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Developing New 2D Materials and Heterostructures for Printed Digital Devices

2D-PRINTABLE - Deliverable report

D6.1. – Beyond-state-of-the-art all-nanosheet TFTs

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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

The main objectives of the deliverable D6.1 is to provide a demonstrator consisting of thin film transistors (TFTs) based on nanosheets that exhibit electrical characteristics beyond state-of-the-art. 2D-PRINTABLE partners successfully integrated developed transition metal dichalcogenides (TMDs) in flexible devices. Optimization of all interfaces and components to maximize charge injection and transport was ensured by employing Langmuir-Schaefer technique as deposition process. The fabricated high-quality networks of nanosheets were embedded in TFTs exhibiting peak mobilities and on/off ratios of 10^1 cm^2 V^{-1} s^{-1} and 10^5, respectively.

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Abbreviations & Definitions

Abbreviation	Explanation
TFT	Thin film transistor
TMD	Transition metal dichalcogenides
2D	Two-dimensional
PET	Polyethylene terephthalate
EMIM TFSI	1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide
V_{ds}	Drain-source voltage
V_T	Threshold voltage
SS	Subthreshold swing

1 Introduction

The field of printed electronics is experiencing rapid growth, with solution processing techniques enabling the fabrication of a diverse array of electronic components.[1] In contrast to traditional silicon-based electronics, printed electronic devices generally exhibit inferior performances. Nevertheless, they offer significant advantages, including low cost, mechanical flexibility, and compatibility with large-area deposition. Consequently, printed electronics hold considerable potential for future applications in wearable devices, healthcare systems, electronic skins, and other emerging technologies. Among different solution-processable materials, two-dimensional (2D) species have emerged as promising candidates due to their outstanding intrinsic electrical, optical and mechanical properties.[2] The family of 2D materials is vast, encompassing thousands of members with diverse characteristics.[3] This includes conductive materials such as graphene, semiconductors like 2H-phase molybdenum disulfide (MoS_2), and insulators such as hexagonal boron nitride (hBN). Inks of these materials can be exploited in printed devices, including transistors, solar cells, photodetectors and light-emitting diodes.[4] To fully harness the potential of 2D materials in these applications, it is crucial to optimize solution-deposition techniques for the fabrication of high-quality networks over large areas. These printed networks must exhibit properties that are suitable for device integration, such as high mobility or conductivity. A significant challenge in printing inks containing nanosheets with low aspect ratios (typically less than 50) is that such networks tend to be highly porous and disordered.[5] As a result, the junctions between nanosheets, which are a key factor in limiting the mobility and conductivity of the network, often form point-like structures with exceptionally high junction resistances. In this framework, we demonstrate the fabrication of high-quality networks of a wide range of 2D materials, which are further integrated in flexible TFTs exhibiting electrical output beyond state-of-the-art solution-processed devices (i.e. 10^1 $cm^2V^{-1}s^{-1}$ field-effect mobilities and 10^5 on/off ratios).

The demonstrator reported in D6.1 “Beyond-state-of-the-art all-nanosheet TFTs” offer several insights for dedicated tasks in WP6, such as T6.2, as well as a solid platform for the achievement of objectives like O6.1 “TFTs with charge carrier mobilities for both p- and n-type exceeding 100 cm^2/Vs” and O6.3 “Demonstration of integration of high-mobility TFTs into simple circuits”.

2 Methods and core part of the report

2.1 Background

Inks of 2D materials have been obtained starting from electrochemical exfoliated bulk crystals. These inks have been exploited to fabricate high-quality networks based on Langmuir-Schaefer technique. Finally, these networks have been integrated on flexible TFTs and their electrical properties benchmarked.

2.2 Procedures

An electrochemical cell with two electrodes is employed to intercalate TMDs (both from HQ graphene and in-house synthesized) crystals (Figure 1a). A small crystal serves as the cathode, while a platinum foil (Alfa Aesar) is exploited as the anode. Crocodile clips are used to hold the electrodes. For the electrolyte, a solution of tetrapropylammonium (TPA) bromide (Sigma-Aldrich, 5 mg/mL) is dissolved in propylene carbonate (approximately 50 mL). A bias of 8 V is applied for 30 minutes across the electrodes to facilitate the intercalation of TPA^{+} cations into the 2D crystal. This process results in a considerable expansion of the pristine 2D crystal, confirming the successful intercalation. Following intercalation, the 2D crystal is immersed in isopropyl alcohol (IPA) overnight to dissolve and remove any residual bromide ions.

The Langmuir−Schaefer technique is employed using a Teflon stand (10 cm) onto which a substrate is placed (Figure 1b). The stand is positioned within a beaker filled with deionized water. Distilled hexane (20 mL) is drop-cast onto the surface of the deionized water to create a water/hexane interface, where the substrate is placed. TMDs inks (140 µL) are then casted onto the hexane surface. The Teflon stand and substrate are subsequently carefully extruded through the 2D crystal layer, facilitating the coating of the substrate surface with the TMD network. Then, the TMD networks are dried for 6 hours in ambient air in a fume hood and further annealed at 120 °C for 1 hour on a hot plate into a N_2 glovebox (Jacomex GP campus) to enhance the adhesion of the 2D flakes onto the substrate. This process is repeated to form a second layer of the TMD network. To build the device, gold electrodes (100 nm) are deposited via evaporation (FC-2000 Temescal Evaporator) through a tailored mask, with a width of 1100 µm and a channel length of 50 µm. Further, gold is also used as the gate electrode (1.5 × 4 mm), 1 mm apart from the source and drain electrodes. Following electrode deposition, 2D materials-based devices are further annealed at 120 °C for 1 hour in a N_2-filled glovebox. Flexible substrates are made with polyethylene terephthalate (PET).

To regulate the injection of ions into the semiconducting channel, the ionic liquid 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide (EMIM, Sigma-Aldrich) is employed. A drop of EMIM is placed onto the TFTs to ensure that the gate, source, and drain electrodes are fully covered with the ionic liquid. Before electrical measurements, the devices are subsequently placed under vacuum ($\sim 1.6 \times 10^{-4}$ mbar) in a Janis Probe Station for 12 hours to remove any residual water. Electrical characterization is performed by contacting the devices with gold-coated probes connected to a Keithley 2612A dual-channel source measurement unit. A gate voltage window of −3 to 3 V is applied for transfer characteristics, with a scan rate of 50 mV s^{-1} and a drain-source voltage (V_{ds}) of 1 V for all the set of devices.

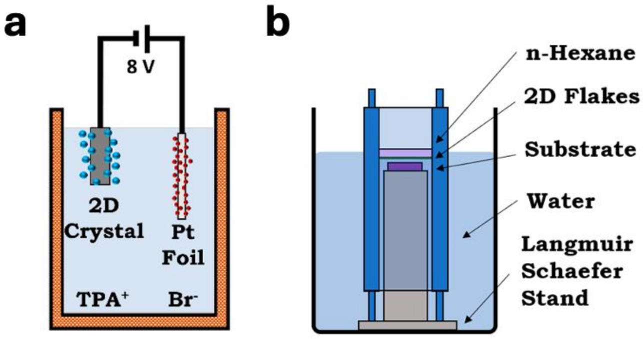

Figure 1. Schematic illustrations of the (a) electrochemical exfoliation and (b) Langmuir-Schaefer setups.

2.3 Data Analysis

OriginLab software was used to carry out data analysis.

3 Results & Discussion

3.1 Results

To characterise the electronic properties of our semiconducting networks, we fabricated TFTs (Figure 2a) made of a wide variety of 2D semiconductor. The device configuration of a demonstrator based on nanosheets network is shown in Figure 2b.

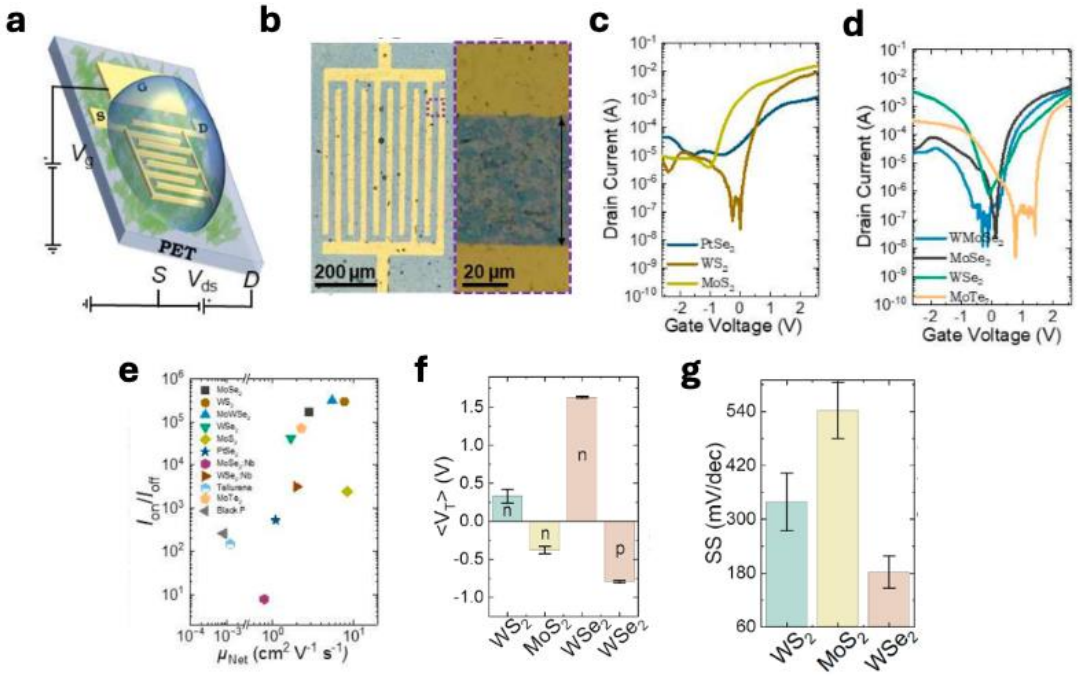

Figure 2. Electrical characterization of TFTs. (a) Schematic illustration of a generic TFT device. (b) Optical images of the nanosheets network embedded in the device. Transfer characteristics of selected (c) n-type and (d) ambipolar electrochemically gated transistors. (e) On/off ratio and field-effect mobility comparisons of different TFTs. V_T (f) and *SS* (g) of selected TFTs.

An n-type behaviour was observed for $PtSe_2$, MoS_2 and WS_2 (Figure 2c). In contrast, $MoSe_2$, WSe_2, $MoTe_2$ and $MoWSe_2$ TFTs exhibited ambipolar characteristics (Figure 2d). Figure 2e shows an overview of the average field-effect mobility and on/off ratio for our TFTs, with the best performing devices displayed at the top right-hand corner of the plot. Average mobilities are in the range of 1 - 8 $cm^2\ V^{-1}\ s^{-1}$ with peak mobilities in the order of 10^1 $cm^2\ V^{-1}\ s^{-1}$ and on/off ratios in the range of 10^0 - 10^5. The mobilities and on/off ratios exhibited by the TFTs in this report, outperform typical ones obtained with liquid-phase exfoliated (i.e. ultrasonication) 2D materials.[6] This is attributed to the larger aspect-ratio and lower defectivity of the electrochemical exfoliated flakes, as discussed in previous deliverables of 2D-PRINTABLE. To further benchmark our devices, V_T was evaluated on selected TFTs. As shown in Figure 2f MoS_2- and WS_2-based TFTs have $\langle V_T \rangle = -0.38 \pm 0.05$ and 0.33 ± 0.09 V, respectively. In ambipolar WSe_2 devices, the n-type $\langle V_T \rangle$ is 1.63 ± 0.01 V, and the p-type $\langle V_T \rangle$ is -0.80 ± 0.01 V, which can likely be attributed to either W or Se vacancies.[7] Moreover, the SS of such TFTs, defined as the change in gate voltage necessary to change the drain current by one decade, was extracted. To reduce the switching power losses, SS should be minimized. In our selected devices, SS values were of 542 ± 62, 339 ± 64 and 182 ± 36 mV/dec for the networks of MoS_2, WS_2, and WSe_2, respectively.

3.2 Contribution to project (linked) Objectives

The demonstrator of this deliverable contributes reaching the targets of objectives reported in WP 6, including O6.1 “TFTs with charge carrier mobilities for both p- and n-type exceeding 100 cm^2/Vs” and O6.3 “Demonstration of integration of high-mobility TFTs into simple circuits”.

3.3 Contribution to major project exploitable result

D6.1 contributes to the development of different major project tasks, particularly T6.2 “Thin-film transistors”. Proof-of-concept TFT devices in D6.1 are engineered toward the optimization of the interfaces and components to maximize charge injection and transport across the system.

4 Conclusion and Recommendation

This deliverable reports on the development of TFTs based on networks of electrochemically exfoliated nanosheets. Langmuir-Schaefer was used to deposit large area films on flexible substrates. This strategy has allowed the fabrication of a wide variety of TFTs with different semiconducting behaviours. Field effect mobilities in the order of 10^1 cm^2 V^{-1} s^{-1} and on/off ratios as high as 10^5 were obtained, beyond state-of-the-art liquid-phase exfoliated analogues, providing a versatile and promising platform for next-generation printed electronic devices. The results obtained in D6.1 can serve as a seed for further improvement of all-nanosheet TFTs.

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
WP6.1	Mobility target of WP6 below the expectations	1	1	Optimization of synthetic parameters and fine tuning of the nanosheets deposition

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

5.2 Interconnections with other deliverables

Interconnections are foreseen with D3.2 and D5.3 since electrical characterizations of networks and heterostructures are carried out.

6 Deviations from Annex 1

Not applicable

7 References

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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
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**
	P. 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?*	No potential IP was identified by partners	No potential IP was identified by partners	No potential IP was identified by partners
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