

Basal-Plane Functionalization of Chemically-Exfoliated Molybdenum Disulfide by Diazonium Salts

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KEYWORDS

Transition Metal Dichalcogenides, Layered Materials, Molybdenum Disulfide, Covalent Functionalization, Basal-plane, Chemical Exfoliation, 1T-polytype

ABSTRACT

Although transition metal dichalcogenides such as MoS₂ have been recognized as highly potent two-dimensional nanomaterials, general methods to chemically functionalize them are scarce. Herein we demonstrate a functionalization route that results in organic groups bonded to the MoS₂ surface *via* covalent C-S bonds. This is based on lithium intercalation, chemical exfoliation and subsequent quenching of the negative charges residing on the MoS₂ by electrophiles such as diazonium salts. Typical degrees of functionalization are 10-20 at% and are potentially tunable by the choice of intercalation conditions. Significantly, no further defects are introduced and annealing at 350 °C restores the pristine 2H-MoS₂. We show that, unlike both chemically exfoliated and pristine MoS₂, the functionalized MoS₂ is very well dispersible in anisole, confirming a significant modification of the surface properties by functionalization. DFT calculations show that the grafting of the functional group to the sulfur atoms of (charged) MoS₂ is energetically favorable and that S-C bonds are formed.

Over the last few years, the study of two-dimensional (2D) materials has blossomed into one of the most exciting areas of materials science.¹⁻⁷ While this field was originally driven by graphene research, more and more attention is turning to inorganic 2D materials such as MoS₂,¹ MnO₂⁷ and phosphorene.⁸ This is mainly due to their diversity, their range of interesting properties and their potential in numerous applications in areas from optoelectronics to catalysis to medicine.¹⁻⁷ Currently, the 2D materials generating the most excitement are probably the family of transition metal dichalcogenides (TMDs) which include members such as MoS₂, WSe₂ and MoTe₂.^{1, 3} Significant progress has been made on the production of atomically thin, high quality TMDs by chemical vapor deposition (CVD) growth,^{9, 10} chemical exfoliation^{3, 11} and liquid phase exfoliation in suitable solvents^{4, 12} or by the aid of surfactants.^{13, 14} However, unlike the situation with graphene¹⁵⁻¹⁷ or even boron nitride (BN),¹⁸⁻²⁰ there are very few reports on covalent functionalization of TMDs. Typically, functionalization of MoS₂ is achieved by ligand conjugation of thiols at sulfur vacancy sites that were either introduced by ion irradiation²¹ or naturally occurring after chemical exfoliation.^{22, 23} Such methods are interesting but clearly limited in their utility. Up until very recently, no reaction had been reported that allows functionalization of layered MoS₂ on its basal plane without the need of defects. There is no doubt that a general functionalization route is required as such methods have proven extremely versatile for tailoring the surface chemistry of nanomaterials. For example, chemical modification of graphene^{15, 16} or BN^{19, 20} has greatly facilitated their integration into polymer matrices. In addition, functionalization can be used to sensitize initially ambipolar materials such as graphene to interact with specific molecules *via* the functional entity.²⁴ Furthermore, entirely new materials can be designed by attaching functional ligands such as photo- or redox-active molecules to the nanomaterial surface.²⁴

With TMDs such as MoS₂, the most obvious form of covalent functionalization would be to form bonds between the functional group and the surface sulfur (or Se or Te in other TMDs).

However, the basal plane of TMDs is considered to be rather inert, making such strategies challenging. Nonetheless, as has previously been shown for BN, aggressive reagents may indeed functionalize nanomaterials that are considered inert.^{19, 20} As we show within this manuscript, such a strategy can also be applied to functionalize MoS₂. We expect that, once a synthetic protocol to achieve the functionalization and to characterize the material is established, the foundation will have been laid for a much broader and richer chemistry on the surface of TMDs.

The first step towards a general route to functionalize TMDs by grafting functional groups to the exposed sulfur atoms was taken by Chhowalla *et al.* who presented a functionalization sequence based on intercalation, chemical exfoliation and subsequent quenching of the negative charges on the MoS₂ by organic halides or other strong electrophiles.²⁵ While the general reaction sequence is similar to the one used throughout this manuscript, there are notable and important differences in the procedure. Prior to functionalization, we tested different intercalation conditions with the goal of generating intercalated and chemically exfoliated MoS₂ with as few defects and as little structural disruption as possible. Herein, we thus show that defects are indeed not required to achieve functionalization. This also allows us to establish spectroscopic fingerprints to track the functionalization. We furthermore show that the functionalized MoS₂ is highly stable in terms of its polytype and that surface properties are significantly altered leading to a dramatically enhanced dispersibility in anisole. DFT calculations shine light on the structure and geometry of the functionalized material.

Results and Discussion

Purification and characterization of chemically exfoliated MoS₂

Chemical exfoliation of TMDs is generally achieved by reacting the 2D nanomaterials with *n*-butyllithium (*n*-BuLi).^{3, 11, 26-28} This leads to the formation of a lithium intercalation compound associated with a widening of the interlayer distance between the individual MoS₂ layers and a charge transfer from *n*-BuLi to the MoS₂ (figure 1). This in turn results in a (usually partial) structural reorientation of the MoS₂ from the thermodynamically more stable, trigonal prismatic, semiconducting 2H polytype to the octahedral, metallic 1T polytype.^{3, 11, 26-28} In contrast to intercalated graphene, the resultant material is reasonably stable under ambient conditions and can be dispersed in water yielding chemically exfoliated *CE*-MoS₂. Mild ultrasonication results in an almost complete exfoliation down to monolayers. In this study, we have modified the well-known intercalation procedures to give a material more suitable for subsequent functionalization (^{3, 11, 26, 28-30} and methods). Usually in the literature, *n*-BuLi is used in excess (2.5-3 equivalents *n*-BuLi per MoS₂ formula unit).^{3, 11, 26, 28, 29} However, as described below, we have found the chemically exfoliated material produced using these standard conditions to be structurally defective. Since we explicitly want to develop a basal-plane functionalization of MoS₂ that does not require defects, we have modified this procedure and used excess MoS₂ in the intercalation. As we will show, the thus produced *CE*-MoS₂ is significantly less disrupted and damaged using our modified intercalation conditions.

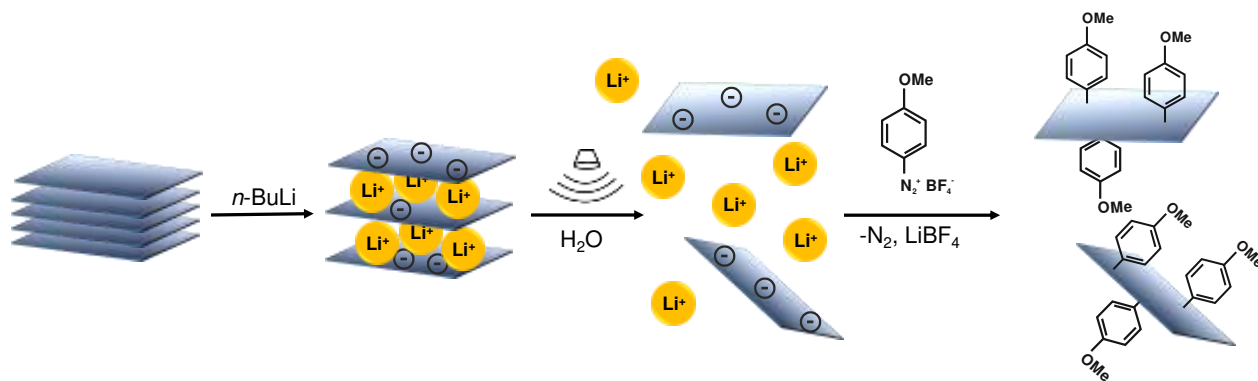


Figure 1: Schematic representation of the basal-plane functionalization of MoS₂. After intercalation with *n*-butyllithium, the negatively charged MoS₂ is dispersed in water by mild bath-type sonication leading to an efficient exfoliation into individual sheets. The charges on the MoS₂ are quenched by the addition of 4-methoxyphenyldiazonium tetrafluoroborate obtaining the functionalized product *f*-MoS₂.

Prior to characterization, purification of the chemically exfoliated MoS₂ is essential. In brief, organic impurities are extracted with *n*-hexane, while inorganic by-products formed during the reaction such as LiOH are removed by several centrifugation-based washing cycles with water (for details see methods and SI section 1). The purified, chemically exfoliated *CE*-MoS₂, prepared using both standard intercalation procedures (*i.e.* using excess *n*-BuLi) and our modified conditions using excess MoS₂, was subjected to X-ray photoelectron spectroscopy (XPS), extinction spectroscopy, thermogravimetric analysis (TGA), zeta potential and atomic force microscopy (AFM). While chemically exfoliated MoS₂ is commonly described as being predominantly in its 1T polytype, we find that this depends on the experimental conditions chosen for the intercalation. Our intercalation conditions using excess MoS₂ yield *CE*-MoS₂ with a lower 1T content as revealed by the XPS Mo3d core level spectra in figure 2a and b. The Mo3d core level spectra show various components that can be assigned to the 2H MoS₂ doublet at binding energies values of 229.2 eV

and 232.2 eV. Both spectra can be fitted with significant additional components (green curves in figure 2a and b) shifted to lower binding energies by ~ 0.8 eV with respect to the main 2H-MoS₂ doublets. These components have previously been observed and identified as related to the 1T-phase of MoS₂.¹¹ In addition, minor contributions from oxides are detected as indicated by the blue and orange traces in the figure.³¹ We further notice that a partial rearrangement to the 2H-polytype occurs more rapidly when using our modified intercalation conditions than in *CE*-MoS₂ produced from intercalation using excess *n*-BuLi (section S3.1). This is unfortunate, as it renders any comparison of the chemically exfoliated precursor system and functionalised MoS₂ challenging in terms of 1T and 2H content, as this means that XPS and functionalization should be conducted the same day.

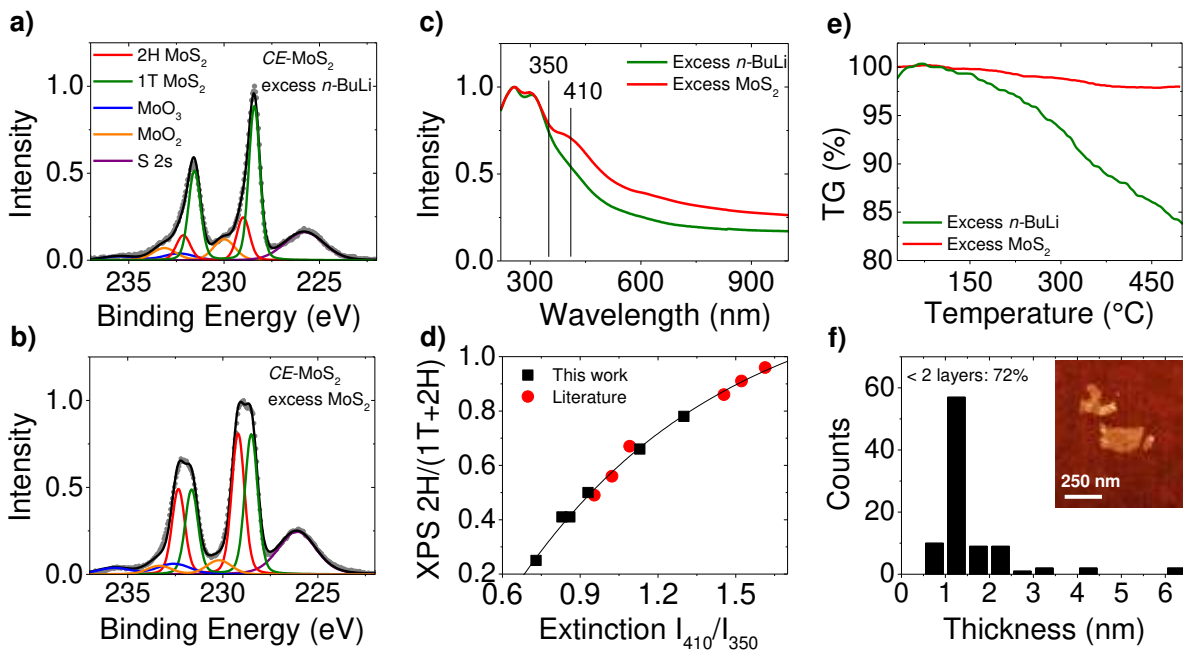


Figure 2: a,b) Fitted Mo3d XPS core level spectra of *CE*-MoS₂ produced using a) excess *n*-BuLi in the intercalation and b) excess MoS₂. Fit components are attributed to 2H-MoS₂, 1T-MoS₂, MoO₂ and MoO₃ in both cases as assigned in the figure legend in a). The 1T content is lower in the case of the chemically exfoliated MoS₂ using excess of MoS₂ in the intercalation. c) Extinction spectra normalized to the maximum of *CE*-MoS₂ produced using excess *n*-BuLi in the intercalation

and excess MoS₂, respectively. The spectral shape is different in both cases clearly showing residual excitonic transitions of 2H-MoS₂ in *CE*-MoS₂ produced using excess MoS₂. This suggests that peak intensity ratios from extinction spectra can be used as metric for the 2H/1T content. d) Plot of 2H/1T ratio determined from fitting the XPS Mo3d core level spectra as a function of extinction peak intensity ratio at 410 nm/ 350 nm. Red data points are extracted from reference 11. The line represents an empirical asymptotic fit. e) Thermogravimetric weight loss of *CE*-MoS₂ produced using excess *n*-BuLi in the intercalation and excess MoS₂, respectively. The significant weight loss of *CE*-MoS₂ produced using excess *n*-BuLi indicates the presence of defects. f) Atomic force microscopy thickness histogram after drop-casting the *CE*-MoS₂ produced using excess MoS₂ onto Si/SiO₂ wafers. 72 % of the nanosheets are < 2 layers with an apparent thickness <1.5 nm. Inset: representative AFM image.

However, we have realized that XPS is not the only technique which can be used to determine the 2H/1T ratio of *CE*-MoS₂. In addition, UV-Vis extinction spectra, as displayed in figure 2c, show marked differences between the two types of *CE*-MoS₂. The extinction spectrum of 1T MoS₂ is characterized by two transitions at 255 nm and 307 nm.¹¹ However, excitonic transitions associated with two sets of excitons are typically observed in 2H MoS₂. These are centered between 350 and 470 nm (D and C-exciton) and 580 and 680 nm (B and A-exciton), respectively.³² These excitonic transitions are also faintly discernible in the extinction spectra of intercalated *CE*-MoS₂ when the material has a higher 2H-polytype content but are absent in the *CE*-MoS₂ with a high 1T content. Particularly striking is the shoulder centered at 410 nm as indicated in figure 2c.

Such spectral changes can be expressed as peak intensity ratios, as we have previously shown for 2H-MoS₂.¹⁴ We therefore suggest that such a peak intensity ratio can also be used to quantify the 2H/1T ratio in *CE*-MoS₂. To test this, we determined the 2H/1T ratio according to XPS on a number of samples and measured extinction spectra the same day the XPS was acquired.

We plot the 2H/1T content as a function of peak intensity ratio in figure 2d. We chose the peak intensity ratio at 410 nm (strong contribution from 2H MoS₂) to 350 nm (strong contribution from 1T MoS₂, local minimum in 2H) as potential metric ratio. We find a very well defined relationship relating the 2H/1T ratio (expressed as 2H/(2H+1T)) to the intensity ratio I₄₁₀/I₃₅₀ according to equation 1:

$$\frac{2H}{2H+1T} = 1.29 - 2.562 * 0.287^x \quad (1)$$

Where x is the extinction intensity ratio

Importantly, data extracted from the literature¹¹ falls on the same curve strongly suggesting that this peak intensity ratio based in the extinction spectra can indeed be used as a metric to quantitatively determine the 2H/1T polytype content of *CE*-MoS₂. This will be important for the analysis of the functionalised material further down below (also see SI section 3.5).

As already mentioned above, we nonetheless consider the chemically exfoliated MoS₂ produced from our modified intercalation conditions using excess MoS₂ to be a better precursor for the subsequent functionalization than the material produced from using excess *n*-BuLi, as the latter is structurally less intact. This is best visualized from the thermogravimetric analysis presented in figure 2e. The *CE*-MoS₂ using our modified reaction conditions (2H/(2H+1T)=0.5-0.6) only shows a minor weight loss of 2 % in the temperature range of 25-500 °C compared to >15 % in the case of intercalation using excess of *n*-BuLi (2H/(2H+1T)=0.25). This suggests a significant disruption of the MoS₂ structure when using excess *n*-BuLi (also see SI figure S3.2) in the intercalation. Transmission electron microscopy (TEM) analysis confirms that considerable damage is done to the MoS₂ nanosheets when using these standard conditions (figure S3.3). Since

our aim is to functionalize MoS₂ which is as structurally perfect as possible, we intercalate using excess MoS₂ throughout the remainder of this study.

We anticipate that an efficient functionalization using electrophiles will depend on two factors: the negative surface charge residing on the MoS₂ and the available surface area which depends on the degree of exfoliation. Measurement of the zeta potential to be -48 mV (SI figure S2.2) shows that the MoS₂ nanosheets are indeed negatively charged. The degree of exfoliation was estimated using atomic force microscopy (figure 2f for representative image) after drop-casting the dispersion on Si/SiO₂ wafers. This showed that 72 % of the chemically-exfoliated nanosheets displayed an AFM height of <1.5 nm consistent with mono- and bilayered species (see histogram in figure 2f).^{11, 33, 34} The mean length of the nanosheets was determined to be 180 nm with a length/width ratio of ~2. The degree of exfoliation in our chemically exfoliated MoS₂ is slightly lower than in some cases reported in literature.^{11, 35} However, a direct comparison with literature is not possible, as the degree of exfoliation of *CE*-MoS₂ in water depends on a number of factors such as MoS₂ starting material, details of sonication and purification and potentially the intercalation conditions. Importantly, the degree of exfoliation using our modified intercalation conditions is similar to that obtained from intercalation using the standard conditions when applying identical purification and sonication protocols (SI section 3.4). We thus conclude that our exfoliated *CE*-MoS₂ produced from the modified, much milder intercalation conditions is an ideal precursor for covalent functionalization.

Functionalization of CE-MoS₂

Since MoS₂ has long been considered to be unreactive and almost inert even after intercalation, we have chosen very aggressive electrophiles, namely diazonium salts (in this case 4-methoxyphenyldiazonium tetrafluoroborate) to quench the negative charges on the MoS₂ and functionalize the material. Diazonium salts have extensively been used in carbon allotrope functionalization and represent a versatile and rich class of suitable electrophiles for reaction with MoS₂.^{17, 36-38} After addition of the diazonium salt, we observe an immediate precipitation of black powder from the yellowish-brown dispersion in water, pointing to an efficient quenching of the charges. As we will show below, this is accompanied by a basal-plane functionalization of MoS₂ to generate *f*-MoS₂. Our XPS analysis strongly suggests that partial negative charges on the S in the *CE*-MoS₂ are neutralized by the addition of the cationic electrophile resulting in the formation of a S-C bond. Owing to the high degree of exfoliation of the *CE*-MoS₂ precursor, both sides of the nanosheets are accessible for potential functionalization in dispersion. However, as we also show, this is not a prerequisite for the functionalization, as it can also be achieved after deposition on a substrate (SI section 7.3).

Bulk characterization of functionalized MoS₂

The immediate flocculation of MoS₂ after addition of diazonium salt due to the quenching of the charges residing on the nanosheets is confirmed by zeta potential measurements (figure S4.1). These show that by 2 min after addition of the diazonium salt, the zeta potential increases from -48 mV to 0. The resultant powder was filtered, washed with water and isopropyl alcohol, and dried before being subjected to thermogravimetric analysis coupled to mass spectrometry (TGA-MS), Raman and IR spectroscopy and XPS as described below.

Thermogravimetry showed no mass loss below 220 °C followed by a 7 % mass reduction in the temperature range 220-450 °C (figure 3a). As small, van der Waals bonded molecules tend to desorb from surfaces below 200 °C,³⁹ this suggests the mass loss to be associated with species which are strongly bonded to the surface or intercalated between restacked sheets.⁴⁰ To test whether the mass loss is due to diazonium salt trapped between restacked layers or noncovalently adsorbed on the MoS₂, we performed reference experiments using liquid exfoliated¹² uncharged MoS₂ (SI section 6). No significant weight loss was observed in the reference experiments confirming that physisorption and trapping between restacked MoS₂ nanosheets is negligible. Significantly, thermogravimetric analysis coupled to mass spectrometry (TGA-MS) allows the association of the moieties which had thermally detached from the functional group or its fragments, respectively (figure 3b). Five main mass fragments with $m/z = 107, 108$ (methoxybenzene), $m/z = 77, 78$ (benzene) and $m/z = 39$ (doubly charged benzene ring) were detected peaking at 360 °C clearly evidencing that the mass loss is due to the detachment of the functional group. Assuming that the weight loss in this temperature regime stems from the functional group itself, we use the associated mass loss of 7 % to determine that every 10th MoS₂ unit bears ~1 functional moiety, *i.e.* the bulk degree of functionalization is 10% per MoS₂ unit.

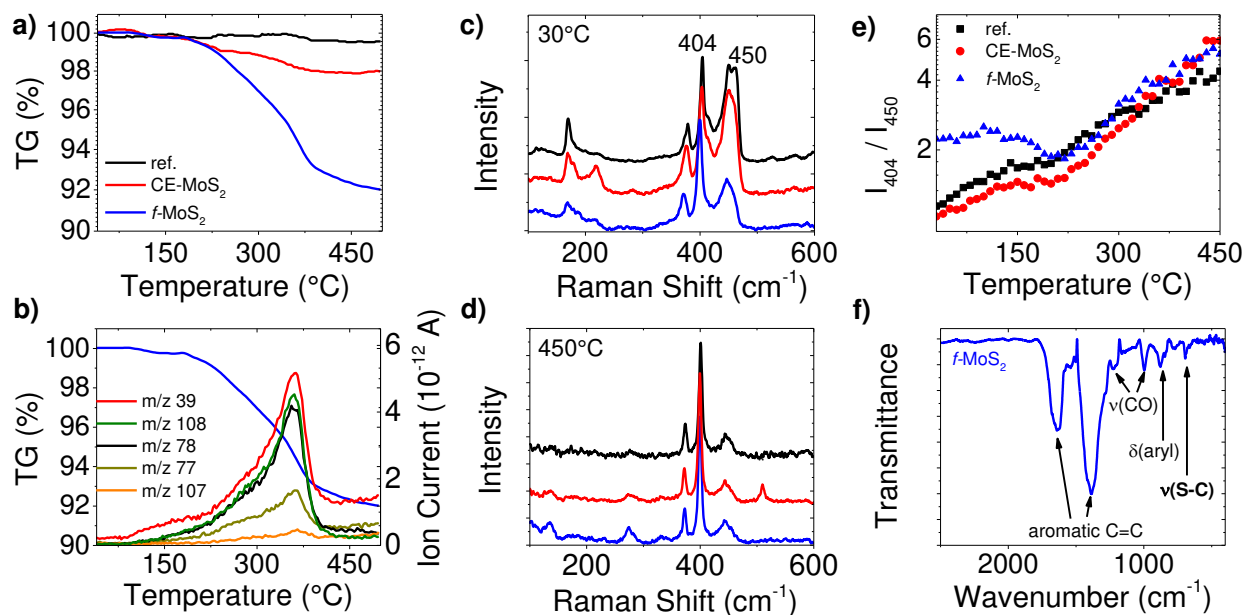


Figure 3: a) Thermogravimetric weight loss of the untreated MoS₂, the CE-MoS₂ and the material after functionalization. The weight loss of 6.7% in the temperature regime of 220-450°C corresponds to a bulk degree of functionalization of 10% per MoS₂ unit. b) Detected mass fragments of *f*-MoS₂ corresponding to methoxybenzene (m/z 107, 108), benzene (m/z 39, 77, 78) evidencing that the mass loss in the temperature range of 200-450°C is due to grafting of the functional group. c, d) Raman spectra (633 nm excitation, average of 250 individual spectra) of the MoS₂ reference, CE-MoS₂ and *f*-MoS₂ normalized to the A_{1g} mode at 404 cm⁻¹ (offset for clarity). Figure legend as in a). c) Spectra measured at 30 °C. The second order longitudinal acoustic phonon (2LA(M) at 450 cm⁻¹) appears decreased in the *f*-MoS₂. d) Spectra measured at 450 °C. e) Plot of the Raman intensity ratio of the A_{1g} mode to the 2LA(M) mode of the MoS₂ reference, CE-MoS₂ and *f*-MoS₂ as a function of temperature. The reference and the CE-MoS₂ follow a very similar trace, while the *f*-MoS₂ deviates significantly at temperatures below 220 °C exhibiting a higher A_{1g}/2LA(M) ratio. This suggests that this peak intensity ratio can be used as indicator for successful functionalization, f) FTIR spectrum (measured in diffuse reflectance mode with CsI as matrix) of *f*-MoS₂. The vibrational modes of the functional group can be clearly identified. In addition, a vibration at 695 cm⁻¹ is detected that can be assigned to a S-C stretching vibration.

Since Raman spectroscopy is a commonly used and powerful tool in nanomaterial characterization, we reasoned that Raman spectra may contain information on the functionalization. The Raman spectrum of MoS₂ when excited off resonance (e.g. $\lambda = 532$ nm) is quite well understood and characterized by two main phonon peaks (the A_{1g} at 404 cm⁻¹ and E¹_{2g} mode at 380 cm⁻¹). However, when resonantly excited with a red laser (633 nm), a number of second order modes are observed and the spectrum is rich in additional features that are not fully understood^{10, 41-45} (for a detailed discussion see SI section 4.2.1). We can nonetheless use the Raman spectrum to trace differences between the MoS₂ reference powder, the chemically exfoliated precursor and the *f*-MoS₂. Low temperature spectra (30°C) are displayed in figure 3c. The spectra are the mean of 250 individual spectra acquired on the respective powder to account for local sample inhomogeneity and changes of the laser focus. Two notable differences between the samples are observed: firstly, the J1-J3 phonon modes (170-300 cm⁻¹) attributed to the 1T phase of MoS₂⁴⁶ are clearly discernible in the chemically exfoliated material, while basically absent in the *f*-MoS₂ and the powder reference. However, at elevated temperatures, they also appear in the *f*-MoS₂ (figures S4.3 and S4.4) suggesting that they are suppressed in the room temperature spectrum of *f*-MoS₂ even though the MoS₂ is still in its 1T conformation. The second pronounced change in the low temperature Raman spectra is the intensity ratio of the A_{1g} mode at 404 cm⁻¹ to the 2LA(M) mode at 450 cm⁻¹. (NB: The peak at 450 cm⁻¹ contains multiple components. But for the sake of simplicity we refer to it as the 2LA(M) mode.) This intensity ratio is significantly higher in the functionalized sample compared to the chemically exfoliated precursor and the starting powder suggesting that the 2LA(M) mode is also suppressed in *f*-MoS₂. To confirm that this change in intensity ratio is attributed to the functionalization, we performed temperature dependent Raman spectroscopy monitoring the evolution of the Raman spectra (mean of 250 spectra each) when heating the sample from room temperature to 500 °C in 10 °C intervals. At high temperatures (450

°C, figure 3d) all features attributed to the 1T polytype have disappeared and the spectra of reference, chemically exfoliated and functionalised MoS₂ are identical suggesting that no permanent harm to the lattice was done by intercalation and functionalization.

To test whether the intensity ratio $A_{1g}/2LA(M)$ is indicative for functionalization, we plot this ratio as a function of temperature in figure 3e. Both the *CE*-MoS₂ and the reference powder follow a similar trace (even though there are differences when looking at individual components as discussed in the SI section 4.2.3). Significantly, the *f*-MoS₂ exhibits a higher $A_{1g}/2LA(M)$ intensity ratio for temperatures up to 220 °C. This coincides with the temperature where the cleavage of the functional group starts according to TGA-MS. We thus propose that this intensity ratio can indeed be used as an indicator for the functionalization of MoS₂. However, we note that a detailed understanding is beyond the scope of this manuscript.

The presence of the functional group is further evidenced by IR spectroscopy (figure 3f). The pattern of the aryl bending mode at ~880 cm⁻¹ suggests a 1,4-substitution pattern on the benzene ring consistent with anchoring of the functional group in *para* position to the methoxy-group.⁴⁷ Most importantly, a vibration at ~695 cm⁻¹ is observed which can be assigned to a S-C stretching vibration strongly suggesting the functional group to be anchored to S atoms of the MoS₂. In addition, we note that no characteristic N₂⁺ vibration (expected at 2,300 cm⁻¹) of the diazonium salt precursor is detected. This indicates that physisorption or intercalation of the precursor salt only occurs to a very minor extent and is not detectable. Annealing at 500 °C to remove the functional groups showed the IR spectra of both *f*-MoS₂ and *CE*-MoS₂ to return to that of the MoS₂ starting powder (figure S4.6). This evidences that the functionalization is fully reversible and the intact MoS₂ can be restored further supporting the conclusion from the Raman spectra.

X-ray photoelectron spectroscopy (XPS)

The data presented above clearly provides evidence for successful grafting of the functional group to the MoS₂ scaffold. IR spectroscopy suggests the formation of a C-S bond. However, IR alone cannot provide unambiguous proof for a covalent functionalization. We have therefore turned to X-ray photoelectron spectroscopy to distinctively probe the chemical environment of the Mo and S, respectively. The fitted Mo3d and S2p core level spectra of the MoS₂ reference powder, the *CE*-MoS₂ precursor, the *f*-MoS₂ and the defunctionalized material (after annealing, *df*-MoS₂) are presented in figure 4. We note that we did not observe any other elements in the survey spectra than Mo, S, C and O (SI table S1).

Both S2p and Mo3d core level spectra (figure 4) show the *CE*-MoS₂ and *f*-MoS₂ to be a mixture of 1T- and 2H-MoS₂. Accordingly, the 1T phase was preserved during the functionalization. We note that the 2H/1T ratio of the *CE*-MoS₂ precursor and the *f*-MoS₂ is slightly different. While the 2H/1T ratio of *f*-MoS₂ according to the Mo3d core level spectra is 0.45, we determined a value of 0.66 in case of the *CE*-MoS₂ (see supporting information table S1). We note that our extinction spectra 2H/1T metric suggests that the 2H/1T ratio of the chemically exfoliated precursor at the time the functionalization was performed was 0.45 (SI section 3.5). However, XPS on the *CE*-MoS₂ was acquired one week later and structural rearrangement to the 2H-polytype had already occurred. While this relatively quick partial rearrangement from 1T to 2H-polytype using our milder, modified intercalation conditions is unfortunate, we nonetheless found the benefits from this modified intercalation (such as lower defect content) to be beneficial over the standard literature conditions when it comes to studying functionalization. Furthermore, the results suggest that the 1T-polytype is stabilized by the functionalization, as no rearrangement to the 2H-polytype was observed in the timeframe of one month (SI section 4.4 and table S1).

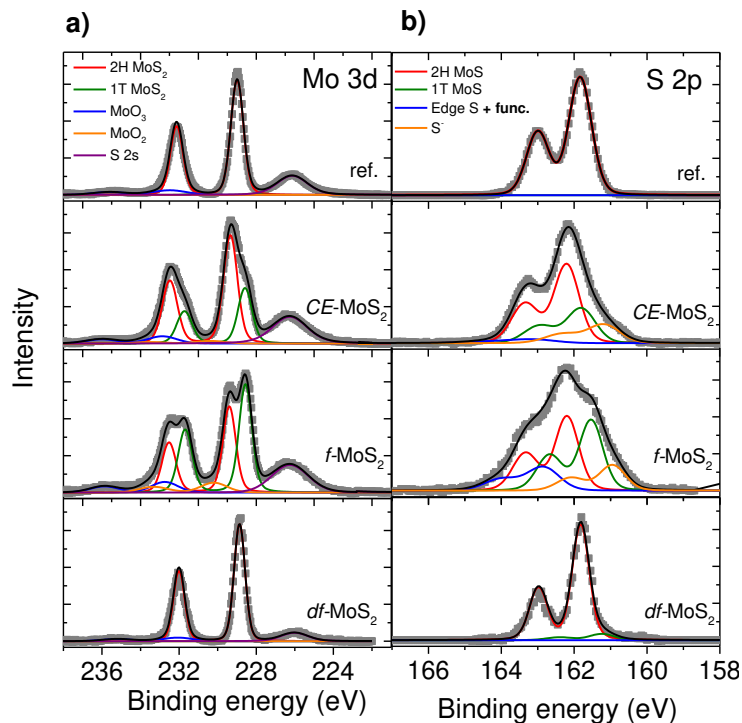


Figure 4: From top to bottom: Fitted XPS core level spectra of the MoS₂ powder, chemically exfoliated CE-MoS₂ (produced from using excess MoS₂ in the intercalation), functionalized *f*-MoS₂ and defunctionalized *df*-MoS₂ (after annealing). a) Mo3d core level, b) S2p core level. The reference is perfectly consistent with 2H-MoS₂, while intercalation yields a mixture of 2H- and 1T-MoS₂ (with a very minor contribution stemming from oxides as indicated by the orange and blue fit lines in the Mo3d core level). Functionalization gives rise to a component at higher binding energies in the S2p core level spectra. The 2H/1T ratio of CE-MoS₂ and functionalized *f*-MoS₂ is different due to rapid rearrangement of 1T-MoS₂ from our intercalation using excess MoS₂ (see SI). The degree of functionalization estimated from the integrated areas of the individual components in the S2p core level spectra is consistent with the 10 % calculated from TGA. After annealing, the MoS₂ is restored to its pristine 2H polytype.

After annealing, the pristine 2H-MoS₂ is completely recovered, consistent with the observation from IR and Raman spectroscopy. While no differences in the Mo3d core level spectra are observed (other than varying 2H/1T contents), the S2p core level spectra are distinct in CE-

MoS₂ and *f*-MoS₂ (figure 4b). The S2p core level spectra of the *CE*-MoS₂ can be fitted with four components: 2H-MoS₂, 1T-MoS₂, a species previously observed in surfactant-exfoliated 2H-MoS₂ associated with edges of the flakes (shifted by ~0.7 eV to higher binding energies relative to 2H-MoS₂)¹⁴ and a component at lower binding energies (~1.2 eV relative to 2H-MoS₂) most likely stemming from electron-rich sulfur from the electron transfer of *n*-BuLi during the intercalation. In the functionalized *f*-MoS₂, the electron-rich sulfur species at lower binding energies decreases in favor of a significantly increased percentage of the “edge-S component” at higher binding energies. This is more pronounced for material obtained from intercalation using excess *n*-BuLi, SI section 7.1. This strongly suggests that any (partial) charges on the sulfur atoms of the chemically exfoliated *CE*-MoS₂ are neutralized by grafting of the functional groups to the sulfur atoms as observed in zeta potential measurements. We can use the integrated areas of the fit components to estimate the degree of functionalization on the basis of XPS. In the *CE*-MoS₂, 4 % of the total sulfur component is attributed to the edge component sulfur at higher binding energies. In turn, in the functionalized *f*-MoS₂, the latter is increased to 15 %. The degree of functionalization can thus be determined to be 11 % per sulfur atom. This coincides with the degree of functionalization obtained from TGA-MS (10 % per MoS₂ unit). Nominally, this appears contradictory, as XPS probes the degree of functionalization on the S atoms, while TGA yields values related to the MoS₂ unit. However, since S atoms bridge the Mo atoms, if every 10th MoS₂ unit bears a functional group, this also means that roughly every 10th sulfur is functionalized. We would like to emphasize that the experimentally observed degree of functionalization of 10% can only be achieved if the functionalization occurs at the basal plane rather than edge sites only. However, it is currently unclear whether edge sites are also affected, or even preferentially functionalized due to their anticipated higher reactivity.

We note that a basal plane functionalization of MoS₂ involving the formation of S-C bonds after intercalation-based activation of the MoS₂ differs significantly from recent functionalization routes,^{22, 23} where S vacancies were filled by coordinating thiols to chemically-exfoliated MoS₂. We are convinced that our route has significant advantages, as it is not limited by the presence of such vacancies and can be applied even to MoS₂ of the highest quality. In addition, the functionalization by forming a covalent bond is in marked contrast to the formation of intercalation compounds from chemically exfoliated MoS₂. This is further illustrated by wide angle X-ray diffraction confirming the absence of *00l* reflections in the *f*-MoS₂ (figure S4.8) and the absence of long range order along the *c*-axis in contrast to intercalation compounds (see ref²⁶ and references therein).

Dispersibility and structural integrity of the lattice

An important point of the functionalization of nanomaterials in general is the alteration of the surface properties due to the attachment of functional moieties. This is expected to change the surface energy of the nanomaterial and as a consequence its dispersibility.⁴⁸ To test this, we have dispersed the MoS₂ reference powder, the *CE*-MoS₂, *f*-MoS₂ (both after filtration and drying) and the defunctionalized *df*-MoS₂ in *N*-methyl-2-pyrrolidone (NMP) and anisole. NMP is known to be a good solvent for MoS₂ with surface energies and solubility parameters matching those of the nanomaterial.^{12, 48, 49} In turn, anisole (methoxybenzene) is chemically well-matched to our functional group. Photographs of the dispersions obtained after mild bath sonication (20 min) and centrifugation at 500 rpm (28 g) are depicted in figure 5a and b. We note that the MoS₂ powder is not a suitable reference for the dispersibility study, as it has a significantly different morphology. Since the crystallites were not broken up by any pre-treatment (*i.e.* chemical exfoliation), much

more energy would be required to efficiently disperse the powder even in good solvents such as NMP. However, for this study, we wanted to keep the sonic energy input to a minimum to avoid potential defunctionalization due to strong local heating during sonication. As expected, the dispersibility of *f*-MoS₂ is significantly altered: compared to the defunctionalized material, the concentration of dispersed *f*-MoS₂ is lower by approximately a factor of three. In turn, *f*-MoS₂ is well dispersible in anisole unlike the chemically exfoliated and defunctionalized MoS₂. This suggests that a degree of functionalization of 10% is already sufficient to significantly alter the surface energy of the MoS₂. In addition, this indirectly evidences that the basal plane is reasonably homogeneously decorated with a neutral functional moiety. If a charge transfer complex between diazonium reagent and *CE*-MoS₂ was formed, no such enhanced dispersibility in anisole would be expected.

The extinction spectra of the NMP dispersions are displayed in figure 5c. The spectrum of the MoS₂ powder is consistent with bulk 2H-MoS₂ showing the characteristic excitonic transitions.^{12, 14, 32} The spectrum of the defunctionalized material resembles that of very small 2H-MoS₂ nanosheets^{14, 50} in analogy to spectra obtained from annealed intercalated MoS₂.¹¹ The spectrum of the redispersed *CE*-MoS₂ resembles a mixture of 2H- and 1T-MoS₂.¹¹ Since the C- and D excitonic transitions centered at 450 nm are slightly better resolved than in the initial chemically exfoliated material in water (figure 2c), we suspect that local heating in the sonication-based redispersion resulted in a partial reconstruction of the 1T- to the 2H-phase. Most interestingly, all excitonic transitions are suppressed in the functionalized material so that optical extinction spectroscopy provides a very quick tool to determine whether functionalization was successful. This also further confirms that the electronic structure of *f*-MoS₂ is significantly different from chemically exfoliated or non-functionalized MoS₂. A more detailed discussion of the redispersion study is presented in the SI (section 5).

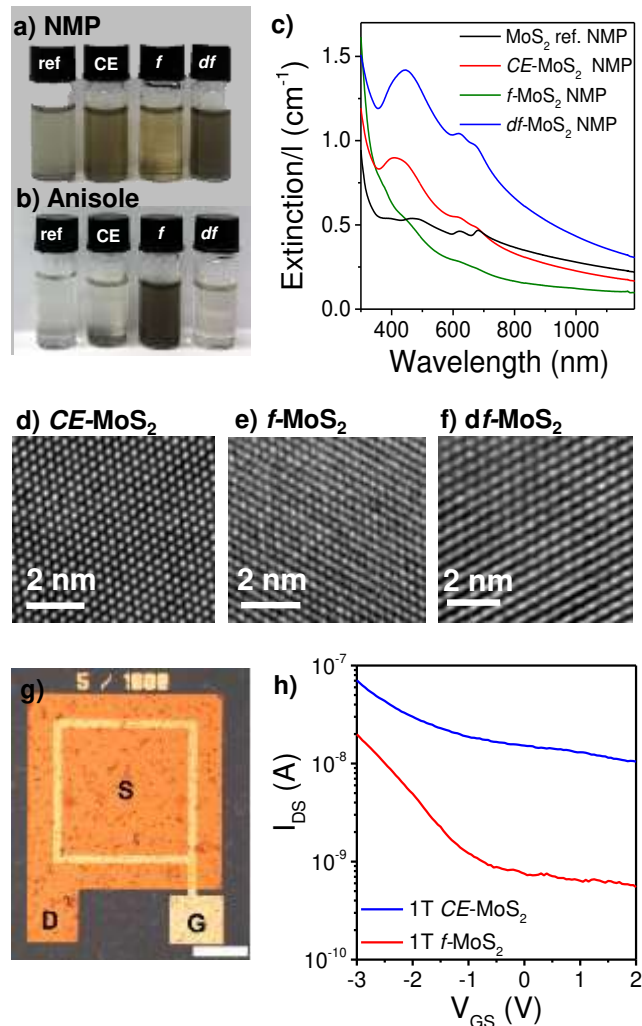


Figure 5: a,b) Redisperison of MoS₂ powder, *CE*-MoS₂, functionalized *f*-MoS₂ and defunctionalized *df*-MoS₂ in a) *N*-methyl-2-pyrrolidone (NMP) and b) anisole. Intercalated and defunctionalized MoS₂ are well dispersible in NMP, while the *f*-MoS₂ is dispersible in anisole opposed to the intercalated and defunctionalized counterparts evidencing a change in solubility parameters due to the functionalization. c) Extinction spectra of the dispersions shown in a) (after mild centrifugation at 500 rpm). Notably, all excitonic transitions are suppressed in *f*-MoS₂. d-f) High resolution transmission electron microscopy (TEM) of the drop-casted dispersions in a) showing the intact lattice of d) *CE*-MoS₂, e) *f*-MoS₂ and f) *df*-MoS₂. g,h) Electrical characterization of network devices. g) Device image with source, drain, and gate electrodes indicated with S, D, and G. The scale bar is 100 μm. The channel length and width of the device are 5 μm and 1000 μm. h) The device transfer curves before and after functionalization. Current on/off ratio increases from 6.7 (before) to 36.1 (after), indicating an enhancement in the semiconducting property.

To confirm that our subsequent intercalation and functionalization sequence does not structurally harm the MoS₂ lattice, we performed a series of high resolution transmission electron microscopic investigations on the MoS₂ reference powder, *CE*-MoS₂, *f*-MoS₂ and the defunctionalized material (figure 5d-f and SI figure S5.5). For this purpose, grids were cast from the NMP dispersions after mild sonication and centrifugation. We note that, in all cases, the MoS₂ is only reasonably well exfoliated and appears as reaggregated agglomerates of formerly individualized nanosheets (see AFM figure 2f and TEM SI figure S3.3). This is attributed to the very gentle redispersion and centrifugation conditions that were chosen to avoid any structural changes of the chemically exfoliated and functionalized MoS₂. Because of that, many small patches were frequently observed on the basal plane of the redispersed material (center images in S5.5). However, apart from that, the lattice is intact over wide regions (figure 5d-f) showing that no severe structural damage to the MoS₂ was induced by our functionalization sequence. We note that an analysis of 2H and 1T polytype content from bright field images is extremely challenging⁵¹ and beyond the scope of the manuscript.

Functionalization after intercalation with excess n-BuLi

The intercalation conditions with excess MoS₂ have proven to be ideal for establishing the characterization protocols to trace the subsequent basal plane functionalization. However, this *CE*-MoS₂ has the disadvantage of undergoing a rather rapid rearrangement from its 1T polytype to its 2H polytype. It is therefore very challenging to compare, for example, electrical properties of *f*-MoS₂ to the *CE*-MoS₂ precursor, as the 2H/1T ratio may vary. Given that the functionalization stabilizes the 1T-phase, which is known to be metallic in chemically exfoliated MoS₂, it is important to test whether this is also the case for *f*-MoS₂. We have therefore performed

functionalization of 1T *CE*-MoS₂ from intercalation using excess *n*-BuLi. A detailed characterization is presented in the supporting information (section 7). The XPS analysis shows that only very minor 2H/1T rearrangement occurs within one month (SI section 7.1). The initial 1T:2H ratio was determined to be ~4 (*via* Mo3d core level X-ray photoelectron spectra, table S2). Thus, both chemically and functionalized MoS₂ can be considered to be predominantly 1T MoS₂. XPS furthermore suggests that the degree of functionalization is 20%.

To test the electrical characteristics of 1T *CE*-MoS₂ and 1T *f*-MoS₂, we have fabricated field-effect transistors (FETs) based on self-assembled monolayers (SAMs) using region-selective deposition of the chemically exfoliated MoS₂. This technique has previously been applied for electrical characterization of functionalized carbon allotropes and is described in detail elsewhere.^{52, 53} In brief, the network devices were produced by immersing pre-patterned chips covered with a positively charged SAM in the channel region (3-methyl-1-(12-phosphonododecyl)imidazolium bromide) in an aqueous dispersion of the 1T *CE*-MoS₂. Due to Coulombic attraction, 1T *CE*-MoS₂ nanosheets are selectively deposited in the channel region (figure 5g).⁵⁴ The network transistor of the chemically exfoliated MoS₂ is difficult to turn off and shows on/off ratios of ~ 7 due to the metallic nature of 1T-MoS₂. After testing, the device was soaked in an aqueous solution of the diazonium salt for 5 min. Successful functionalization was confirmed by Raman spectroscopy (figures S7.4 and S7.5). The transistor showed a clear improvement in on/off ratios (up to ~36) suggesting that the *f*-MoS₂ exhibits semiconducting properties even though the 1T-polytype is maintained (figure 5h). The device exhibits a typical p-type characteristic which could be due to the electrostatic doping from the SAM layer underneath.⁵⁴ The hole mobility decreased from 3.9×10^{-4} cm²/Vs before functionalization to 1.2×10^{-4} cm²/Vs after functionalization. This could be attributed to the extra scattering centers introduced by the

functionalization. However, we have to note that the decrease is not pronounced at all and the electric property of the network transistor is largely preserved.

Modelling

In order to gain further insights in the structure and bonding in the functionalized MoS₂, we have performed density functional theory calculations (DFT). We propose a reaction model implying dissociative chemisorption of n (number of molecules) 4-methoxyphenyldiazonium cations on a MoS₂ surface with net charge of $-|e|n$, producing the release of n N₂ molecules. To test whether steric hindrance may occur for degrees of functionalization of 20% per MoS₂ unit, functionalized surfaces with low and high coverage have been modelled being equivalent to grafting one or four molecules ($n = 1$ or 4) per MoS₂ unit cell, respectively.

The reaction energy is evaluated as

$$E_{\text{react}} = [E_{\text{MoS}_2} + nE_{\text{cat}}] - [E_{\text{funct}} + nE_{\text{N}_2}]$$

where, n is the number of chemisorbed molecules, E_{MoS_2} and E_{funct} are the energies of the clean and the functionalized surfaces, respectively and E_{cat} and E_{N_2} are the energies of the isolated cation and the released N₂ molecule. The reaction is largely energetically favorable, with a reaction energy of $E_{\text{react}} = 2.33$ eV per molecule at low coverage. At high coverage, the reaction energy per molecule becomes even larger. We note that this reaction energy is much larger than calculated adsorption energies for physisorbed molecules which are in the range of 0.5 eV per molecule.⁵⁵ This suggests

that, even though physisorption may occur, the reaction is thermodynamically driven towards a covalent functionalization. This agrees well with our experimental data from TGA-MS showing that the mass fragments attributed to the functional group are detected in a temperature range of 270-450°C with only traces being detected at lower temperatures where physisorbed species would be expected.

After geometry relaxation, the 1T-MoS₂ monolayer shows a 2×1 reconstruction, known as $1T'$ phase (see SI section 8). In the charged MoS₂ parent system, we observe a bidental Mo-S bonds distribution (centered around 2.42 Å and 2.48 Å, respectively). This structure relaxes after functionalization in such a way that all Mo-S bonds are distributed around an average Mo-S bond length of 2.45 Å. The grafted molecule is approximately perpendicular to the surface (92.8°) (figure 6, bottom right) and the dihedral angle between molecular plane and (100) surface is 30.22° (figure 6, bottom left). The analysis of the electronic structure of the clean and functionalized monolayer shows that they are both semiconductors with a very tiny band-gap (see SI section 8).

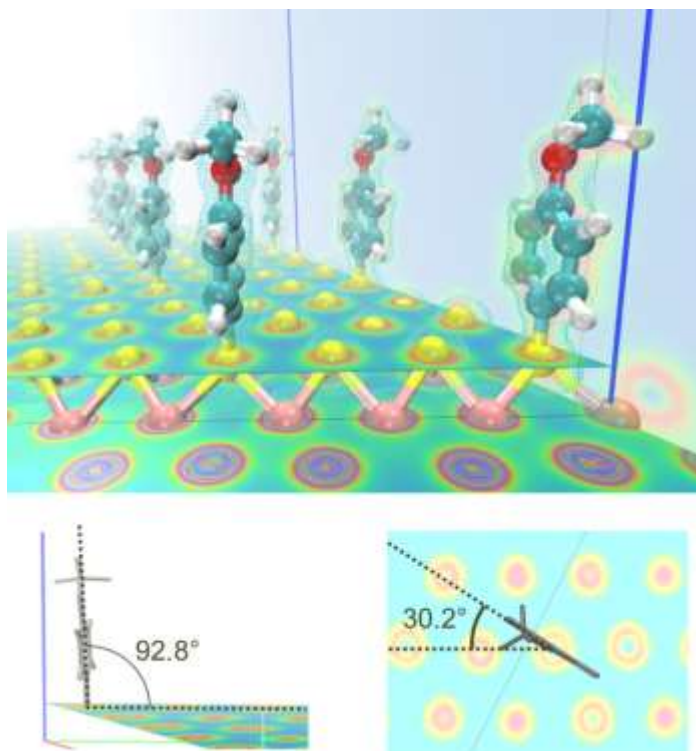


Figure 6: Top: Ball and stick representation of the functionalized monolayer with high coverage. Red, blue, yellow, pink and white balls represent O, C, S, Mo and H atoms, respectively. The dotted area reproduces the total electronic charge (isosurface with a contour level of 0.8 electrons). The two (001) planes (perpendicular to z axis) depict volume slices of the total electronic charge on Mo (below) and S (above) surfaces. (010) plane is also highlighted by a transparent slice. The position of this plane along y axis is highlighted by the thin grey line perpendicular to (001) plane, corresponding to where S-C bonds lie. Red and blue on the planes indicate high and low charge values, respectively. Bottom left: Tilt angle between y and molecular axis. Bottom right: Dihedral angle between molecular plane and (100) surface. In both panels the molecule is schematically sketched and the electron charge on the reference grafting S plane at low coverage is also represented. Y axis is represented in top and bottom right insets by a grey line lying on the (001) plane. In bottom left inset, red, green and blue lines represent x, y and z axis, respectively.

The analysis of the Bader charges⁵⁶ of the clean (uncharged and non-functionalized) MoS₂ system show a charge polarization with S atoms bearing partial negative charges and Mo atoms being partially positively charged (quantitative analysis see SI section 8). When excess charges are

added to the overall neutral system (such as experimentally achieved after intercalation with *n*-BuLi), these distribute over the external S atoms. This is rather important, as a chemical reaction with a positively charged reagent is likely to occur on the negatively charged reaction site, *i.e.* the S atoms. The Coulombic attraction between the negatively charged S surfaces and the positively charged diazonium reagent also accounts for the spontaneous reaction experimentally observed and the strongly negative reaction energy. Our calculations confirm that S-C chemical bonds are formed. The C atom grafted to the surface withdraws 0.15 |e| from its neighbor S, which is about 0.2 |e| less charged than the other surface S atoms. A very similar picture is observed when the coverage is higher (figure 6, top).

This clearly confirms the experimental observations that basal-plane functionalization on the S atoms of chemically exfoliated MoS₂ is readily accessible by reaction of *CE*-MoS₂ with strong electrophiles such as diazonium salts.

Conclusion

In conclusion, we have demonstrated a novel functionalization sequence for transition metal dichalcogenides such as MoS₂. The functionalization is based on reacting intercalated, chemically-exfoliated MoS₂ with electrophiles such as diazonium salts. The use of chemically-exfoliated MoS₂ is beneficial due to the good exfoliation in water making both sides of the nanosheets accessible. This yields typical degrees of functionalization of 10-20 at%. The successful functionalization was evidenced by zeta potential measurements, IR, Raman and extinction spectroscopy, TGA-MS and XPS.

The basal-plane functionalization is fully reversible and annealing restores predominantly pristine 2H-MoS₂. High resolution TEM confirms the lattice to be widely intact. The basal-plane

functionalization furthermore yields *f*-MoS₂ with different surface properties or surface energies which is reflected in an enhanced dispersibility in solvents that are compatible with the functional group. In the functionalized MoS₂, the 1T-polytype that is typical for intercalated MoS₂ is maintained and even stabilized. However, in contrast to intercalated 1T-MoS₂ which is known to be metallic, *f*-MoS₂ exhibits semiconducting properties as concluded from electrical characterization of network transistor devices before and after functionalization. DFT calculations show that the reaction is energetically very favorable and that a S-C bond is formed.

We believe this work is important, as it establishes spectroscopic fingerprints of covalently functionalized MoS₂. We also show that this method is intrinsically not reliant on the presence of defects or vacancies and so can potentially be applied to high-quality nanosheets. In addition, the method is versatile, with functionalization achievable both in solution and for nanosheets deposited on surfaces. Importantly, this approach is not limited to MoS₂ but is applicable to any TMD (or indeed any layered compound) which can be intercalated with lithium. We anticipate that this ability to easily functionalize TMDs is only the first step toward the development of secondary functionalization routes leading to the bonding of complex molecular systems to the nanosheet surface.

Methods

Sample preparation: More details on materials and methods are presented in the SI.

Synthesis of diazonium compound: In a 500 mL three neck flask equipped with a stir bar, gas outlet and a dropping funnel 10 g (81 mmol) *p*-anisidine were suspended in 250 mL water. 6 g (89 mmol) sodium nitrite were added and the suspension was cooled with an ice bath. Dropwise addition of

50 mL (36 g, 48 wt% in H₂O, 200 mmol) tetrafluoroboric acid yielded the crude product as fine white needles. After washing, it was recrystallized from diethyl ether.

Intercalation/Chemical exfoliation: Under argon atmosphere 1.5 mL *n*-BuLi (2.0 M) in cyclohexane was added to 1.5 g (9.4 mmol) MoS₂. After the addition of 10 mL of dry hexane as solvent, the dispersion was heated to 65 °C overnight. 100 mL distilled water was added to the cooled reaction mixture under hydrogen evolution. After the decrease of the gas formation, organic impurities were removed by extraction with hexane (two times), the aqueous phase was collected. A portion of the concentrated black aqueous phase was diluted further with distilled water to obtain a yellowish-brown dispersion which was bath-sonicated for 20 minutes at 50 °C and pre-centrifuged at 750 rpm (62 g) for 1:30 h at 20 °C in order to remove non-exfoliated material as sediment. Four further centrifugation steps at 14 krpm (21,475 g, 1:30 h, 20 °C) removed very small MoS₂ material and LiOH generated during the reaction as supernatant. After each high speed centrifugation step, the sediment was collected with fresh distilled water shaken by hand and subjected to the next centrifugation step. After the washing procedure the final sediment was redispersed in distilled water by bath sonication (30 min, 50 °C) yielding a highly stable dispersion. To obtain *CE*-MoS₂ predominantly as 1T polytype, 1.5 g MoS₂ and 15 mL *n*-BuLi (2.0 M) were used for intercalation. The material thus obtained is denoted as 1T *CE*-MoS₂. Unless otherwise noted, *CE*-MoS₂ refers to the chemically exfoliated material obtained from intercalation using excess MoS₂.

Functionalization: 4-Methoxyphenyldiazonium tetrafluoroborate dissolved in distilled water was added to the dilute yellowish/brownish purified *CE*-MoS₂ dispersion dropwise under exposure to light. After addition of only a few drops of reagent, a black precipitate formed. The reaction mixture was stirred overnight and filtered through a 0.2 µm reinforced cellulose membrane filter (Sartorius).

Washing with isopropanol to remove organic side-products and with distilled water yielded the functionalized MoS₂ product after drying under vacuum.

Characterization: Optical extinction was measured on a Perkin Elmer Lambda 1050 in quartz cuvettes with a pathlength of 0.4 cm. Raman spectroscopy was performed using a Horiba Scientific LabRAM Aramis equipped with a motorized sample holder. TGA-MS analysis was carried out on a Netzsch STA 409 CD with EI ion source and quadrupole mass spectrometer on a 10 K/min temperature ramp using helium as inert gas. Zeta potential measurements were carried out on a Malvern Zetasizer Nano system with irradiation from a 633 nm He-Ne laser. X-ray Photoelectron Spectroscopy was performed under ultra-high vacuum conditions ($< 5 \times 10^{-10}$ mbar), using monochromated Al K α X-rays (1486.6 eV) from an Omicron XM1000 MkII X-ray source and an Omicron EA125 energy analyzer. An Omicron CN10 electron flood gun was used for charge compensation and the binding energy scale was referenced to the adventitious carbon 1s core-level at 284.8 eV. Mo3d and S2p core-level regions were recorded at an analyzer pass energy of 15 eV and with slit widths of 6 mm (entry) and 3 mm x 10 mm (exit), resulting in an instrumental resolution of 0.48 eV. After subtraction of a Shirley background, the core-level spectra were fitted with Gaussian-Lorentzian line shapes and using Marquardt's algorithm. IR spectra were acquired using a Perkin Elmer Frontier spectrometer equipped with a diffuse reflectance unit and CsI as matrix. Atomic force microscopy (AFM) was carried out on a Solver Pro scanning probe microscope (NT-MDT) equipped with a Sony Exwave HAD camera optical zoom (6.5) in tapping mode. Low resolution bright field transmission electron microscopy (TEM) imaging was performed using a JEOL 2100, operated at 200 kV on holey carbon grids (400 mesh). Prior to HRTEM imaging, the samples were drop-cast onto grids that were then kept at 120 °C overnight under vacuum to remove excess surfactant. HRTEM imaging was then performed on an FEI Titan

TEM operated at 300 kV. The network transistor devices based on region-selective assembly of *CE*-MoS₂ were prepared in analogy to reference⁵³ (see also SI). In brief, the pre-patterned chip is immersed in 0.2 mM isopropanol solution of 12-mercaptododecylphosphonic acid (HS-C₁₂-PA) for 70 hours to form the nonpolar self-assembled monolayer (SAM). The SAM in the channel region is removed with O₂ plasma and replaced by the positively charged SAM 3-methyl-1-(12-phosphonododecyl) imidazolium bromide. *CE*-MoS₂ in aqueous solution is selectively deposited by dip-coating for 24 hours.

Modelling: The simulation scheme adopted throughout this work is based on Density Functional Theory (DFT) as implemented in AIMS and CP2K codes.⁵⁷ PBE⁵⁸ exchange and correlation functional with Van der Waals correction at the Grimme-D3 level⁵⁹ has been used. In CP2K the wave-functions are expanded on a Gaussian basis set, whereas an auxiliary plane-wave expansion of the electronic density is used to efficiently evaluate the Hartree part of the Coulomb interactions and the exchange-correlation energy. Goedecker-type pseudopotentials are used for all atoms with triple- ζ plus polarization (TZVP) Gaussian basis sets. A kinetic cutoff of 300 Ryd is used for the plane-wave expansion of the electronic density and BZ integration is restricted to the Γ -point. The geometry is relaxed until the maximum force on each atom is less than 0.01 eV/Å.

To model both the clean and functionalized MoS₂ monolayers we used hexagonal cells obtained replicating 6x6 times the hexagonal MoS₂ unit cell, with 1T symmetry and lattice parameter $a = 3.16$ Å. The use of this cell guarantees a sampling of the Brillouin zone which leads to an error on the evaluation of total energy smaller than 0.001 eV/cell. Different images of the monolayer along z are separated by a vacuum region of approximately 45 Å. Neutral and charged (with $-1 |e|$ and $-4 |e|$ excess charge) substrates have been compared. An energy correction for multipole error in Hartree potential has been added.

ASSOCIATED CONTENT

Supporting Information: Purification of *CE*-MoS₂, comparison of intercalation conditions, further characterization of functionalized MoS₂ (zeta potential, Raman, XPS, XRD), details on redispersion experiments, functionalization of chemically exfoliated MoS₂ from intercalation using excess *n*-BuLi, functionalization after deposition on substrates, details DFT calculations. Supporting Information is available free of charge from the ACS Nano home page.

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The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

Acknowledgements

The research leading to these results has received funding from the European Union Seventh Framework Program under grant agreement n°604391 Graphene Flagship. In addition, CB acknowledges the German research foundation DFG (BA 4856/1-1). JNC acknowledges the European Research Council grant SEMANTICS for financial support. KCK, IA, PV, FH, AH, ZW and MH acknowledge the Collaborative Research Centre SFB953 “Synthetic Carbon Allotropes”. KCK acknowledges the Erlangen Graduate School Molecular Science (GSMS).

HCN and VN acknowledge ERC 2DNanoCaps, SFI PIYRA and FP7 MoWSeS. GSD, NMcE and NB acknowledge SFI for PI_10/IN.1/I3030. ZW and MH acknowledge the Cluster of Excellence “Engineering of Advanced Materials”. SS and CSC have been supported by the European Research Council (Quest project). All calculations were performed on the Parsons cluster maintained by the Trinity Centre for High Performance Computing, under project ID: HPC_12_0722. This cluster was funded through grants from Science Foundation Ireland.

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