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Developing New 2D Materials and Heterostructures for Printed Digital Devices

2D-PRINTABLE - Deliverable report

D4.2. – Characterization of new materials identified through theory

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Project Scientific Abstract

The 2D-PRINTABLE project uses sustainable liquid-phase exfoliation (LPE) techniques to produce inks of a wide range of novel 2D materials (2DMs), including conducting, semiconducting, and insulating nanosheets, identified through comprehensive computational screening. These inks are then utilized in liquid phase deposition methods 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.

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Abbreviations & Definitions

Abbreviation	Explanation
2DM	2D material
AFM	Atomic force microscopy
AR	Aspect ratio
EDX	Energy-dispersive X-ray
EE	Electrochemical exfoliation
FIB-SEM-NT	Focused beam ion-scanning electron microscopy-nanotomography
LCC	Liquid cascade centrifugation
LPE	Liquid phase exfoliation
LS	Langmuir-Schaefer
NS	Nanosheets
SAED	Selected-area electron diffraction
SEM	Scanning electron microscopy
TEM	Transmission electron microscopy
XRD	X-ray diffraction

1 Introduction

The exfoliation and use of novel 2D materials (2DM) obtained from exfoliation of previously (widely) unexplored bulk materials is a core contribution to the main objective of 2D-PRINTABLE, namely to use sustainable liquid-exfoliation techniques to develop a wide range of new 2DMs and to develop the printing and liquid-deposition methods required to fabricate networks and multicomponent heterostructures with unprecedented properties, enabling the production of next-generation printed electronic devices. Ideally, the exploration of new materials is guided through theoretical prediction of their properties, followed by synthesis of the bulk layered materials in large quantity. These aspects are described in Deliverables D1.1 “Database on available materials”, D1.2 “Theory-identified novel 2D materials” and D1,3 “Synthesis of bulk materials” which show that significant progress has been made within the project lifetime. After bulk materials are available, in our workflow, they are typically first subjected to sonication-based liquid phase exfoliation (LPE). This is because this process is routinely used and established and can give valuable information on the ease of exfoliation, nanosheet moprhology as well as the stability of the materials in the form of nanosheets. Most importantly, it can be applied to insulators, as well as metals and semiconductors unlike electrochemical exfoliation. Only materials that are found to be intact after exfoliation and show good environmental and colloidal stability will be potentially selected for further electrochemical exfoliation to produce high aspect nanosheets which are often key for device performance.

In this deliverable, we describe the progress in exfoliating new layered materials that have not been previously (or not comprehensively) studied in LPE. As such, the report is directly connected to objectives of WP1, i.e. O1.3: Liquid-based exfoliation of bulk 3D layered materials to yield novel 2D materials and builds on O1.1: Prediction of a portfolio of new 2D materials with ad-hoc designed (opto)electronic properties. O1.2: Synthesis of bulk 3D layered materials. For any research related to 2DM, state-of-the-art characterization is of utmost importance which is addressed within 2D-PRINTABLE through workpackage 4 dedicated to characterization. Here, the basic characterization of newly exfoliated 2DM is described within Task 4.1 with the linked objective O4.1: Basic characterization of as-exfoliated and functionalized nanosheet building blocks. The specific materials described below are metal diborides, TaS_2, Bi_2SeO_5, CrSBr, $Na_2Cu_2TeO_6$.

2 Methods

2.1 Background

Exfoliation of new materials always requires a careful characterisation to assess whether structural integrity of the nanosheets is preserved after exfoliation and to identify nanosheet size/thickness and morphology which gives important information for further processing. As described for nanosheets of Bi_2SeO_5, CrSBr, $Na_2Cu_2TeO_6$.in this report, a range of spectroscopic and microscopic techniques are used, typically including but not limited to X-ray diffraction (XRD), Raman spectroscopy, UVVis extinction and absorbance spectroscopy, transmission electron microscopy (TEM) and selected area diffraction (SAED), scanning electron microscopy (SEM), often coupled to energy disperse X-ray (EDX) analysis, and atomic force microscopy (AFM). When nanosheets are found promising, additional characterisation is performed such X-ray photoelectron spectroscopy and high resolution TEM.

Further, previous work on many materials beyond graphene, boron nitride and transition metal dichalcogenides showed that the nanosheets can be prone to degradation in the presence of water and oxygen. To address this, we have established inert exfoliation that also allows us to track degradation through simple spectroscopy after exposing the sample to ambient conditions. Such work can be relatively time consuming and is carried out on a subset of materials. Here, it was applied to the metal diborides and TaS_2.

2.2 Procedures

The sonication assisted liquid phase exfoliation (LPE) of Bi_2SeO_5 , CrSBr, $Na_2Cu_2TeO_6$ in isopropanol (IPA) has been used for the production of nanosheets (NSs) processed in WP1. The LPE was performed for 8 hours, whilst ensuring that the temperature of the sonication bath did not exceed 40°C. The exfoliated material in solvent was centrifuged at 4500 rpm for one hour. The solvent was discarded and the precipitate redispersed in fresh IPA. After 1 hour of gravitational sedimentation, upper part of supernatant was collected for further characterization.

The exfoliation of metal diborides is described in detail in *ACS Nano* 2024, 18, 42, 28596-2860.

The exfoliation of TaS_2 was performed in dried and degassed NMP through bath sonication under argon atmosphere or tip sonication in a nitrogen filled glovebox for 7h. Unexfoliated material was first removed through centrifugation at 100 *g* for 2h. The supernatant was subjected to cascade centrifugation at sequentially increasing centrifugation speeds and the sediment containing size-selected fractions was collected after each step in fresh NMP. All decanting was performed inside the glovebox. Degradation kinetics were investigated after exposure to ambience through extinction spectroscopy.

The characterisation of the 2D materials in bulk and exfoliated form was performed using a range of standard techniques such as SEM (e.g. using the SEM 6492LA instrument), TEM (e.g. using the JEOL JEM 1011 microscope operated at 100 kV), AFM (e.g. employing the NX10 AFM from Park Systems) in non-contact or tapping mode, XRD (e.g. using the PANalytical Empyrean with Cu Kα radiation), Raman spectroscopy (e.g. using Renishaw microRaman inVia 1000 spectrometer), and extinction and absorbance spectroscopy (e.g. using Perkin Elmer Lambda 1050 with and without integrating sphere). The sample preparation for microscopy involved drop-casting the dispersion onto suitable substrate and evaporating the solvent.

2.3 Data Analysis

The data analysis was performed using specialized software for each technique applied, such as Digital Micrograph for TEM and SEM images, the Gwyddion 2.61 for AFM data, WIRE 5.5 for Raman spectra and HighScore Plus for XRD data or OriginPro for other spectroscopy.

3 Results & Discussion

3.1 Production of novel 2D nanosheets by sonication-assisted LPE

Since 2D conductors beyond graphene are scarce, the LPE of conductive materials was investigated. Metal diborides represent a family of layered non-van der Waals crystals with semimetallic properties for all nanosheet thicknesses. While previous reports show that the exfoliated nanomaterial is prone to oxidation, we demonstrate a readily accessible inert exfoliation process to produce quasi-2D nanoplatelets with intrinsic material properties. For this purpose, we demonstrate the exfoliation of three representative metal diborides (MgB_2, CrB_2, and ZrB_2) under inert conditions, see Figure 1 (https://pubs.acs.org/doi/full/10.1021/acsnano.4c04626). The nanomaterial is characterized using a combination of transmission electron microscopy, scanning electron microscopy, atomic force microscopy, IR, and UV–vis measurements, with only minimal oxidation indicated postprocessing. By depositing the pristine metal diboride nanoplatelets as thin films using a Langmuir-type deposition technique, the ohmic behavior of the networks is validated. Furthermore, the material decomposition is studied by using a combination of electrical and optical measurements after controlled exposure to ambient conditions. Finally, we report an efficient, low-cost approach for sample encapsulation to protect the nanomaterials from oxidation. This is used to demonstrate low-gauge factor strain sensors, confirming metal diboride nanosheets as a suitable alternative to graphene for electrode materials in printed electronics.

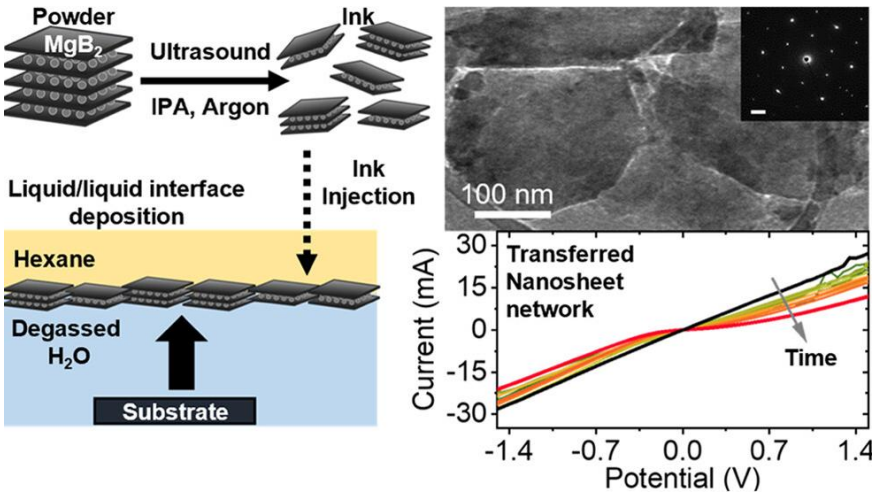

Figure 1: LPE of metal diborides. Left) Schematic of the structure of the metal diborides, their exfoliation and deposition using a Langmuir Schaefer type technique. Right: TEM image of the deposited film with SAED patterns as inset and I-V characteristics of the NS network.

Another promising conductor is TaS_2 which is stable as different polytypes. 1T-TaS_2 exhibits charge density wave phases, while 2H-TaS_2 is metallic at room temperature. Unfortunately, phase-pure synthesis of the bulk materials is challenging to date. Since LPE of this material has not been described in detail, we subjected different batches of bulk materials to LPE under inert conditions using both

bath and tip sonication in dried and degassed NMP. Nanosheets were then purified and size-selected by cascade centrifugation. Extinction spectra of one size-selected fraction are compared in Figure 2a. Bath and tip sonication yielded similar results. However, one batch showed a strikingly different extinction spectrum which suggests that the polytype can be identified through UV-Vis. Future work will be conducted for clarification. The extinction spectra of the size-selected fractions show systematic changes with NS size (Figure 2b) including blue shift in the peak position with decreasing NS size/thickness and changes in relative intensities. This is illustrated by the plot of the extinction intensity ratio at 700 nm / 320 nm as function of central centrifugal acceleration in Figure 2c. Again, data from bath and tip sonication agrees very well. The nanosheets were deposited into thin films using the Langmuir Schaefer type deposition at the water-hexane interface. Representative SEM images, which also confirm successful size selection are shown in Figure 2d.

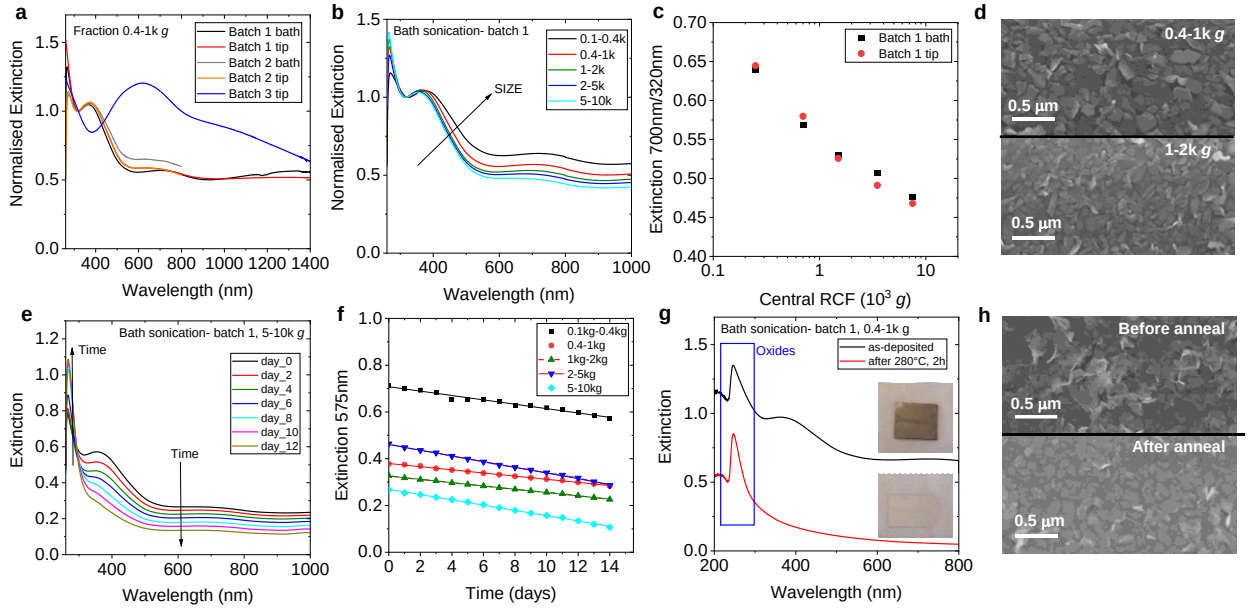

Figure 2: Characterisation of LPE TaS_2 exfoliated under inert conditions. A) Normalised extinction spectra of one size-selected fraction obtained from different batches after tip and bath sonication. B) Extinction spectra of size-selected fractions showing size-dependent changes. C) Intensity ratio of extinction at 700 nm / 320 nm as function of central centrifugal acceleration used in size selection. D) SEM images of two fraction after Langmuir Schaefer deposition. E) Extinction spectra measured at different time intervals after exposure to ambience. F) Extinction at 575 nm as function of time for the different fraction indicating degradation according to (pseudo) 0 order kinetics. G) Extinction spectra of a Langmuir-Schaefer deposited film (2 subsequent cycles) and the same film after annealing showing complete conversion to an opaque film. H) SEM images of the film in G) before and after annealing.

To investigate the degradation of the TaS_2, the dispersion were exposed to ambient conditions and the extinction measured at different time intervals. A set of spectra in Figure 2e illustrate distinct changes: A decrease in extinction over the entire Vis/nIR region and an increase in the extinction in the UV region which is assigned to tantalum oxide. The kinetics (Figure 2f) indicate unusual (pseudo) 0 order kinetics due to the linear decrease of extinction over time. Time constants vary across the size selected

fractions with the tendency that degradation is faster in fractions of small/thin NSs. The UVVis spectroscopic fingerprint of degradation can also be used to assess whether NSs are intact after deposition. Extinction spectra of Langmuir-Schaefer deposition are shown in Figure 2g. Already immediately after deposition, the oxides can be identified in the UV region, as the sample was exposed to ambient conditions and water during the deposition. After annealing at 280°C for 2h, the film turns completely transparent/opaque suggesting complete conversion to an oxide. Interestingly, SEM images (Figure 2h) reveal that the films are more ordered after annealing with well-defined nanosheets. In future work, such films will be tested as dielectrics.

Furthermore, more exotic, less well-known layered materials were investigated in LPE. The NSs of Bi_2SeO_5 , a known high-κ dielectric, have been produced by LPE for the first time by sonication in IPA. The NSs exhibited notable colloidal stability in the exfoliation media, IPA in this case, remaining suspended for several weeks. The nature of this enhanced stability achieved without additional functionalization of the NSs or the addition of dispersants in the solvent/ink will be studied in future work. The characterisation is summarised in figure 3. The diffraction pattern (Figure 3b) indicates polycrystallinity or randomly restacked nanosheets. TEM (Figure 3c) and AFM (Figure 3f) show NSs typical for LPE with well-defined shape and sharp edges which are very polydisperse in thickness (Figure 3e). XRD (Figure 3d) and Raman spectroscopy (Figure 3g) confirm that the nanosheets are structurally intact after LPE.

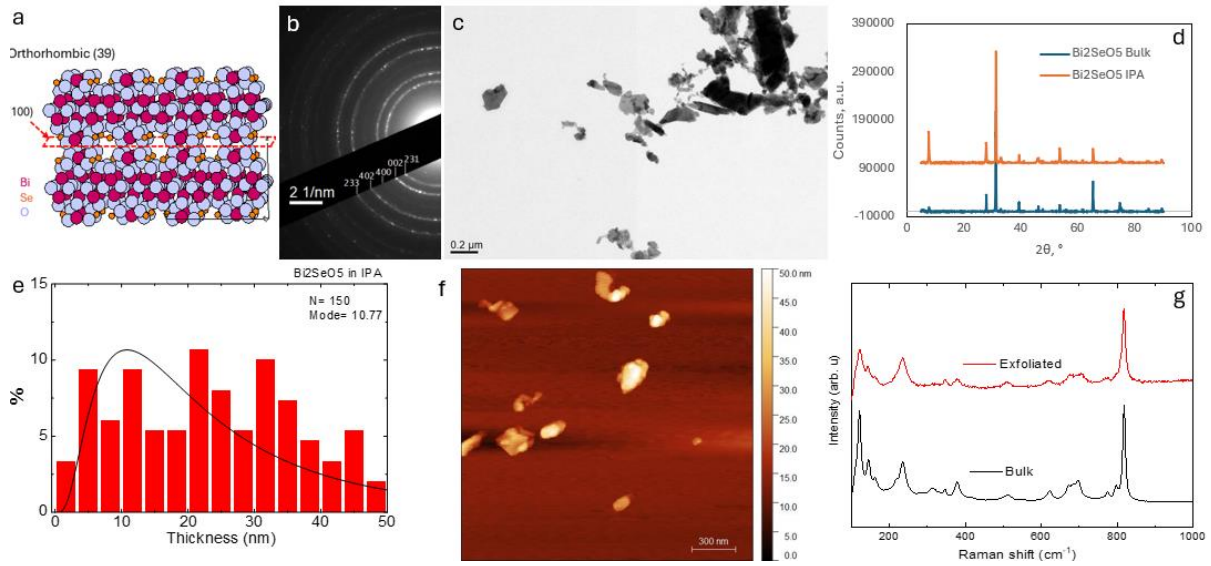

Figure 3. Bi_2SeO_5 NSs produced by LPE and their structural characterization. a) model of the orthorhombic crystal structure of Bi_2SeO_5 with the cleavage plane, (100), indicated. b) electron diffraction pattern matched with the reference structure of Bi_2SeO_5, PDF 01-070-5102 and c) TEM image of the exfoliated NSs. d) comparison of XRD spectra from bulk and exfoliated materials, both matching the reference structure of Bi_2SeO_5. The AFM statistical analysis (e) and a typical image (f) indicate that most flakes were around 10 nm thick. The Raman spectroscopy characterization (g) confirms that the structure of the material has been preserved through the exfoliation process.

The NSs obtained by sonication-assisted LPE of CrSBr, a 2D magnetic semiconductor, resemble the anisotropic morphology and growth pattern of the corresponding bulk single crystals, which crystalize in the form of needles. The exfoliated NSs are also distinctly elongated or wire-shaped, with many of these elongated NSs fragmented to smaller rectangular sheets. The characterisation in summarised in Figure 4. Interestingly, AFM shows a relatively narrow thickness range. XRD and Raman confirm the structural integrity.

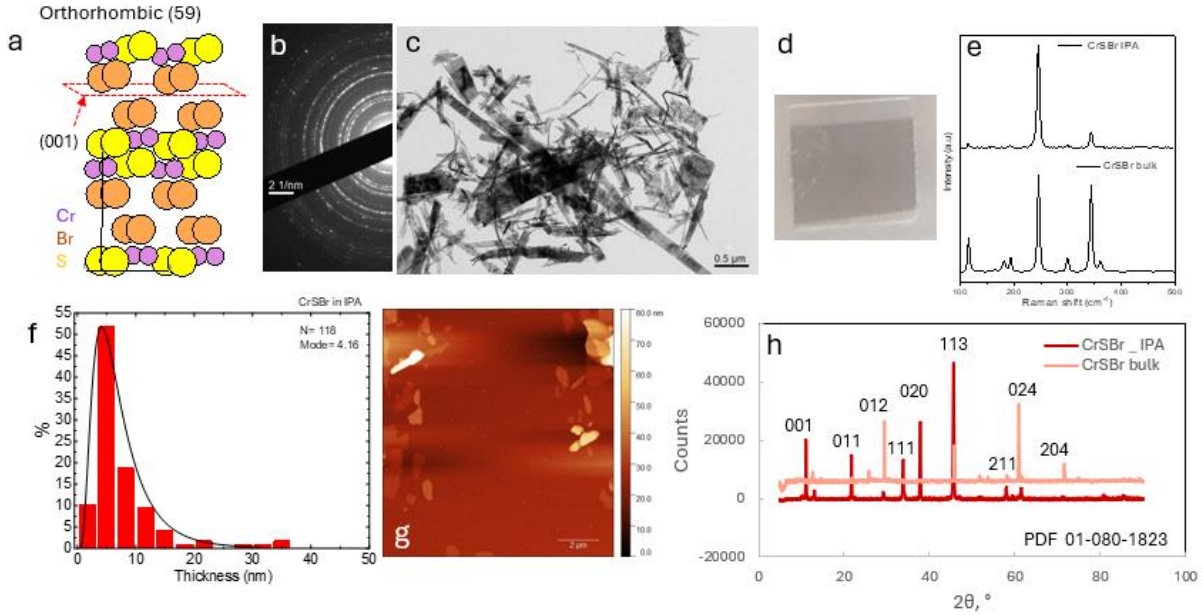

Figure 4: Exfoliated NSs of CrSBr and their characterization. a) model of the orthorhombic crystal structure of CrSBr with the (001) cleavage plane indicated. b) an electron diffraction pattern from the exfoliated NSs indexed according to CrSBr reference pattern PDF 01-080-1823 and c) the corresponding TEM image. d) A thin film produced by spray printing of CrSBr ink on glass substrate, e) the Raman spectra from the exfoliated and bulk materials indicate no changes in the structure because of the exfoliation. f) AFM statistical analysis of the NSs such as those shown in g) indicates that most NSs were around 4 nm thick. The XRD analysis of bulk and exfoliated materials confirms no structural changes in the material following the exfoliation.

The NSs of $Na_2Cu_2TeO_6$ have also been produced by sonication-assisted LPE and exhibit irregular morphology with relatively wide size distribution in terms of both lateral size and thickness (Figure 5). The electron diffraction pattern from the exfoliated product is matched with the standard monoclinic structure, while Raman spectroscopy and XRD confirm that the structure of the bulk material has been preserved after exfoliation.

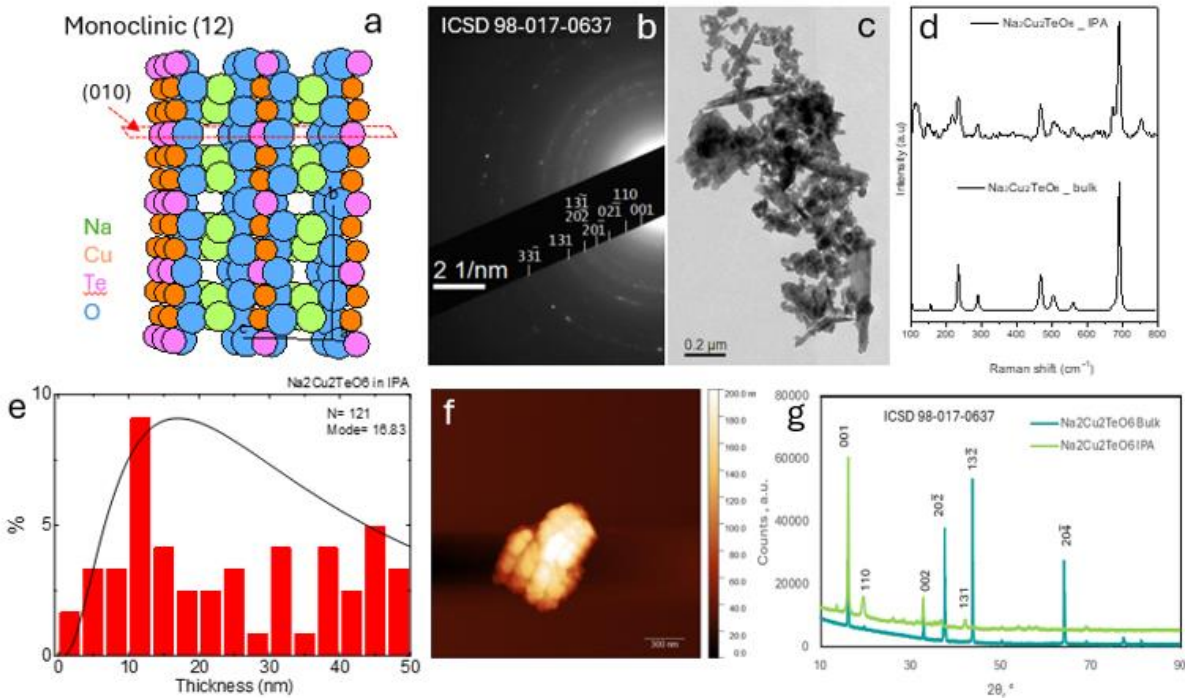

Figure 5: Exfoliated $Na_2Cu_2TeO_6$ NSs and their characterization. a) model of the monoclinic crystal structure adopted by this quaternary compound b) an electron diffraction pattern from the exfoliated NSs indexed according to reference pattern ICSD 98-017-0637 and c) the corresponding TEM image. d) The Raman spectra from the exfoliated and bulk materials indicate no changes in the structure because of the exfoliation. e) AFM statistical analysis of the NSs such as those shown in f) indicates that most NSs were around 17 nm thick. The XRD analysis of bulk and exfoliated materials (g), confirms no structural changes in the material following the exfoliation.

3.2 Contribution to project (linked) Objectives

The exploration of novel, previously unexplored 2DM is directly related to the main objective of 2D-PRINTABLE, namely to use sustainable liquid-exfoliation techniques to develop a wide range of new 2DMs and to develop the printing and liquid-deposition methods. The results summarised greatly contribute to O1.3: Liquid-based exfoliation of bulk 3D layered materials to yield novel 2D materials and O4.1: Basic characterization of as-exfoliated and functionalized nanosheet building blocks. The requirement for the study is the availability of new bulk materials, and hence a connection to O1.1: Prediction of a portfolio of new 2D materials with ad-hoc designed (opto)electronic properties and O1.2: Synthesis of bulk 3D layered materials

3.3 Contribution to major project exploitable result

Not applicable

4 Conclusion and Recommendation

This deliverable describes the characterisation of 5 new materials exfoliated materials: metal diborides, TaS_2, Bi_2SeO_5, CrSBr, $Na_2Cu_2TeO_6$. Some of these (Bi_2SeO_5, CrSBr, $Na_2Cu_2TeO_6$) are unexplored, while others (metal diborides, TaS_2) have been reported in literature, but not comprehensively. One objective of 2D-PRINTABLE is to identify and explore >10 materials. Considering that theory-driven identification of interesting materials and synthesis of the bulk materials require some time, we are well on track at the current state at project midterm, as many new bulk materials are already available by now (see D1.3).

Perhaps not surprisingly, we found that some materials (metal diborides, TaS_2) are prone to degradation under ambience. However, we also demonstrate that this can be mitigated through inert exfoliation and importantly, for metal diborides, it was shown that tiled nanosheet networks with good conductivities can nonetheless be fabricated. For TaS_2 we plan to showcase that degradation can also be an opportunity when it is controlled, as it allows a conversion to insulating oxides which can be promising dielectrics which are typically more difficult to make due to limited exfoliation strategies.

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
WP1,2,4	Stable, narrow linewidth emitter from earth abundant elements with high PLQY cannot be found within project lifetime	2	2	Up to now, no new, stable emitter material was found. For light emitting dioides, work will focus on monolayered TMDs and InSe

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

5.2 Interconnections with other deliverables

The current deliverable is closely related to the D4.1 “Characterization of nanosheets, networks and heterostacks built from initially available 2D materials” which describes the established characterisation routines in more detail as well as the upcoming D4.3 “Protocols for new characterization methodologies”. Further, it builds on D1.1 “Database on available materials”, and D1.3 “Synthesis of bulk materials”.

Since characterisation of nanosheets and their networks is an integral part of the process chain from production to applications, it is directly or indirectly connected to all tasks and deliverables within 2D-Printable.

6 Deviations from Annex 1

Not applicable

7 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.

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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