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Developing New 2D Materials and Heterostructures for Printed Digital Devices

2D-PRINTABLE - Deliverable report

D3.4 – Heterostructures from CVD + printing

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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 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 design and fabrication of novel device structures involving 2D materials prepared through both bottom-up and top-down methods.

Chemical vapor deposition (CVD) is widely used to produce high-quality 2D nanosheets and thin films on selected substrates. Although CVD-grown materials have enabled advanced heterostructured devices, their integration typically depends on complex and time-intensive transfer steps, which hinder large-scale application. In contrast, electrochemically exfoliated (EE), solution-processable 2D nanosheets provide a scalable pathway for fabricating large-area films on a variety of substrates using straightforward techniques such as printing. Their atomic thicknesses and mechanical flexibility promote intimate coupling with other materials, making them well-suited for efficient heterostructure formation. For 2D materials lacking surface dangling bonds, such as transition metal dichalcogenides (TMDs), 2D/2D heterostructures represent a powerful platform to investigate new electronic phenomena and develop scalable device architectures.

In this report, we chose to use another bottom-up method called thermally assisted conversion (TAC) to fabricate tungsten disulfide (WS_2) layer. This method overcomes the limitation of CVD that it cannot be patterned on a substrate. The successful fabrication of WS_2 layer was verified by Raman spectroscopy characterisation. Subsequently, EE MoS_2 dispersion was spin-coated to form 2D/2D heterostructures. The device was completed by spin coating another p-type NiO semiconductor and evaporating gold electrode. The device was examined regarding its current-voltage characteristics and electroluminescence performances. Due to the large sheet resistance coming from the bottom electrode, the device cannot be operated as a diode and no light emission was detected. However, it is believed that further optimisation on the bottom electrode will improve the device electrical behaviours.

Electrochemically exfoliated 2D nanosheets offer distinct advantages due to their solution processability and scalability. When integrated with nanoflakes or nanofilms through bottom-up approaches, they expand the diversity of device architectures and open new opportunities for exploration and application.

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Abbreviations & Definitions

Abbreviation	Explanation
CVD	Chemical vapor deposition
SP	Solution-processed
PVD	Physical vapor deposition
TAC	Thermally assisted conversion
PPF	Pyrolyzed photoresist film
THAB	Tetraheptylammonium bromide
EL	Electroluminescence
TMDs	Transition metal dichalcogenides

1 Introduction

This deliverable report deals with the Task 3.6 in WP3: Combining CVD growth and solution processing to produce novel heterostructures.

Chemical vapor deposition (CVD) is a common method for synthesizing high-quality 2D nanosheets and thin films on specific substrates. While CVD-grown materials have enabled various heterostructured devices, their integration often relies on complex, time-consuming transfer processes that limit scalability. Alternatively, electrochemically exfoliated, solution-processable 2D nanosheets offer a scalable route for large-area film fabrication on diverse substrates through simple techniques like printing or coating. Their atomic thickness and flexibility allow for intimate contact with other materials, ideal for forming efficient heterostructures. For 2D materials without surface dangling bonds, such as transition metal dichalcogenides (TMDs), 2D/2D heterostructures provide a promising platform to explore novel electronic behaviours and scalable device architectures.

In this deliverable, we introduce the device design, aiming to combine both CVD type WS_2 and liquid based type MoS_2 nanosheets to form novel heterostructures. However, we realised that CVD type thin film still needs to be mechanically transferred from one substrate to another one and there will also be an issue to spatially align with other layers on a substrate. Therefore, we decide to use thermally assisted conversion (TAC) method to convert metal layer such as tungsten W into WS_2. This method allows us to spatially pattern the substrate to selectively coat the target materials. Solution-processable nanosheets can be subsequently coated on top of TAC-2D layers to form novel vertical heterostructures. The fabrication processes are illustrated, and the electrical performance was examined. Eventually, we investigated the electrical behaviours of the fabricated devices. It is expected that the protocol can be easily applied to other types of materials, leading to new device designs and applications.

2 Methods and core part of the report

2.1 Background

Chemical vapor deposition (CVD) is a widely employed technique for synthesizing high-quality single or polycrystalline two-dimensional (2D) nanosheets and thin films at elevated temperatures on specific substrates.[1] Over the past few decades, CVD-grown 2D materials have enabled the fabrication of various heterostructured devices.[2, 3] However, the integration of these materials often requires complex and time-consuming transfer processes, which significantly hinder their scalability and compatibility with large-area device manufacturing.

In contrast, solution-processable 2D nanosheets produced via electrochemical exfoliation present a promising alternative.[4] These exfoliated nanosheets can be easily dispersed in solvents, enabling straightforward and scalable techniques such as printing or coating to fabricate large-area thin films on a wide range of substrates, including flexible and unconventional ones. Moreover, their atomic thickness and mechanical flexibility allow them to form intimate interfaces with other materials, an essential feature for building efficient heterostructures.

Particularly for 2D materials with no surface dangling bonds—such as transition metal dichalcogenides (TMDs)—the formation of 2D/2D heterostructures offers a unique opportunity to harness their intrinsic properties without the need for complex surface engineering. This approach enables the exploration of novel electronic behaviours and device architectures, driving forward the development of next-generation flexible and scalable electronic systems.

2.2 Procedures

The solution-processable MoS_2 nanosheets were obtained by electrochemical exfoliation. The crystal was held by a copper clip as the anode and graphite foil was used as the cathode. 12.5 mg/mL tetraheptylammonium bromide (THAB) solution in acetonitrile was used. A DC voltage of 7 V was applied for 30-60 min. The intercalated crystal was removed from the clip and was immediately immersed in 2 wt% PVP/DMF solution. The solution was ultra-sonicated in a sonic bath for 30 min. To remove the un-exfoliated nanosheets, the dispersion was centrifuged at 3000 rpm for 30 min and the supernatant was carefully collected. The supernatant was further centrifuged at 6000 rpm for 60 min and the resultant supernatant was decanted. The sediment was washed by DMF to remove excess PVP and was finally re-dispersed by anhydrous DMF.

The device fabrication will be introduced in the result part.

2.3 Data Analysis

The collected data is plotted and analysed in Origin.

3 Results & Discussion

3.1 Results

3.1.1 Device design

The proposed device structure is PPF/TAC-WS_2/SP-MoS_2/NiO/Au, as shown in Figure 1A. In this structure, WS_2 is used as electron transport layer, as the sulfur vacancies will endow it n-type electrical behaviours. The dangling-bonding free surface of both WS_2 and MoS_2 will form a seamless and high-quality 2D/2D interface for a facile charge transfer across interfaces. The bandgap of WS_2 is also larger than that of MoS_2, so the light emission from MoS_2 will not be absorbed by it. Further, the shallower electron affinity of WS_2 will enable a favoured electron injection into MoS_2. NiO is used as the hole transport layer.

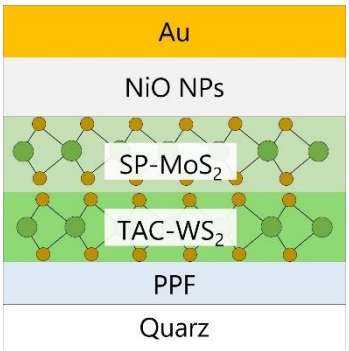

Figure 3.1 Device design. Schematic demonstration of device structure (A) and energy bands (B).

3.1.2 Device fabrication

Pyrolyzed photoresist film (PPF) on quartz was selected as an alternative of graphene electrode described in T3.4. PPF is fabricated by the pyrolysation of photoresist films to glassy carbon to temperatures above 900°C. As a result, conducting, transparent and temperature stable layers can be formed on quartz substrates. This is import for subsequent CVD deposition of TMD which typically use temperature > 600°C. Moreover, patterned carbon layer of PPF can formed on quartz substrate using photolithography. This methodology developed at UniBW M enables to fabricate the hybrid LED structures based on CVD and EE TMD films.

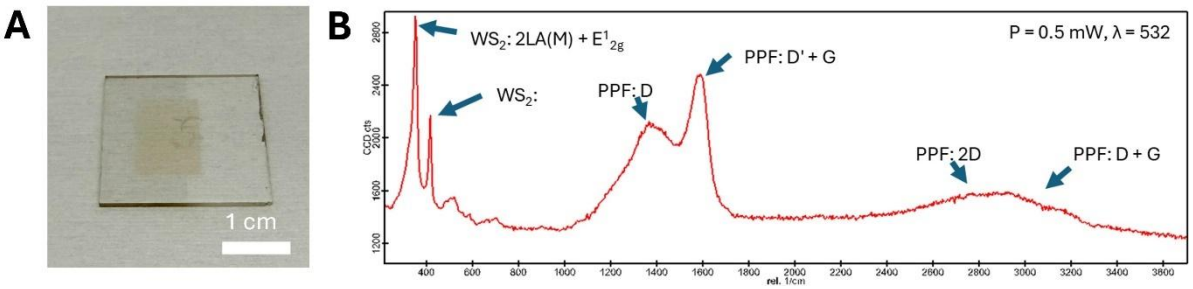

Figure 3.2 (A) Photograph of the fabricated PPF/W/WS_2 layer. (B) Raman spectrum of TAC-WS_2 on the PPF carbon layer.

UniBw M fabricated the WS_2 layers thermally assisted conversion (TAC) a combination of physical and chemical vapor deposition (PVD & CVD) on the PPF/quartz substrates. The TAC method is advantageous for area selective deposition. In here a sputtered tungsten (W) pattern was defined by photolithography on the PPF layers and subsequently converted to WS_2 through sulfurization in a CVD furnace. The results is shown in Fig 1 a). The photograph shows a quartz substrate, which left half is coated with a transparent PPF layer, appearing slightly grey. In the middle a square of TAC deposited WS2 is visible in a amber colour. The composition is confirmed by Raman spectrum shown in Figure 3.2. WS_2 and PPF characteristic peaks can be observed.

The patterned PPF/TAC-WS_2 substrate was sent to TCD, which was subsequently transferred into N_2-filled glovebox. A monolayer enriched EE MoS_2 dispersion with a concentration of 20 mg/mL was spin coated on the substrate at a speed of 1500 rpm for 60 s. The substrate was baked on a hotplate at 110 °C for 10 min. It resulted in a MoS_2 thin film of approximately 15 nm. NiO nanoparticle ethanol dispersion was spin coated at a speed of 2000 rpm for 60 s to obtain 40 nm thick NiO layer and no annealing was used. The substrate was taken out of glovebox and transferred into metal deposition chamber, where top electrodes of 30 nm gold were evaporated by e-beam evaporator (Temescal) at a rate of 0.15 nm/s under vacuum. A shadow mask was used during evaporation. After evaporation, silver paste was applied for electrical connection purposes. The device area is taken as the overlapping area between the top and bottom electrodes and is indicated in the figure with a dashed red line. The device area is around 7 mm^2. The completed device was measured in ambient immediately after fabrication.

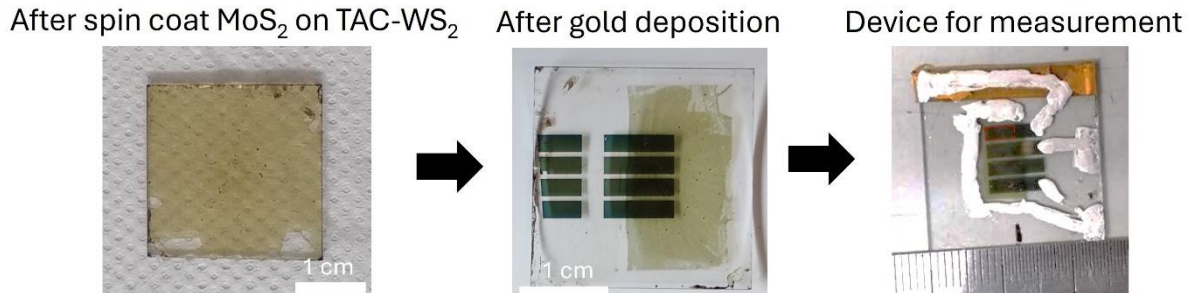

Figure 3.3 Device fabrication process: from MoS_2 spin-coating, gold evaporation to applying silver paste for electrical contacts. The red dashed square in the last figure indicates the overlapping area between top and bottom electrodes, which is defined as the device area around 3.5 cm by 2 cm.

3.1.3 Electrical characterisations

To assess the electrical behaviour, the current-voltage (I-V) characteristics was collected in the range of -10 to 10 V (Figure 3.2A). The obtained I-V curve is linear and shows no rectification behaviour. The device was further swept from 0-20 V and the electroluminescence (EL) intensity was monitored during sweeping (Figure 3.2B). The device showed no EL. It is likely that the WS_2 and MoS_2 layer are not conductive enough. The available carriers within MoS_2 layer are not enough for radiative recombination to emit detectable EL signals. Further optimisation of WS_2 and MoS_2 layer will be required to improve its conductivity.

3.2 Contribution to project (linked) Objectives

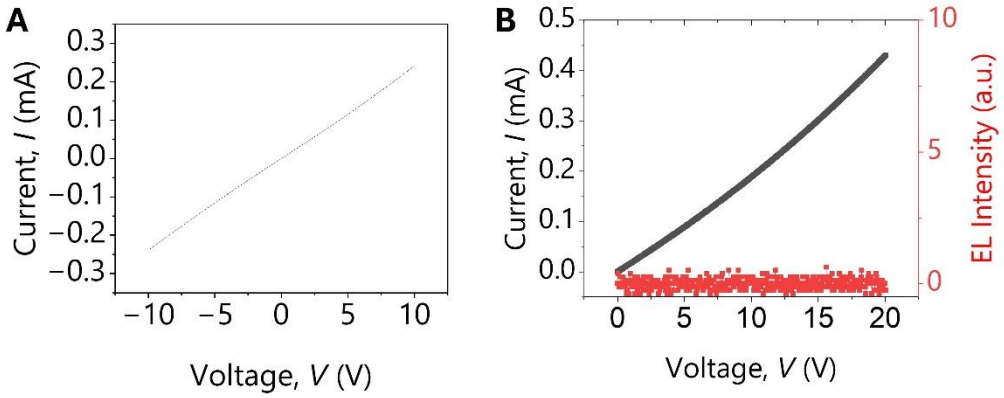

Figure 3.4 Electrical characterisations. (A) I-V curve and (B) I-EL intensity-V curves.

In this deliverable, we demonstrated the fabrication protocols of a novel structured diodes combining both TAC 2D and solution-processable 2D. Previous stacked 2D devices were made with complicated and unscalable flake level transfer and stacking methods. Our protocols could be easily applied to other types of 2D materials and device structures, producing more types of novel heterostructures.

3.3 Contribution to major project exploitable result

The novel device structure design and its fabrication protocol will contribute to KER for WP3: Printed networks.

4 Conclusion and Recommendation

In conclusion, we reach the objective that novel structured devices were designed and fabricated with both TAC and solution-processable 2D materials.

Firstly, we identified the potential issue could arise from patterning of different materials that will be layer-by-layered stacked together. This has been solved by choosing TAC rather than CVD so we can avoid sophisticated film transfer procedures. Secondly, we proposed a potential light-emitting device structure combining both TAC WS_2 and SP MoS_2 thin films to form 2D/2D heterostructures, where TAC WS_2 can be served as the electron transport layer and SP MoS_2 serves as light-emissive layer. Thirdly, the fabrication process was demonstrated with potential to be applied to other materials and applications. At last, the electrical characterisation showed that the electrical conductivity of functional layers should be further resolved to fully reveal the device capabilities.

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
WP3	The TAC-WS_2 and SP-MoS_2 are resistive	2	2	Systematic vary their thicknesses to study its electrical conductivity

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

5.2 Interconnections with other deliverables

The electrical characterisations are related to deliverable D5.3:Electrical characterization of films and vertical heterostructures.

6 Deviations from Annex 1

A minor deviation is that we are not using CVD 2D materials. We chose another method (TAC) to allow a patterning of the device region which is more advantageous than CVD based methods.

7 References

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[3] Y. Beckmann, H. Myja, T. Kramberg, J. Konietzka, M. Abdelbaky, A. Grundmann, A. Ghiami, M. Heuken, H. Kalisch, A. Vescan, W. Mertin, T. Kümmell and G. Bacher, "Self-Powered Photodetectors Based on Scalable MOCVD-Grown WS_2–MoS_2 Heterostructures," *ACS Photonics*, vol. 11, no. 6, pp. 2228-2235, 2024.

[4] S. Wang, J. Xue, D. Xu, J. He, Y. Dai, T. Xia, Y. Huang, Q. He, X. Duan and Z. Lin, "Electrochemical molecular intercalation and exfoliation of solution-processable two-dimensional crystals," *Nat Protoc*, vol., DOI: 10.1038/s41596-023-00865-0, no. 18, pp. 2814-2837, 2023.

8 Acknowledgement

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Project partners:

#	Partner short name	Partner Full Name
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
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**
	NAME (Organisation)	NAME (Organisation)	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