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Developing New 2D Materials and Heterostructures for Printed Digital Devices

2D-PRINTABLE - Deliverable report

D2.3 – Formation of discrete assemblies of 2DMs

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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 2DM films 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

The report outlines the progress in the formation of discrete assemblies of two-dimensional (2D) materials based on the use of bidentate molecular linkers. To synthesize solution-processed heterostructures, an approach based on defect-engineering of liquid-phase exfoliated nanosheets to control the in-plane growth of their discrete assemblies in the form of heterostructures from inks of different 2D transition metal dichalcogenides (TMDs) has been devised and exploited. The major achievements of the deliverable D2.3 reported in this document are:

- **Design of a novel stepwise microfluidic strategy** to fabricate discrete assemblies of 2D TMDs (i.e. MoS_2 and WS_2 as 2D building units). To ensure selective bridging, cyclic and sequential deposition of MoS_2, π-conjugated dithiolated molecules and WS_2 has been designed. The use of thiolated molecules was chosen in order to selectively bridge sulfur vacancies, which are mainly located at the edges of MoS_2 and WS_2 flakes.

- **Multiscale characterization protocol** of the synthesized solution-processed discrete heterostructures to validate the methodology and investigate characteristics features of such discrete assemblies. Stepwise optical and scanning electron microscopy (SEM), in-situ electrochemical impedance spectroscopy (EIS), Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) provided full feedback on the formation mechanism.

The work described in this report provides a foundational framework for the assembly of a diverse range of printable low-dimensional complex systems, enabling the realization of precisely engineered discrete assemblies beyond the state-of-the-art.

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Abbreviations & Definitions

Abbreviation	Explanation
2DM	Two-dimensional material
APTES	(3-Aminopropyl)triethoxysilane
BDT	1,4-benzenedithiol
EIS	Electrochemical impedance spectroscopy
FWHM	Full-weight half maximum
IPA	Isopropanol
LPE	Liquid-phase exfoliation
NMP	N-Methyl-2-pyrrolidone
SEM	Scanning electron microscopy
XPS	X-ray photoelectron spectroscopy

1 Introduction

The deliverable D2.3 “Formation of discrete assemblies of 2DMs” mainly focuses on the development of novel chemical routes to modify the nanosheets synthesized in Work Package 1 (WP1), such as defect engineering, and the investigation of physical properties of the newly synthesized discrete assemblies. To this end, key is the identification of anchoring groups and straightforward functionalization strategies for the 2D materials, which represents the foundation of Task 2.1. For instance, as edge-chalcogen vacancies are the most abundant defects in TMDs, these anomalies can be exploited as reactive sites to covalently bridge adjacent flakes to form controlled discrete assemblies. Nevertheless, conventional techniques that use liquid-phase exfoliated (LPE) nanosheets to yield solution-processed heterostructures, such as spin-coating, spray-coating, drop-casting, etc., do not allow selective functionalization and formation of controlled heterostructures in terms of componential selectivity. Indeed, these techniques are governed by deposition randomness that leads to uneven coatings that do not grant full access to the defective vacancies of nanosheets, thus hindering effective functionalization.

Hence, to achieve the objectives of this deliverable, a versatile solution-processed strategy based on defect-engineering and covalent functionalization to selectively control the assembly of discrete assemblies through lateral hetero-junctions from inks of 2D TMDs has been developed. Sequential and cyclic deposition of MoS_2, dithiolated molecules and WS_2 into a microfluidic setup ensures the assembly of preferential in-plane growth of MoS_2-WS_2 heterostructures. The choice of dithiolated organic moieties is critical to bridge adjacent flakes through sulfur vacancies between MoS_2 and WS_2. Moreover, to improve percolation of charges across the system, a conjugated molecule, such as 1,4-benzenedithiol (BDT) has been exploited.

To benchmark other tasks in WP2 (i.e. Tasks 2.2 and 2.4), multiscale characterizations on the assembled solution-processed heterostructures using bidentate molecules have been carried out. Therefore, a characterization protocol for the formation of discrete assemblies od 2DMs has been established.

The results obtained by the activities included in this report are key to the further development of two-dimensional materials-based (2DMs) assemblies endowed with characteristic and on-demand features that go beyond the state-of-the-art. For instance, next deliverables (i.e. D3.3) can benefit from the work carried out in D2.3.

2 Methods and core part of the report

2.1 Background

In this deliverable, inks of LPE MoS_2 and WS_2 were used. As LPE TMDs are mostly endowed with 0D defects, such as sulfur-vacancies, BDT was employed as molecular bridge to assemble lateral assemblies of MoS_2-WS_2. To covalently connect neighbouring MoS_2 and WS_2 nanosheets, a microfluidic setup was designed and a stepwise strategy developed, as microfluidic flow can be exploited to regulate the diffusion of molecules in a controlled manner. To shed the light on the importance of BDT in facilitating the assembly of MoS2-WS2 heterostructures from solution methods, a multiscale characterization has been carried out.

2.2 Procedures

MoS_2 and WS_2 inks were obtained by using established exfoliation protocols,[1] carrying out sonication of pristine powders in N-Methyl-2-pyrrolidone (NMP). The powders were initially dispersed in NMP at a concentration of 20 mg/mL and sonicated for 1 hour using a horn tip-sonicator at 60% amplitude. Then, the dispersions were centrifuged at 3218 g for 1 hour using a Hettich Mickro 220R, and the supernatant was discarded to remove any contaminants. The sediment was then redispersed in fresh NMP and sonicated for additional 5 hours, producing polydisperse stock dispersions. To separate flakes of different sizes, the stock was centrifuged stepwise. First, the largest aggregates were removed by centrifuging at 106.4 g for 90 minutes, and the sediment was kept for further exfoliation. The supernatant was then centrifuged at 425 g for 90 minutes to collect the smaller fraction of flakes. Finally, the sediment was redispersed in isopropanol (IPA).

The discrete assemblies of 2D TMDs were grown stepwise using a microfluidic setup, which included a chamber (Figure 1) with an internal volume of 12 µL and a peristaltic pump. The flow rate was kept steady at 0.6 mL/min throughout the process. To prevent flakes from aggregating and causing clogging, a tube with a diameter of 0.8 mm was used. First, the substrate (previously coated with (3-Aminopropyl)triethoxysilane – APTES – to facilitate the adhesion of single TMDs on the surface of the substrate) was placed in the chamber, and IPA dispersion of MoS_2 was flowed for 3 minutes, resulting in a random distribution of MoS_2 flakes. Next, a 50 mM solution of BDT in IPA was circulated for 2 minutes to functionalize the defect sites on the MoS_2 flakes. Then, a dispersion of WS_2 in IPA was flowed for 10 minutes to enable the functionalization with BDT anchored on previously deposited MoS_2 through the free thiol groups, creating MoS_2-BDT-WS_2 in-plane heterojunctions. After this, BDT was used again, and the previous steps were repeated to build a lateral discrete assembly. Between each step, the entire system was flushed with IPA to clean out any excess material and remove any TMD flakes or unbound BDT molecules.

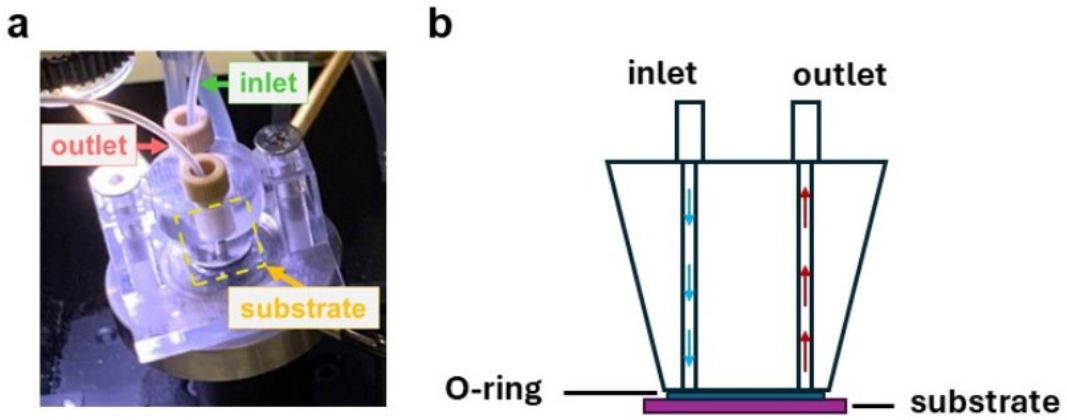

Figure 1. Microfluidic setup. (a) Optical image of the microfluidic chamber and (b) schematic illustration of the microfluidic setup.

The assemblies underwent through an extensive characterization including stepwise optical and electron microscopy investigation, X-ray photoelectron spectroscopy (XPS), in-situ electrochemical impedance spectroscopy (EIS) and Raman spectroscopy.

2.3 Data Analysis

The data was generally analysed using OriginPro. In addition, EIS data was analysed with the software NOVA, Metrohm Autolab. The peak fitting of high-resolution XPS spectra for the S2p, Mo3d, and W4f regions was carried out using characteristic doublets with the following fitting parameters: i) for S2p, the L/G mix was set to 30%, spin-orbit splitting was fixed at 1.20 ± 0.1 eV, and the intensity ratio of the S2p3/2 to S2p1/2 components was 0.511; ii) for Mo3d, the L/G mix was also 30%, spin-orbit splitting was set at 3.15 (+0.2, -0.1) eV, and the intensity ratio of the Mo3d5/2 to Mo3d3/2 components was 0.690; iii) for W4f, the L/G mix was 30%, spin-orbit splitting was 2.15 ± (+0.2, -0.1) eV, and the intensity ratio of the W4f7/2 to W4f5/2 components was 0.788. For quantification, atomic scattering factors were obtained from the quantification library of the Avantage software and were automatically corrected for the instrument transmission function.

3 Results & Discussion

3.1 Results

The solution-based growth based on microfluidics developed in the tasks that led to this deliverable represents the first successful example of structurally controlled formation of in-plane heterostructures from LPE 2DMs. This strategy leverages structural defects at the edges of TMDs to drive the formation of in-plane heterojunctions by covalently linking flakes with dithiolated molecules through sulfur vacancies. The inherent rigidity of the BDT molecules prevents them from backfolding or linking both thiol groups to a single nanosheet, ensuring that the molecules bridge adjacent flakes. However, despite the precise control over the process, vertical stacking of flakes may still occur, leading to the formation of homojunctions. The morphology of the MoS_2–WS_2 assemblies mediated by BDT was characterized using optical microscopy and SEM. In particular, in order to fine-tune the process, these microscopies were employed to monitor the growth of the assemblies after each LPE TMD deposition step (Figure 2).

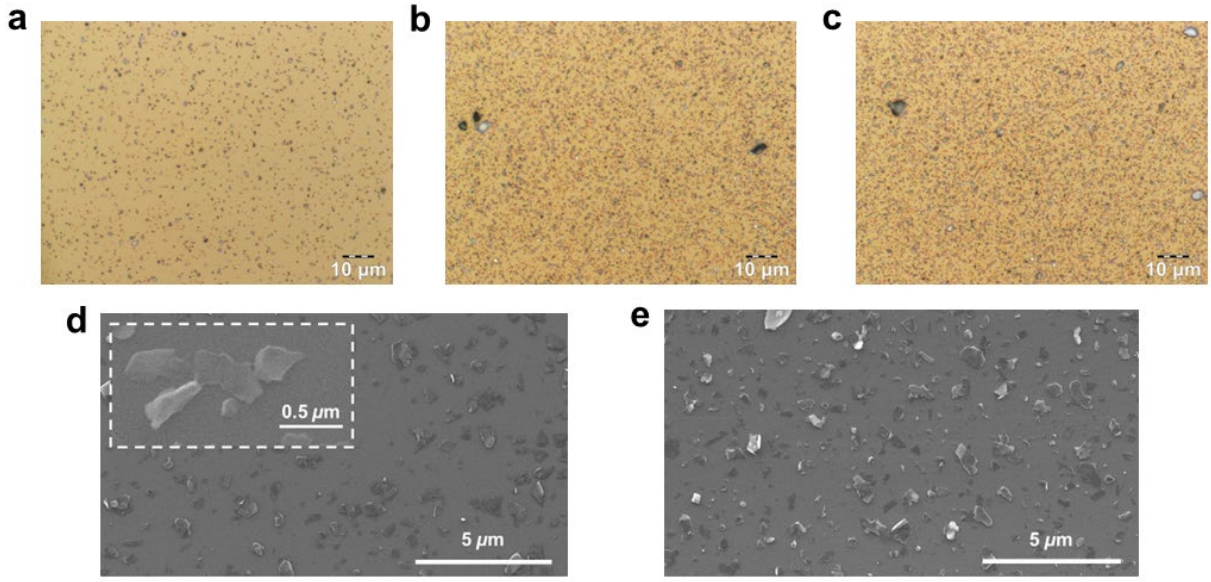

Figure 2. Stepwise optical microscopy and SEM survey. Optical microscopy analysis after deposition of (a) MoS_2, (b) WS_2 and (c) second cycle of MoS_2. SEM images of the (d) intermediate step of the lateral heterostructure corresponding to the deposition of Mo_2 and WS_2 and (e) final step related to the stepwise deposition of MoS_2-WS_2-MoS_2.

The successful functionalization of both LPE MoS_2 and WS_2 with BDT was evaluated using XPS and Raman spectroscopy. XPS analysis was conducted on BDT-bridged assemblies as well as on pristine LPE MoS2 and WS2 nanosheets. The high-resolution S 2p spectrum of TMDs reveals defects in the system and serves as a useful tool for studying the healing of sulfur vacancies after selective chemical functionalization.[2] Figures 3a and 3b show the core-level S 2p spectra of pristine LPE MoS_2 and WS_2 coatings, displaying the main S 2p3/2 and S 2p1/2 components at around 162.0 eV and 163.2 eV for

MoS_2, and 162.4 eV and 163.6 eV for WS_2. Additionally, a third component at approximately 161.4 eV for MoS_2 and 161.7 eV for WS_2 corresponds to defects in the crystal structure, such as sulfur vacancies. The significant reduction in the relative area of this defect-related component in the BDT-functionalized discrete MoS_2-WS_2 assemblies (Fig. 3c), from 7.2 ± 1.4% for MoS_2 and 25.3 ± 2.1% for WS_2 to 2.8 ± 1.6%, indicates a clear decrease in sulfur vacancies, suggesting effective healing through BDT covalent functionalization.

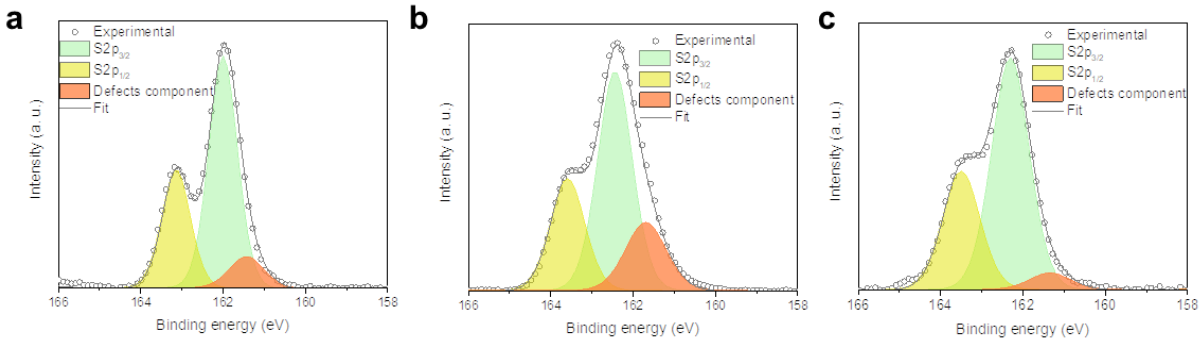

Figure 3. High-resolution S 2p XPS spectrum. (a) pristine MoS_2, (b) pristine WS_2 and (c) MoS_2-BDT-WS_2 lateral assembly.

Further confirmation of the healing of sulfur vacancies is obtained by comparing the Mo 3d and W 4f spectra of BDT-functionalized assemblies with those of the pristine LPE MoS_2 and WS_2.[3,4] For MoS_2, the relative area of the defect component (Figure 4a), that can be deconvoluted at 231.5 and 234.7 eV, is reduced from 16% to 8.6% upon formation of the heterojunction (Figure 4b). Similarly, for WS_2, the relative area ascribed to the defect component (Figure 4c), at 31.5 and 33.7 eV, is reduced from 18% to 7% after yield BDT-mediated heterojunctions.

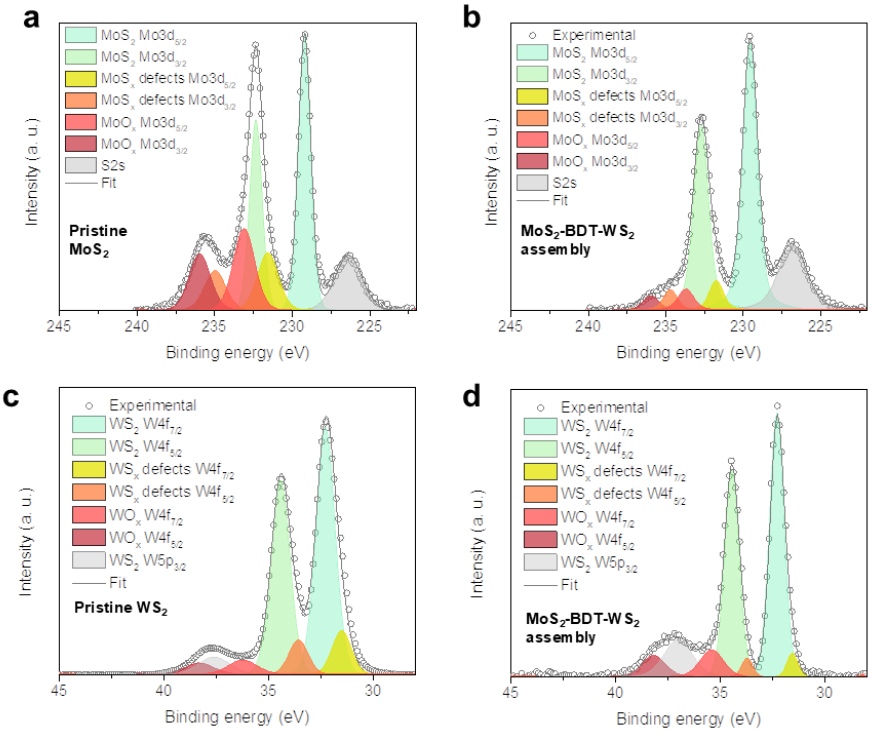

Figure 4. HR-XPS spectra of Mo 3d and W 4f peaks. HR-XPS spectra of Mo 3d peak in (a) pristine MoS_2 and (b) discrete MoS_2-BDT-WS_2 assembly. HR-XPS spectra of W 4f peaks in (c) pristine WS_2 and (d) discrete MoS_2-BDT-WS_2 assembly.

Raman spectroscopy has been exploited to further validate the healing of sulfur vacancies in TMDs by the thiolated molecules. The Raman features typical of MoS_2 and WS_2 remain unchanged, suggesting that the interaction with BDT does not affect the inherent structural properties of the materials (Figure 5). A clear blue shift is observed in the E^1_{2g} and A_{1g} bands, which originate from the in-plane and out-of-plane vibrations, respectively, for both MoS_2 and WS_2 in the synthesized discrete MoS_2-BDT-WS_2 assembly (Figure 5). This shift is consistent with the reduction of defect-driven modes as BDT helps to heal the material.[5] As the nanosheets get closer to the substrate surface, the out-of-plane mode is stabilized, causing a significant blue shift in the A_{1g} modes of both MoS_2 and WS_2. In addition, BDT cross-linking enhances the rigidity of the structure, further restricting the out-of-plane mode. Since the frequency of the E^1_{2g} mode is closely related to defect density, the blue shift indicates a decrease in defects. This is further supported by the narrowing of the full width at half maximum (FWHM) of the characteristic Raman bands of both MoS_2 and WS_2 in the BDT-assisted discrete assembly (Table 1).[5]

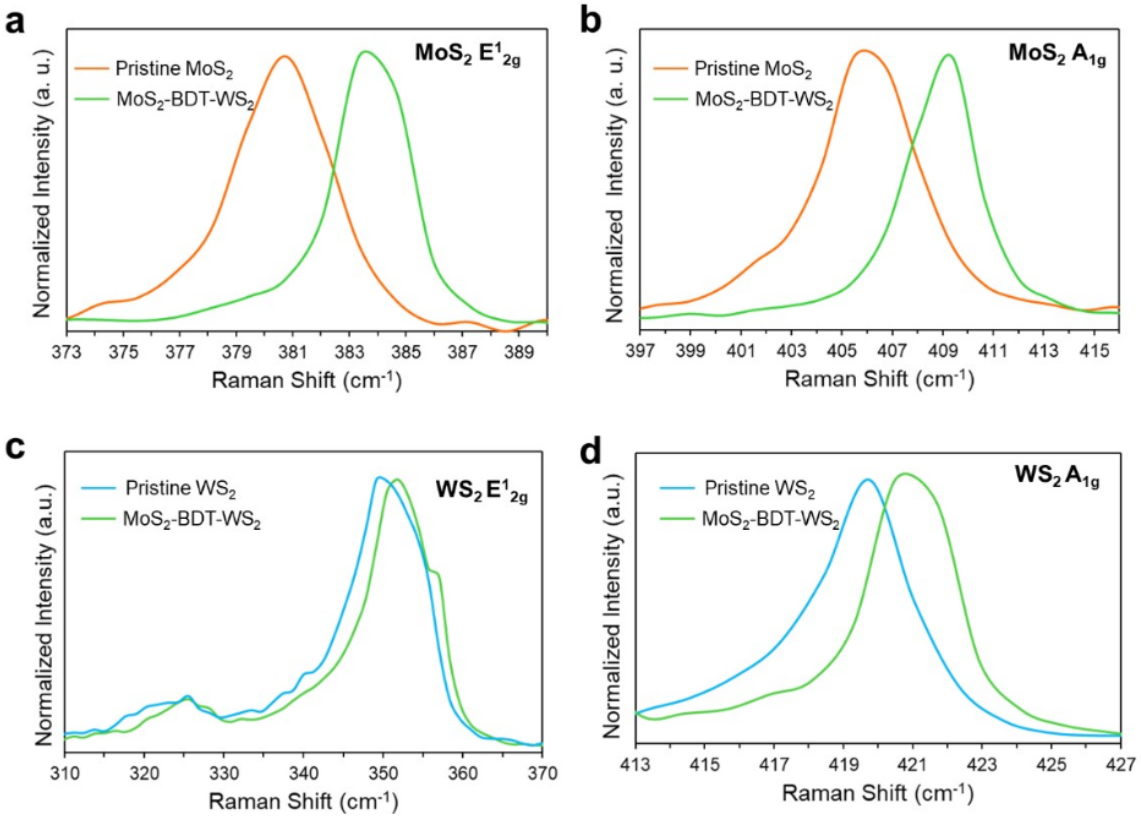

Figure 5. Raman characteristics. Comparison of (a) E^1_{2g} and (b) A_{1g} Raman bands of MoS_2 in pristine LPE MoS2 and discrete MoS_2-BDT-WS_2 lateral assembly. (c) E^1_{2g} and (d) A_{1g} Raman bands of WS_2 in pristine LPE WS_2 and discrete MoS_2-BDT-WS_2 lateral assembly.

Table 1. FWHM of the characteristic Raman bands of MoS_2 and WS_2 in pristine LPE materials and heterostructures.

Material	FWHM E^1_{2g} (cm^{-1})	FWHM A_{1g} (cm^{-1})
MoS_2	4.20 ± 0.25	4.36 ± 0.25
MoS_2 (heterostructure)	2.82 ± 0.48	3.45 ± 0.49
WS_2	11.39 ± 0.37	3.35 ± 0.15
WS_2 (heterostructure)	10.63 ± 0.24	3.01 ± 0.23

To investigate the effective role of BDT as a linker between adjacent flakes, promoting the formation of discrete assemblies, electrochemical impedance spectroscopy (EIS) was exploited with *in-situ* measurements. The assemblies were grown onto substrates patterned with interdigitated gold electrodes, as the growing assemblies would result in the formation of a barrier for the ionic conductivity. As the continuous growth of the 2D assembly restricts ionic conductivity between the electrodes, in situ EIS measurements show a notable increase in impedance after each TMD deposition step (Figure 6a). This serves as an internal gauge, enabling real-time monitoring of the stepwise assembly formation through the microfluidic strategy. To confirm the crucial role of bidentate molecules in assembling the heterostructures in a planar fashion, EIS was carried out after each MoS_2 and WS_2 deposition step without employing BDT in between each TMD loading. As a result, no significant change was detected at increased TMD loading (Figure 6b), indicating inefficient assembly formation, and thus suggesting uneven coatings of the flakes within the interdigitated electrodes. Finally, a standard Randles equivalent circuit was used to fit the Nyquist plots and extract the charge transfer resistance (R_{ct}),[6] which measures the resistance to ionic conduction at the electrolyte-electrode interface. In the discrete MoS_2-BDT-WS_2 assembly, a noticeable increase in R_{ct} was observed, as a result of the in-plane growth of the assembly (Figure 6c). On the other hand, when nanosheets are deposited without a molecular bridge, R_{ct} shows negligible variation, as a result of random and inefficient coating of TMDs flakes.

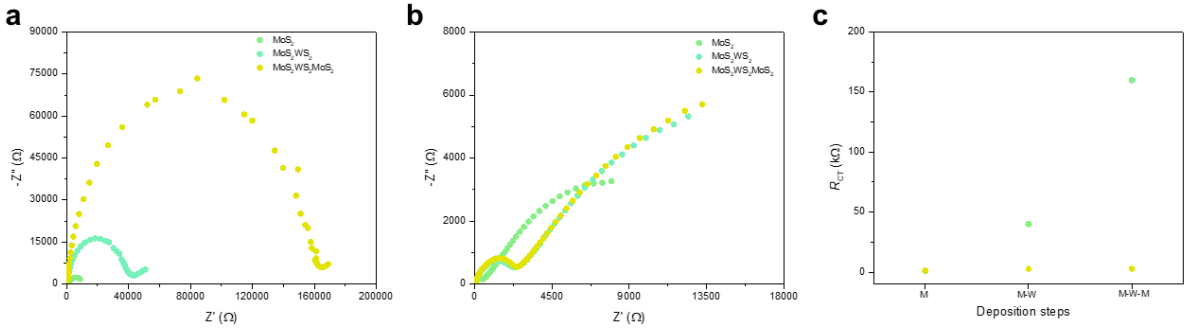

Figure 6. EIS analysis. (a) Evolution of the Nyquist plot when BDT is introduced into the microfluidic chamber between each MoS_2 and WS_2 deposition step. (b) Nyquist plots after each TMD deposition step for in the absence of BDT as intermediate step. (c) Comparison of R_{ct} as a function of TMD deposition for discrete MoS_2-BDT-WS_2 assemblies and coatings without using BDT, displayed in green and yellow, respectively.

3.2 Contribution to project (linked) Objectives

The results discussed in this deliverable significantly contributed to different specific objectives of WP2. As the goal of WP2 is to develop novel chemical routes to modify the nanosheets synthesize by other partners of the consortium (see WP1) through selective defect functionalization and covalent functionalization, the findings in D2.3 represents a step forward towards the realization of endless possibilities in the formation of discrete assemblies and their characterization. These are core units for objectives such as O2.1 “O2.1 Push the boundaries of defect engineering and functionalization in 2DM” and O2.3 “Use chemical modification for controlled nanosheets linkage through chemical coupling into discrete assemblies and synthesis of flake-level heterostructures”.

3.3 Contribution to major project exploitable result

This deliverable contributed reaching different project targes, such as novel discrete assemblies that goes beyond state-of-the art though the design of novel synthetic strategies to enable the formation of tailored solution-processable heterostructures with in-plane configuration.

4 Conclusion and Recommendation

In conclusion, we have presented the planar growth of solution-processed discrete assemblies based on 2D TMDs exploiting intrinsic material defects. To this end, a facile new sequential microfluidic approach has been designed. Sulfur vacancies in MoS_2 and WS_2, most abundant at the edges, have been healed by using bidentate π-conjugated molecules. Such healing process has the dual role of anchoring adjacent nanosheets and promoting the preferential formation of in-plane discrete assemblies. The BDT-linked MoS_2–WS_2 discrete assemblies were thoroughly characterized. The developed microfluidic approach to assembling discrete assemblies from solution-processed TMDs nanosheets can be easily adapted to other classes of 2DMs by using appropriately functionalized bidentate linkers. Thus, the choice of anchoring groups that selectively bind specific 2DMs, combined with cores that introduce new functionality, provides endless possibilities for embedding innovative printable 2D assemblies into ultrathin next-generation printed (opto-)electronic devices. Furthermore, the microfluidic approach based on defect-engineering to assemble heterostructures of 2DMs can be extended and optimized to yield heterostructures and hetero-networks that will be developed in future 2D PRINTABLE tasks.

5 Risks and interconnections

5.1 Risks/problems encountered

Risk No.	What is the risk	Probability of risk occurrence[1]	Effect of risk[1]	Solutions to overcome the risk
WP2.new	Aggregation can occur during the microfluidic process.	3	1	Tailor equipment tools (i.e. pipe size), wash between each deposition step and dilute the dispersion/solution

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

5.2 Interconnections with other deliverables

D2.3 is mainly interconnected with D3.2, as the latter exploits the of bi- or multidentate molecular linkers to fabricate networks of 2DMs.

6 Deviations from Annex 1

Not applicable

7 References

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Project partners:

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2	UNISTRA	UNIVERSITE DE STRASBOURG
3	UKa	UNIVERSITAET KASSEL
4	BED	BEDIMENSIONAL SPA
5	TUD	TECHNISCHE UNIVERSITAET DRESDEN
6	VSCHT	VYSOKA SKOLA CHEMICKO-TECHNOLOGICKA V PRAZE
7	UNR	UNIRESEARCH BV
8	UniBw M	UNIVERSITAET DER BUNDESWEHR MUENCHEN
9	EPFL	ECOLE POLYTECHNIQUE FEDERALE DE LAUSANNE

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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**
	Paolo Samorì UNISTRA	Georg Duesberg UniBw M	Jonathan Coleman TCD
1. *Do you accept this Deliverable as it is?*	Yes	Yes	Yes
2. *Is the Deliverable complete?* - *All required chapters?* - *Use of relevant templates?*	Yes	Yes	Yes
3. *Does the Deliverable correspond to the DoA?* - *All relevant actions preformed and reported?*	Yes	Yes	Yes
4. *Is the Deliverable in line with the 2D-PRINTABLE objectives?* - *WP objectives* - *Task Objectives*	Yes	Yes	Yes
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
6. *Is created and potential IP identified and are protection measures in place?*	Yes	Yes	Yes
7. *Is the Risk Procedure followed and reported?*	Yes	Yes	Yes
8. *Is the reporting quality sufficient?* - *Clear language* - *Clear argumentation* - *Consistency* - *Structure*	Yes	Yes	Yes