

HORIZON EUROPE PROGRAMME
HORIZON-CL4-2023-DIGITAL-EMERGING-01-33

GA No. 101135196

Developing New 2D Materials and Heterostructures for Printed Digital Devices



2D-PRINTABLE - Deliverable report

D2.1. – Tuneable functionalization of TMDs



Funded by
the European Union

Deliverable No.	D2.1	
Related WP	WP 2	
Deliverable Title	Tuneable functionalization of TMDs	
Deliverable Date	2024-06-30	
Deliverable Type	REPORT	
Dissemination level	Public (PU)	
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Approved by	Jonathan Coleman (TCD) - Project Coordinator	24.6.2024
Status	Final	24.6.2024

Document History

Version	Date	Editing done by	Remarks
V1.0	5.6.2024	CB	
V1.1			
V2.0	24.6.2024	CB	
V3.0			
FINAL			

Project Scientific Abstract

The 2D-PRINTABLE project aims to integrate sustainable large-scale liquid exfoliation techniques with theoretical modelling to efficiently produce a wide range of new 2D materials (2DMs), including conducting, semiconducting, and insulating nanosheets. The focus includes developing the printing and liquid phase deposition methods required to fabricate networks and multicomponent heterostructures, featuring layer-by-layer assembly of nanometer-thick 2DMs into ordered multilayers. The goal is to optimize these printed networks and heterostructures for digital systems, unlocking new properties and functionalities. The project also seeks to demonstrate various printed digital devices, including proof-of-principle, first-time demonstration of all-printed, all-nanosheet, heterostack light-emitting diodes (LEDs). In conclusion, 2D-PRINTABLE will prove 2D materials to be an indispensable material class in the field of printed electronics, capable of producing far-beyond-state-of-the-art devices that can act as a platform for the next generation of printed digital applications.

Public summary

This report deals with progress of defect (and covalent) functionalisation of 2D materials using transition metal dichalcogenides (TMDs) as model substance. While many different functionalisation strategies for TMDs are described in literature to date, the mechanistic understanding is very premature due to a range of complex interactions that can occur between functional group and the TMD itself, as well as the different types of defects that might be present. In order to exploit chemical functionalisation for next generation printed electronics, e.g. to achieve controllable and stable chemical doping, nanosheet cross-linking in networks or further tune nanosheet properties, e.g. enhance photoluminescence quantum yields, it is of importance to fundamentally understand the underlying interactions. This will be key to develop chemical intuition on the one hand and give access to rational design of chemical modification on the other.

In the first few months of 2D PRINTABLE, we focused on the two most widely used functionalisation strategies: i) Filling of chalcogen vacancy defects with thiols and ii) Electrophilic radical addition using diazonium salts. For the thiol-based functionalisation, we could further extend the versatility of the approach by applying the concept also to telluride-based TMDs and by using disulfides instead of thiols which was previously shown to reduce side reactions and dimerization when applied to the functionalisation of Au.

For the diazonium functionalisation, the main aim was to gain deeper understanding of the chemical binding and the role of defects by using the same reaction sequence in comparative studies using MoS₂ produced by different exfoliation methods (sonication-assisted liquid phase exfoliation, chemical exfoliation using n-BuLi and electrochemical exfoliation using tetraalkyl ammonium salts as intercalant). For the first time, diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy, allowed the identification of characteristic vibrations from the grafting to the MoS₂ surface providing evidence that both a covalent S-C bond is formed, as well as anchoring to oxygen containing defects (e.g. sulfonyl and sulfoxides) occurs. The binding state is comparable for different exfoliation techniques, but the degree of functionalisation is tuneable showing a significantly higher degree of functionalisation for chemically exfoliated nanosheets (up to 40% of S) compared to liquid exfoliated MoS₂ (~2% of S).

Characterisation of electrochemically exfoliated MoS₂ was hindered through the presence of adsorbates that are added as stabiliser after the electrochemical intercalation. These organic residues can hinder the covalent and defect-based binding of the reagent and at the same time, can alter the intrinsic nanosheet properties and likely also affect the junction resistance in networks. To this end, the newly established DRIFT spectroscopy was exploited to design washing protocols to remove the organic residues.

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Abbreviations

Abbreviation	Explanation
AFM	Atomic force microscopy
CE	Chemical exfoliation
DMF	Dimethylformamide
DRIFT	Diffuse reflectance infrared Fourier transform
EE	Electrochemical exfoliation
FIR	Far-infrared
IPA	Isopropanol
LPE	Liquid Phase exfoliation
MIR	Mid-infrared
MS	Mass spectrometry
PVP	Poly vinyl pyrrolidone
SEM	Scanning electron microscopy
TGA	Thermogravimetric analysis
TMD	Transition metal dichalcogenide
XPS	X-ray photoelectron spectroscopy

1 Introduction

This deliverable reports on progress within the Task 2.1 “Defect engineering and functionalization” and Task 2.2. “Covalent functionalization”. The overall aim is phrased as objective 2.1, namely to push the boundaries of defect engineering and functionalization in 2D materials.

Gaining control and fundamental understanding of the functionalisation is the foundation to use chemical modification to tailor nanosheet properties, control interfaces and achieve chemical cross-linking, e.g. in networks as well as discrete homo- and heterostructures to for example improve network mobility, reduce charge traps, and controllably dope nanosheets. As such, these tasks are at the beginning of the process chain towards printed high performance devices. The results will directly feed into Task 2.4. “Synthesis of flake-level homostructures and heterostructures” and Task 3.3. “Printing high-mobility films of chemically coupled nanosheets forming networks” aiming at objective O2.3 to “Use chemical modification for controlled nanosheets linkage through chemical coupling into discrete assemblies and synthesis of flake-level heterostructures”.

Before moving on to new types of nanosheets, the initial studies described here focus on transition metal dichalcogenides (TMDs). A number of functionalisation strategies have been developed and described in literature. However, comparative studies are often lacking leading to a pre-mature understanding of the underlying chemical mechanisms. To this end, we explore mainly two different strategies for defect and covalent grafting: i) The established thiol chemistry which is extended to selenide and telluride based TMDs. ii) Diazonium chemistry for a comparative study on the reactivity of nanosheets produced by different methods (liquid phase exfoliation, chemical and electrochemical exfoliation).

An important aspect within these projects is to identify versatile characterisation techniques to understand both binding, as well as degree of functionalisation. This is essentially Task 4.2. “Basic characterization of functionalized/doped nanosheets and flake-level homo- and heterostructures” of the DOA. To this end, we now established diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy as new technique within the consortium and also the community. As such, the results described here are also important first steps for Task 4.5. “Methodological development”.

All tasks and objectives linked to this deliverable will commence through the entire duration of 2D-PRINTABLE. Based on the results discussed below obtained within the first 9 months, we are confident that the objectives related to this deliverable will be achieved.

2 Methods

2.1 Background

For the results described in this deliverable, transition metal dichalcogenides (TMDs) were used as model substance for chemical defect functionalisation. While proof of concept reactions for TMDs are described in literature,¹ a fundamental understanding of reaction mechanisms and the binding state of the functional group is still lacking due to challenges associated with the characterisation. In particular, comparative studies between nanosheets produced by different techniques, e.g. sonication-assisted liquid phase exfoliation (LPE), chemical exfoliation (CE) through intercalation and electrochemical exfoliation (EE) have not been described in a comprehensive way. As such, it is not clear in which way the reactivity is distinct between different production methods due to different types and content of defects. Further, defect functionalisation through filling of S vacancies with thiols is commonly employed and already showed success in enhancing mobilities in networks through cross-linking.² However, it is not clear in which way the same strategy can be applied to Se and Te-based TMDs.

2.2 Procedures

Samples were produced through established procedures of sonication-assisted LPE,³ chemical exfoliation after intercalation with n-BuLi⁴ and electrochemical exfoliation⁵ using alkyl ammonium electrophiles. The nanosheet size distribution was typically narrowed through cascade centrifugation.⁶ Functionalisation with thiols² and diazonium salts⁷ was conducted in analogy to previous work in the respective groups. Characterisation through optical extinction spectroscopy, Raman spectroscopy, microscopy (optical, SEM, AFM) and XPS is also well established within the consortium and was applied according to typical workflows.

For diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy in the mid-infrared (MIR) and far-infrared (FIR) bulk powders of exfoliated and functionalised MoS₂ were obtained through freeze drying and mixed with dry CsI as matrix and subjected to the diffuse reflectance measurement. Typically, multiple spectra were measured on each sample with a resolution of 1 cm⁻¹. The CsI background was subtracted as baseline prior to the measurement of the samples.

A number of washing protocols were tested to remove adsorbates (e.g. surfactant, polymeric stabiliser) from LPE and EE MoS₂. For this purpose, MoS₂ nanosheets were centrifuged at high speeds to obtain a pellet as a sediment which was subsequently redispersed in the washing solution and centrifuged again.

2.3 Data Analysis

The data was typically analysed using OriginPro. XPS fitting was conducted using CasaXPS processing software. For DRIFT spectroscopy, a constant baseline was first subtracted, the reflectance signal converted to Kubelka Munk units followed by a second manual baseline subtraction.

3 Results & Discussion

3.1 Results

3.1.1 Functionalisation with Thiols

Defect engineering of sulfur vacancies in disulfide TMDs have been the subject of extensive work during the last decade as a route to anchor thiolated molecules to the basal plane or edges of MoS_2 as well as WS_2 and ReS_2 .^{1, 8} It was also recently shown that such thiol end group can be used to anchor molecules to diselenides such as WSe_2 .⁹ To address the general applicability, we have explored the same defect healing process of thiolated molecule in case of Te vacancies on the basal plane of MoTe_2 (Figure 3.1A). The efficient healing was demonstrated by Raman spectroscopy, XPS and back gated field effect transistors.

Along a similar line, the presence of a thiol end group in molecules, in particular when exposing a polyaromatic chain, is known to lead to a notable instability due to the tendency of dimerizing into disulfides. Because of this reason, disulfide molecules are used for example to control their chemisorption on Au electrodes, in view of their higher stability. Such a strategy is of course a source of inspiration, inspiring the curiosity of scientists to explore whether a disulfide containing molecule can be anchored on the basal plane of MoS_2 in a process that first involves the breaking of the S-S bond, followed by the linkage on the sulfur vacancy. To address this question, we have anchored two disulfide molecules on MoS_2 that by design can n- or p-dope the 2D semiconductor (Figure 3.1B). Such an efficient functionalization and electronic modulation was demonstrated by Raman spectroscopy, XPS and backgated field-effect transistors.

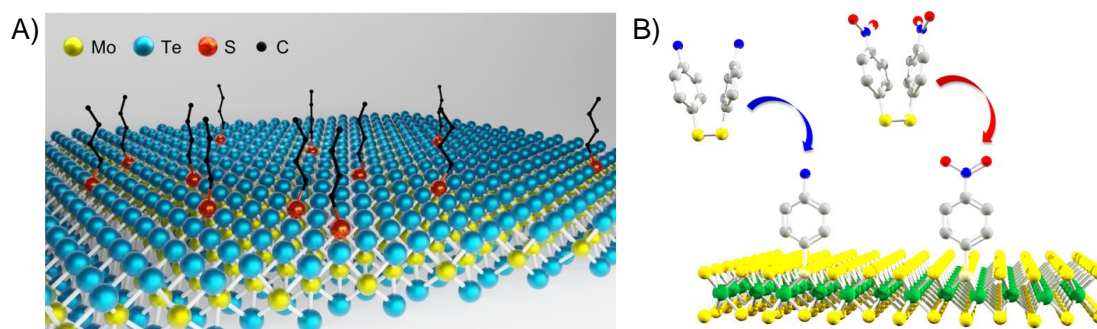


Figure 3.1: Schematics of thiol functionalisation of TMDs. A) Cartoon of MoTe_2 lattice with point S-vacancies healed with butanethiols, B) Cartoon of MoS_2 vacancy healed with two differently functionalized disulfides molecules.

3.1.2 Functionalisation with Diazonium Salts

Another strategy for the covalent and/or defect functionalisation of TMDs is based on the reaction with strong electrophiles such as diazonium salts. This was first demonstrated for chemically-exfoliated nanosheets.¹⁰ These are negatively charged 1T' nanosheets which readily react in an anticipated radical reaction which quenches the negative charge. Previous work described that the functional group is anchored through a sulfur-carbon bond with strongly covalent character.^{7, 10} In turn, diazonium functionalisation has also been achieved for charge neutral nanosheets, such as CVD-grown MoS_2 or

LPE nanosheets.¹¹ Here, it was suggested that also S-C bonds are formed, albeit through a cooperative, defect-mediated mechanism. To date, it is not clear whether the binding to LPE and CE nanosheets is indeed similar and where EE nanosheets should be placed in this sequence (Figure 3.2). This is due to challenges associated with directly characterising the binding state of the functional group. Even if the binding state was comparable, degrees of functionalisation vary.^{7, 10, 11} One hypothesis is that the grafting density of the electrophilic diazonium salt is governed by the charge density of negative charges. Zeta potential measurements suggest that LPE nanosheets are relatively charge neutral in neat solvents (i.e. the absence of surfactants), while CE nanosheets are strongly negatively charged and EE nanosheets have intermediate zeta potential. This would suggest that the grafting density of the functional groups can be easily varied through the exfoliation method.

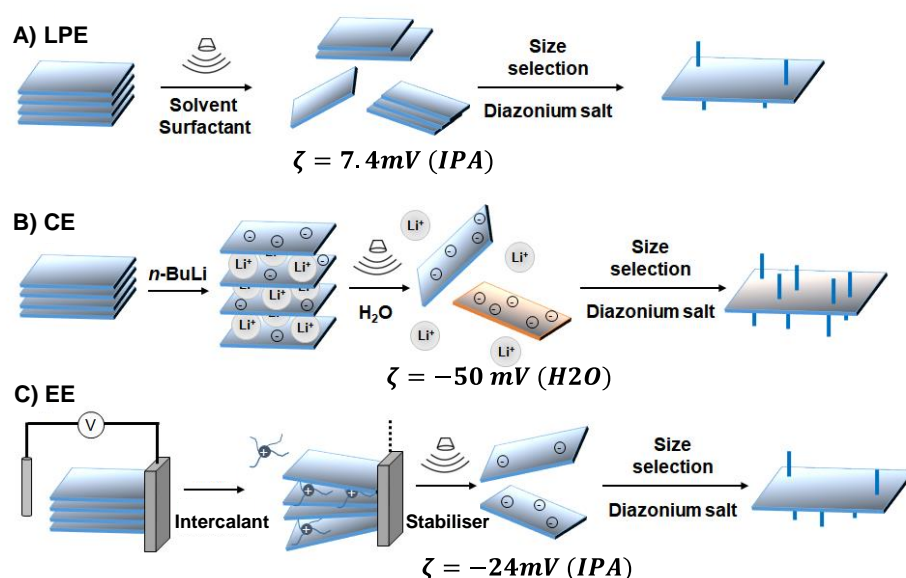


Figure 3.2: Schematic of the exfoliation and diazonium functionalisation sequence using A) Sonication-assisted liquid exfoliation, B) Chemical exfoliation and C) Electrochemical exfoliation. The measured zeta potentials of the MoS₂ nanosheets is indicated. Based on this, one would expect the lowest grafting density with the electrophile for LPE and the highest for CE.

To investigate this, nanosheets were produced by sonication-assisted LPE in aqueous surfactant, CE and EE using established protocols. After exfoliation, the size distributions were narrowed through centrifugation and the nanosheets were washed with water and isopropanol (IPA) to remove as much stabiliser as possible prior to addition of the diazonium salt. After the reaction, side products and unreacted diazonium salt were again removed by centrifugation-based washing. Reference samples were produced undergoing the same work-up.

Optical extinction spectra of the as-produced samples are shown in Figure 3.3A-C. For LPE nanosheets, these can be interpreted in terms of increased nanosheet lateral size and thickness based on the changes in the optical profile.¹² This can be a result of the centrifugation-based washing which removes the smallest nanosheets in the supernatant along with impurities, as well as aggregation. This effect is less pronounced for the functionalised samples compared to the reference. Optical microscope

images of thin films (inset in Figure 3.3A) produced by Langmuir Schafer type deposition show relatively homogeneous films suggesting aggregation to play a minor role. The optical profile of CE MoS₂ is characteristic of the 1T phase (Figure 3.3B). The transitions in the UV region are smeared out after functionalisation consistent with literature (albeit not understood).⁷ The EE MoS₂ nanosheets (Figure 3.3B) show a sharpening of the A and B excitonic transitions (600-700 nm), especially after functionalisation, as well as an increase in the nonresonant scattering >700 nm. The former could be a signature of dedoping, while the latter suggests aggregation which is in this case confirmed by optical spectroscopy on thin films.

Dried powders of the nanosheets were subjected to DRIFT in the FIR-MIR range. In the FIR region, calculations predict¹³ the presence of IR active out of plane and in plane Mo-S vibrations of 2H MoS₂. These have not been previously studied experimentally for exfoliated nanosheets. The in plane Mo-S vibration is well discernible for 2H LPE MoS₂ (Figure 3.3D) and also present in EE MoS₂ (Figure 3.3F). No changes between reference and functionalised samples are observed suggesting that the majority of the nanosheets are structurally intact. The FIR region of CE MoS₂ (Figure 3.3E) is mostly bereft of features consistent with the presence of a distorted 1T polytype where 2H MoS₂ vibrations are expected to be absent. While this might not be surprising, it is unfortunate, as it does not allow for a normalisation to the Mo-S vibration in the wider MIR-FIR spectral range which can be used for a semi-quantitative assessment of the presence of the functional group.

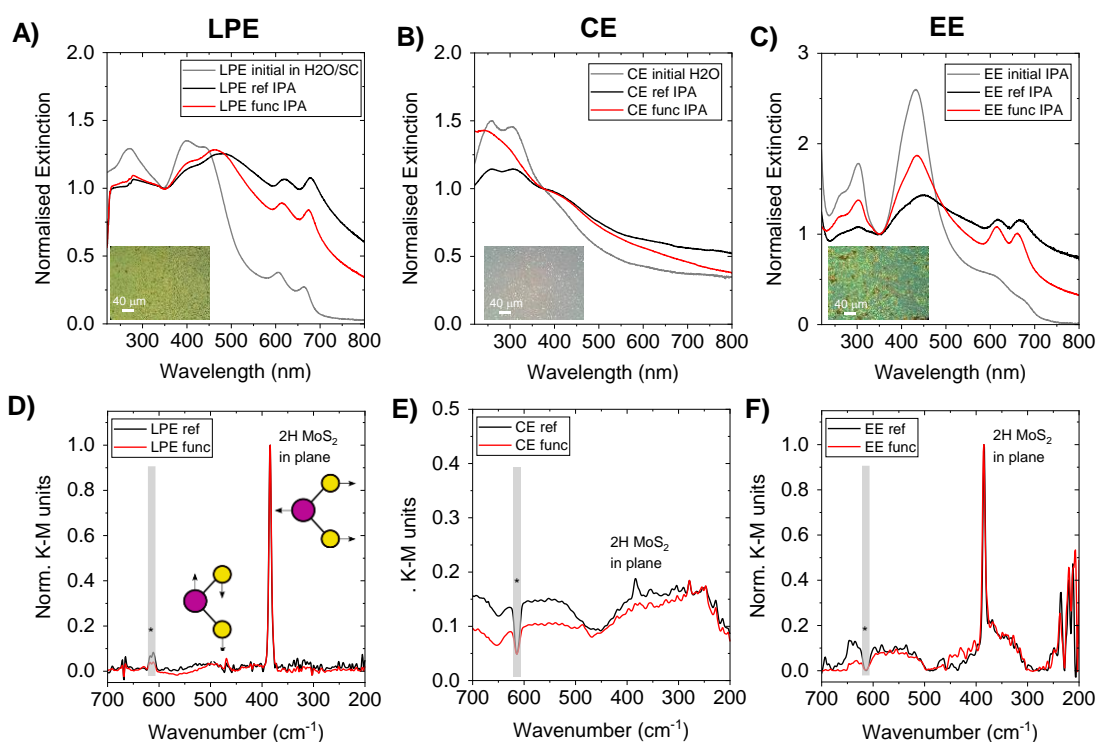


Figure 3.3: Optical characterisation of functionalised nanosheets compared to the reference material. A-C) Optical extinction spectra of A) LPE nanosheets, B) CE nanosheets, C) EE nanosheets. The inset shows an optical micrograph of Langmuir-Schafer type films. D-F) DRIFT in the FIR of D) LPE nanosheets, E) CE nanosheets, F) EE nanosheets

The MIR spectral range clearly shows the presence of the functional group for LPE and CE nanosheets (Figure 3.4). Unfortunately, the spectra of EE MoS₂ (not shown) are dominated by poly-vinyl

pyrrolidone (PVP) which was used as stabiliser after exfoliation. Obviously, different washing protocols are required in this case (addressed in section 3.1.3). This is not only important in terms of characterisation, but also to achieve a controlled reaction since diazonium salts are highly reactive and side reactions with adsorbates cannot be excluded. Therefore, only LPE and CE nanosheets are discussed in the following.

In the MIR, vibrations that can be clearly assigned to the functional group (shaded in blue) are observed for both LPE and CE MoS₂ (Figure 3.4). In the reference samples, no distinct vibrations are observed except for alkyl vibrations from hydrocarbons that are often associated with MoS₂.¹⁴ In addition, a number of vibrations can be observed which give indications of the binding state. For both LPE and CE MoS₂, signals attributed to organic sulfonyl, sulfoxide and C-S are detected, albeit with different relative intensities. Note that the sulfonyl and sulfoxide vibrations are absent in the reference. On the one hand, this confirms that the binding state of the functional group is similar for LPE and CE MoS₂ with the exception of a feature at ~940 cm⁻¹ in LPE MoS₂ which could not yet be assigned. On the other hand, the data evidences that diazonium functionalisation is a mixture of both covalent (formation of C-S) and defect functionalisation (anchoring to sulfonyl and sulfoxides).

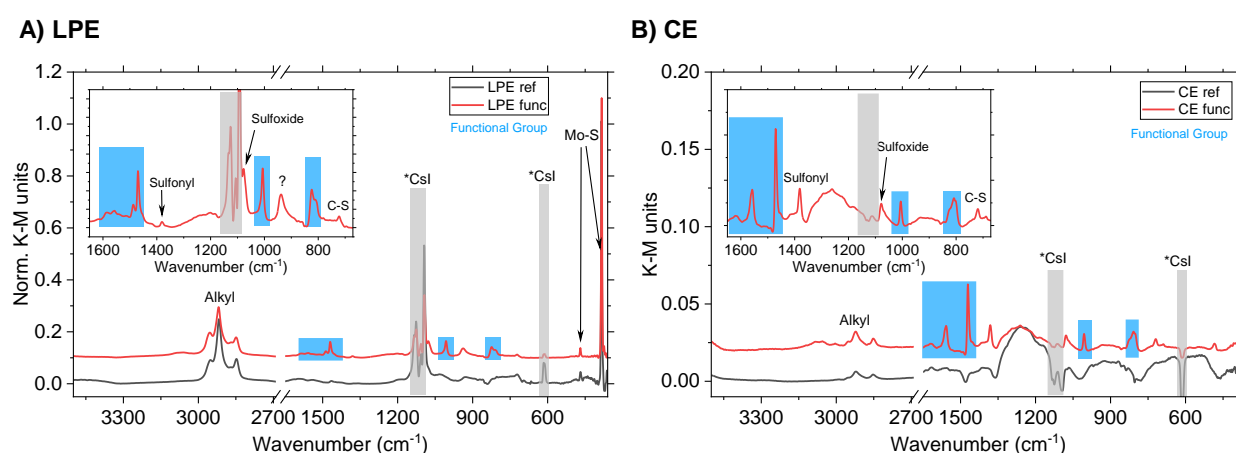


Figure 3.4: DRIFT spectra over the FIR-MIR spectral range of A) LPE MoS₂ and B) CE MoS₂ showing similar vibrations in both cases assigned to the functional group (shaded blue area) as well as the binding to the MoS₂ scaffold.

To estimate the degree of functionalisation, XPS was performed. The Mo3d and S2p core level spectra are shown in Figure 3.5. The core level spectra of LPE nanosheets are characteristic for such type of samples with signals for 2H MoS₂ and traces of MoO₃ in the Mo3d core level (Figure 3.5A) and only a single S species in the S2p core level (Figure 3.5B). The spectra of reference and functionalised sample are virtually identical showing no sign of functionalisation. In the survey spectra, a characteristic element of the functional group is detected with an intensity ratio that suggests 2% of the S atoms bear a functional group. While this could be physisorbed functional group, it is emphasized that defect/covalent functionalisation is evidenced by DRIFT. Obviously, the degree of functionalisation is too low to be reliably detected by fitting S2p core level spectra. This is surprising, as XPS is usually considered a major characterisation technique for functionalisation of TMDs.

In contrast, the core level spectra of functionalised CE MoS₂ show obvious differences to the reference. In the Mo3d core level (Figure 3.5C), three Mo components are observed assigned to 2H MoS₂, 1T MoS₂ as well as MoO₃. The 1T/2H ratio in the functionalised sample (1.1/1) is higher than in the

reference (0.5/1) consistent with literature⁷ which reported that functionalisation stabilises the 1T polytype which is otherwise metastable and rearranges to 2H with time. The S core level spectrum (Figure 3.5D) of the reference is best fitted with 2 components corresponding to 2H and 1T MoS₂, respectively. In the functionalised sample, an additional doublet is required at higher binding energy, i.e. higher oxidation state. This makes up ~40% of the S signal and is attributed to a contribution from “defective” S (organic sulfonyl, sulfoxide), as well as the covalently functionalised S. A deconvolution is not possible within the accuracy of the measurement/fitting. Thus, the XPS demonstrates an ~20x higher degree of functionalisation of CE MoS₂.

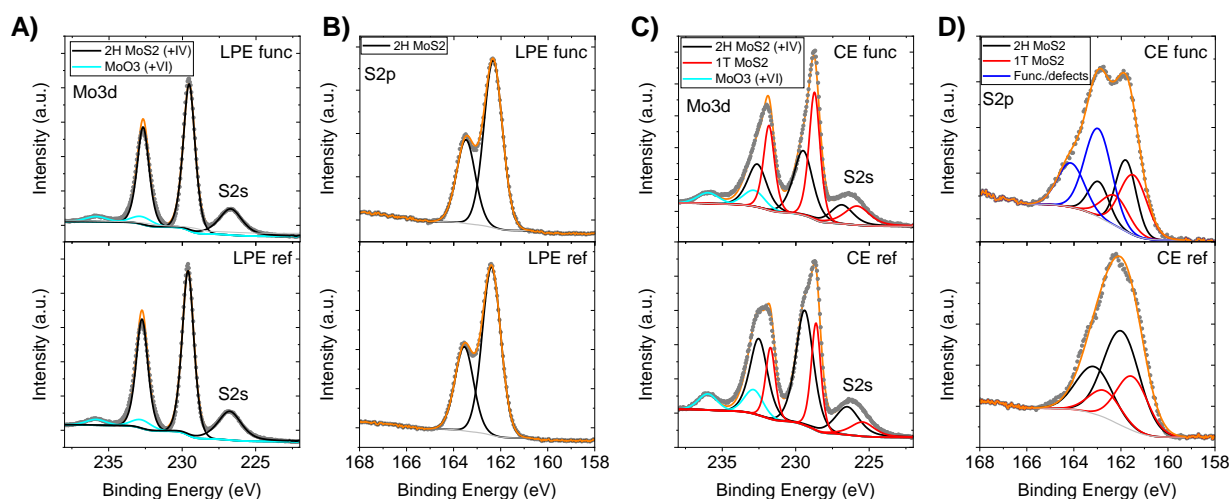


Figure 3.5: Fitted XPS core level spectra of functionalised MoS₂ compared to the respective reference samples from A-B) LPE and C-D) CE. A, C) Mo3d core level spectra; B, D) S2p core level spectra.

Note that thermogravimetric analysis coupled to mass spectrometry (TGA-MS) was also planned, but could currently not yet be conducted. The delivery of a new instrument at UKa was delayed, while the MS coupling at UNISTRA is currently not functional and the setup at TUD requires relatively large masses not suitable for this work.

In summary, the study clearly showed that diazonium functionalisation leads to the formation of a C-S bond, but also functionalisation of oxygen-containing defects. The binding state for LPE and CE MoS₂ is similar, but the grafting density is much higher for CE nanosheets. Further, DRIFT spectroscopy was shown to be an excellent characterisation tool with a better sensitivity to detecting the functionalisation than XPS core level spectra. Characterisation and likely functionalisation of EE MoS₂ was hindered through surface adsorbates.

3.1.3 Purification of the TMD surface

In light of the finding that EE MoS₂ nanosheets contain a significant amount of surface adsorbates in spite of attempted washing procedures that were successful for LPE and CE nanosheets, it was investigated in greater detail how surfactants and stabilisers can be efficiently removed make the surface of nanosheets accessible for reagents in the liquid phase. The washing procedure was followed by UVVis extinction spectroscopy as well as DRIFT in the MIR and FIR. Here, a normalisation to the Mo-S vibration in the FIR enables a direct comparison across washing steps and across procedures. This is

important, as previously, such information was only reliably accessible using TGA-MS or time-of-flight secondary ion mass spectrometry.

Figure 3.6 shows four sequences of washing LPE nanosheets produced in different small molecule surfactants or popular solvents. After 2-3 washing steps, small molecule surfactants are removed to below the detection limit (Figure 3.6A,B). Further, it was possible to identify solvents that leave only negligible or no adsorbates making washing obsolete (Figure 3.6C), while other solvents leave residues that are much harder to remove than small molecule surfactants (Figure 3.6D). This can be a result of sonication-induced polymerisation of the solvent which then leaves a residue on the surface that cannot be removed through simple washing at room temperature.

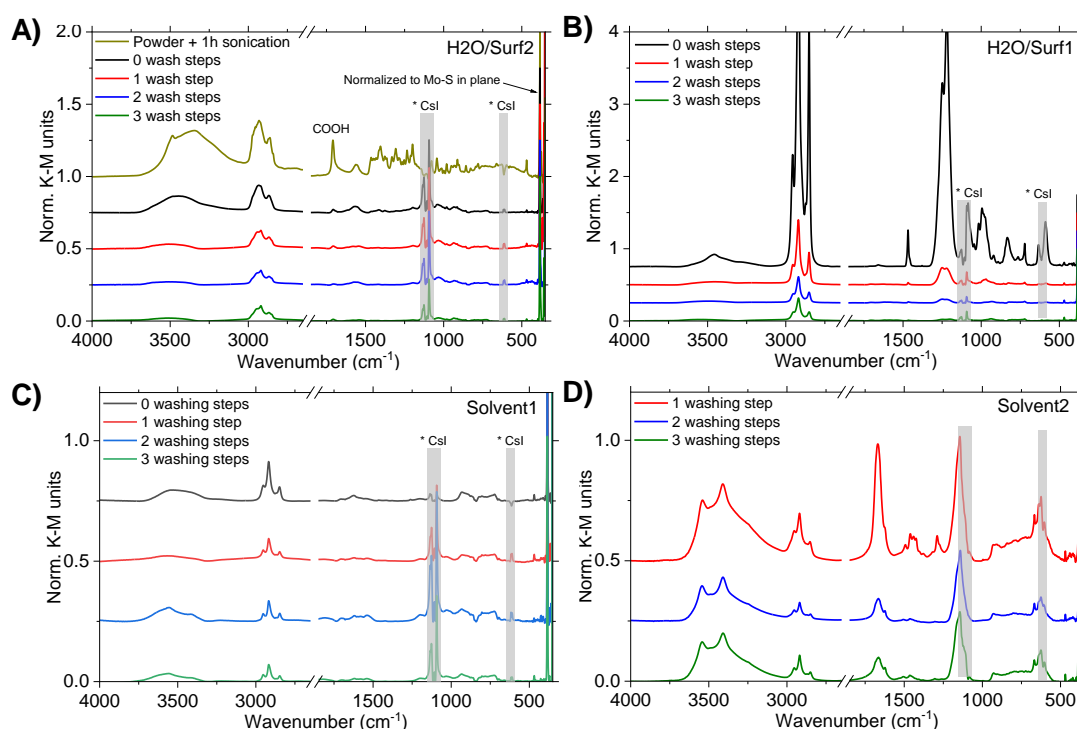


Figure 3.5: Removal of surface adsorbates from LPE MoS₂: DRIFT spectra in the MIR-FIR spectral range for washing sequences of LPE nanosheets. A-B) Data for MoS₂ stabilised by small molecule surfactants. C-D) Data for solvent-stabilised nanosheets

For EE MoS₂ produced through electrochemical intercalation of tetrapentyl and tetrahexyl ammonium bromide, respectively, PVP in dimethylformamide (DMF) was used to stabilise the nanosheets. For such dispersions, typically washing with DMF and IPA is performed to remove a majority of the surface adsorbates. However, no systematic report is found in the literature to the best of our knowledge. Due to their high aspect ratio, EE nanosheets are ideal as components in physically coupled nanosheet networks after Langmuir Schafer-type deposition due to the possibility of forming conformal junctions with low junction resistance.^{5, 15} For such nanosheet networks, adsorbates on the surface are problematic for two reasons: First, they might still contribute to junction resistance. Second, they can intrinsically dope the nanosheets and thus impede with controlled doping. Thus, it is important to be able to measure in which way these adsorbates can be removed. To allow for functionalisation and potentially nanosheet cross-linking during film formation, it is desired that this can be achieved in the liquid phase prior to film formation. However, when performing a purification of the nanosheet surface

in the liquid phase, there is always a risk that colloidal stability is lost and nanosheet aggregation occurs.

The removal of surface adsorbates was first followed by UVVis extinction spectroscopy (Figure 3.7A). While DMF as solvent strongly absorbs at wavelength < 270 nm, making this spectral region inaccessible, measurement in IPA allows to observe an absorption onset in supernatants after centrifugation-based washing. While this onset is not characteristic, it is clearly reduced in intensity from step to step confirming the removal of surface adsorbates. The effect of the purification can also be seen in the extinction spectra of the MoS₂ dispersion (Figure 3.7B). After the removal of surface adsorbates, the spectral profile is different in the UV region, i.e. the absorption onset at ~ 270 nm is no longer observed. The profile of the excitonic MoS₂ transition is similar, with slightly increased nonresonant scattering suggesting minor aggregation.

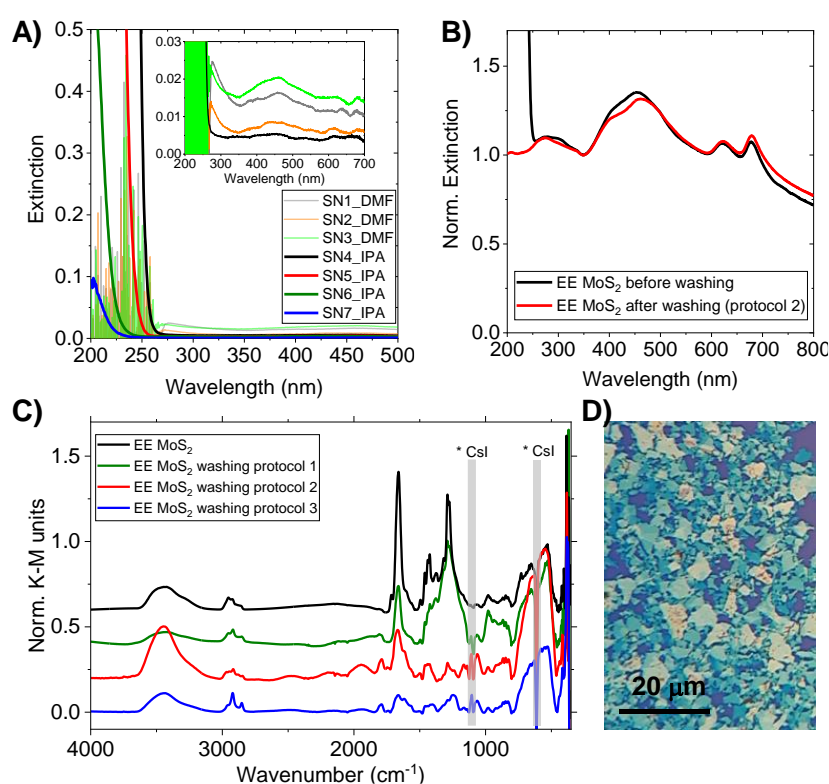


Figure 3.7: Removal of surface adsorbates from EE MoS₂. A) UVVis extinction spectra of a washing sequence showing supernatants after subsequent centrifugation-based washing. B) UVVis extinction spectra before and after washing. C) DRIFT spectra in MIR and FIR normalised to the Mo-S vibration comparing the final samples using different washing protocols. D) Optical micrograph of a MoS₂ nanosheets deposited after liquid-liquid interface assembly after applying washing protocol 3.

As in the case of LPE nanosheets, the nanosheets were collected and dried after the washing protocols and subjected to MIR and FIR DRIFT. Normalisation to the Mo-S out of plane vibrations allows for a direct comparison of the intensity of the organic molecules associated with the MoS₂ surface. The spectra in Figure 3.7C show that it was possible to elaborate a washing protocol, which reduced the characteristic PVP vibrations to almost only the noise level in the spectra. Figure 3.7D shows an optical micrograph of the purified nanosheets deposited by liquid-liquid interface assembly which confirms that, with our new protocol, nanosheet aggregation can also be negligible.

3.2 Contribution to project (linked) Objectives

The results described in this deliverable will greatly contribute to the overall project objectives, in particular to developing advanced chemical modification methods to further tune the properties of nanosheets and achieve chemical coupling to enhance nanosheet mobility. While the functionalisation strategies described here are not novel as such, the comparative study of LPE, EE and CE MoS₂ greatly improved our fundamental understanding of underlying chemical reactions.

Secondly, any controlled functionalisation will be hindered by surface adsorbates from the production, which was shown to be particularly problematic for the high aspect ratio EE nanosheets. The newly developed ability to measure the surface contamination (and subsequent functionalisation) easily, as well as the new protocols to purify the surface will be the foundation to improve network mobility in both physically and chemically coupled nanosheet networks. Further, the purification will be key to achieve controlled chemical doping.

3.3 Contribution to major project exploitable result

N/A

4 Conclusion and Recommendation

In conclusion, we are well on track in fulfilling the objective of controlled defect and covalent functionalisation even though hiring of researchers was delayed for some partners (e.g. UKa).

Firstly, we could demonstrate the versatility of thiol chemistry also for selenide and telluride-based TMDs. Secondly, we gained a deeper understanding in diazonium-based functionalisation for nanosheets produced by different exfoliation strategies. Thirdly, we could establish DRIFT as novel characterisation tool to assess the presence of organic molecules on the nanosheet surface in a semi-quantitative way and to gain insights into the nature of the chemical binding.

The DRIFT investigations also clearly showed that controlled chemical modification of high aspect ratio electrochemically exfoliated nanosheets can be more challenging than anticipated due to the presence of the stabilisers added after electrochemical intercalation. Therefore, significant efforts were redirected to purify the nanosheet surface in the liquid phase to make the material accessible for further derivatisation. While this caused a slight delay in addressing chemical coupling in networks during or after film formation, the findings are extremely important for all types of devices targeted where clean interfaces will be key.

5 Risks and interconnections

5.1 Risks/problems encountered

The following new risk was identified and successfully mitigated during the course of the project resulting in a minor delay with respect to the progress in Task 3.3 (High mobility films of chemically-coupled nanosheets).

Risk No.	What is the risk	Probability of risk occurrence ¹	Effect of risk ¹	Solutions to overcome the risk
WP2.new	The surface of nanosheets is covered by adsorbates potentially interfering with functionalisation	1	3	Design washing protocols to remove adsorbates

¹⁾ Probability risk will occur: 1 = high, 2 = medium, 3 = Low

5.2 Interconnections with other deliverables

This deliverable is naturally connected to D4.1 “Characterization of nanosheets, networks and heterostacks” built from initially available 2D materials due in month 12, as characterisation is an integral part for all aspects of 2D-PRINTABLE.

In particular, the designing of washing protocols described in section 3.1.3. was enabled by establishing DRIFT-IR spectroscopy as new characterisation tool for the semi-quantitative analysis of organic moieties on the nanosheet surface. This is also the foundation for parts of D4.3 “Protocols for new characterization methodologies” (month 24).

6 Deviations from Annex 1

None.

7 References

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8 Acknowledgement

The author(s) would like to thank the partners in the project for their valuable comments on previous drafts and for performing the review.

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1	TCD	TCD THE PROVOST, FELLOWS, FOUNDATION SCHOLARS & THE OTHER MEMBERS OF BOARD, OF THE COLLEGE OF THE HOLY & UNDIVIDED TRINITY OF QUEEN ELIZABETH NEAR DUBLIN
2	UNISTRA	UNIVERSITE DE STRASBOURG
3	UKa	UNIVERSITAET KASSEL
4	BED	BEDIMENSIONAL SPA
5	TUD	TECHNISCHE UNIVERSITAET DRESDEN
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7	UNR	UNIRESEARCH BV
8	UniBw M	UNIVERSITAET DER BUNDESWEHR MUENCHEN
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This project has received funding from the European Union's Horizon Europe research and innovation programme under grant agreement No 101135196. Views and opinions expressed are however those of the author(s) only and do not necessarily reflect those of the European Union. Neither the European Union nor the granting authority can be held responsible for them.

9 Appendix A - Quality Assurance Review Form

The following questions should be answered by all reviewers (WP Leader, reviewer, Project Coordinator) as part of the Quality Assurance procedure. Questions answered with NO should be motivated. The deliverable author will update the draft based on the comments. When all reviewers have answered all questions with YES, only then can the Deliverable be submitted to the EC.

NOTE: This Quality Assurance form will be removed from Deliverables with dissemination level “Public” before publication.

Question	WP Leader	Reviewer	Project Coordinator
	Xinliang Feng (TUD)	Zdenek Sofer (VSCHT)	Jonathan Coleman (TCD)
1. Do you accept this Deliverable as it is?	Yes	Yes	Yes / No (elaborate)
2. Is the Deliverable complete? - All required chapters? - Use of relevant templates?	Yes	Yes	Yes / No (elaborate)
3. Does the Deliverable correspond to the DoA? - All relevant actions performed and reported?	Yes	Yes	Yes / No (elaborate)
4. Is the Deliverable in line with the 2D-PRINTABLE objectives? - WP objectives - Task Objectives	Yes	Yes	Yes / No (elaborate)
5. Is the technical quality sufficient? - Inputs and assumptions correct/clear? - Data, calculations, and motivations correct/clear? - Outputs and conclusions correct/clear?	Yes	Yes	Yes / No (elaborate)
6. Is created and potential IP identified and are protection measures in place?	NA	NA	Yes / No (elaborate)
7. Is the Risk Procedure followed and reported?	Yes	Yes	Yes / No (elaborate)
8. Is the reporting quality sufficient? - Clear language - Clear argumentation - Consistency - Structure	Yes	Yes	Yes / No (elaborate)