

Liquid Phase Exfoliation, characterization, and printing of SnSe and PtSe₂ devices



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Declaration

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Abstract

The demand for optical-to-electrical and/or electrical-to-optical transducers is growing exponentially as optics are increasingly adopted for energy-efficient data transmission. Displays and light sensors are increasingly being integrated in ever more everyday objects. Indeed, optoelectronics is at the core of countless science disciplines and technological applications and there is a clear roadmap towards achieving not only broader band, faster and higher sensitivity (or brighter) devices, but also to develop devices with new functionalities. Since 2010–2011, the relatively young field of two-dimensional materials has experienced a new interest, originating from the research on graphene, and other related atomically thin 2D semiconductors. Recent breakthroughs have shown these 2D materials to cover a broader bandwidth range in the electromagnetic spectrum.

This is due to their unique property of encompassing large exciton binding energies and exceptionally strong light-matter interaction. This makes 2D semiconductors extremely appealing for optoelectronic applications where conventional semiconductors cannot provide the same performance nor added functionality.

Due to the increasing demand for energy and the ongoing climate crisis, it is crucial to develop sustainable materials, and devices able to produce and store solar energy and exploit sustainable processes like hydrogen evolution. Current sustainable devices, such as solar cells and heterojunctions, can be improved with the addition of 2D materials.

This work studies the properties of two materials, SnSe and PtSe₂, for applications in optoelectronic devices.

SnSe has demonstrated versatility in thermoelectronics, photodetectors, solar cells, photocatalysts, phase change memory, and gas sensors. The indirect bandgap of SnSe is ≈ 0.9 eV, and the direct is ≈ 1.3 eV.

Our interest towards PtSe₂ grew due to its photonic, physical, and chemical properties. The exfoliation of PtSe₂ allows us to modulate the electronic structure, resulting in a tuneable bandgap, which allows a transition from semimetal to semiconductor when exfoliated to less than three layers, with a monolayer bandgap of 1.17 eV.

Liquid Phase Exfoliation (LPE) is versatile, scalable, and sustainable and allows processes that would be impossible otherwise. This technique can obtain free-standing films, facilitating

nanomaterial mixing to form heterostructured solids and enabling insertion in a polymer matrix.

In this work, LPE methodologies are developed for the exfoliation of both SnSe and PtSe₂. The obtained dispersions were characterized with UV-Vis, SEM, TEM, and AFM. These dispersions were then printed on a substrate and the obtained device underwent photoelectrical characterization with current-voltage, photo response and power dependence studies.

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Abbreviations

2D	Two-dimensional
AFM	Atomic Force Microscopy
AJP	Aerojet printing
IPA	Isopropanol
IR	Infrared radiation
LCC	Liquid Cascade Centrifugation
LPE	Liquid Phase Exfoliation
NMP	N-Methyl-2-Pyrrolidone
PtSe₂	Platinum selenide
SEM	Scanning Electron Microscopy
SnSe	Tin selenide
TEM	Transmission Electron Microscopy

Table of content

Declaration.....	i
Abstract.....	ii
Acknowledgements	iv
Abbreviations	v
1. Introduction.....	1
1.1 TMDs and 2D materials.....	1
1.2 Exfoliation techniques	2
1.2.4 Liquid Phase exfoliation	5
1.3 Applications ultimately sought by this project	8
1.3.1 Principles of solar cells	8
1.3.2 Principles of heterostructure for water splitting photocatalysis.....	9
1.4 Objective of this work.....	11
2. Experimental techniques	13
2.1 Transmission Electron Microscopy	13
2.2 Scanning Electron Microscopy	14
2.3 Atomic Force Microscopy (AFM)	14
LiteScope™ (AFM+SEM system)	15
2.4 UV-VIS	16
2.5 Inkjet printing.....	17
2.6 Aerosol jet printing	18
3. SnSe, exfoliation and characterization.....	20
3.1 Introduction.....	20
3.2 Materials and Methods.....	21
Ultrasonic bath.....	21
Sonic tip	21
Liquid cascade centrifugation	21
3.3 Results.....	22
3.3.1 Analysis of SnSe exfoliated with sonic bath.....	22
3.3.2 Analysis of SnSe exfoliated by sonic tip	28
3.4 Conclusions.....	31
4. PtSe₂, exfoliation and characterization	32
4.1 Introduction.....	32

4.2 Materials and methods	32
Ultrasonic bath	33
Sonic tip	33
4.3 Results.....	33
4.3.1 Analysis of PtSe ₂ exfoliated with sonic bath	33
4.4 Conclusions.....	36
5. Devices.....	37
5.1 Deposition devices	37
5.1.1 Results with SnSe	37
5.1.2. Results with PtSe ₂	46
5.2 Printed devices	51
5.2.1 Printing of SnSe dispersions	51
5.2.2 Printing of PtSe ₂ dispersions.....	53
5.3 Film deposition	55
5.4 Conclusions.....	56
6. Conclusions and future work.....	57
7. References.....	59

1. Introduction

1.1 TMDs and 2D materials

In the last decade, the interest of the scientific community has been directed on on the study of two dimensional (2D) materials, with this interest going beyond graphene.¹ 2D materials have advantages that arise only when their thickness is near-atomic, allowing thus easy regulation of their properties by surface modification and superb robustness, beside the already mentioned increase of surface area², thus opening the door to various applications across diverse scientific and technological domains.

Among the plethora of 2D nanomaterials, semiconducting 2D nanomaterials distinguish as particularly significant due to their intrinsic electronic properties and potential applications in electronics³, photonics⁴, optoelectronics³, and beyond.^{5,6,7,8}

Semiconducting 2D materials exhibit unique electronic band structures and unprecedented physical properties that are not observed in bulk semiconductors³. Due to their ultrathin nature, these materials possess excellent mechanical strength, flexibility, optical transparency which are fundamental for the next generation of optoelectronic devices; and the large lateral size while maintaining atomic thickness confers them ultrahigh specific surface area.⁹

One of the most prominent semiconducting 2D nanomaterials is graphene, single atomic layer derived from graphite, in which the carbons are bonded with each other in a honeycomb lattice¹⁰. Graphene's superior characteristics such as excellent thermal conductivity and ultra-high carrier mobility¹¹ makes it suitable for many applications such as transparent conductive electrodes¹² and flexible electronics¹³.

Following graphene's discovery, the exploration of other ultrathin 2D materials expanded towards materials with distinct properties and compositions.

Transition metal dichalcogenides (TMDs), such as molybdenum disulfide (MoS₂), have raised interest due to their layer-dependent bandstructure, strong light-matter interactions and high carrier mobility.¹⁴ These materials can find applications in optoelectronic, comprising photodetectors¹⁵, light-emitting diodes (LEDs)¹⁶ and solar cells¹⁷.

Research efforts worldwide have focused on the synthesis, characterization, and manipulation of semiconducting 2D nanomaterials. Techniques such as chemical vapor deposition (CVD)^{11,18}, molecular beam epitaxy (MBE)¹⁹, and liquid-phase exfoliation^{20,21} have been developed to meet the objective of controlling the growth and properties of these materials. The thus synthesised nanosheets can be studied and characterized at the nanoscale with

advanced techniques including scanning probe microscopy²², transmission electron microscopy²³ and atom force microscopy²⁴.

This research examines the qualities of SnSe and PtSe₂, which have the potential for use in optoelectronic devices^{15,25,26,27}.

SnSe has demonstrated its versatility across various applications including thermoelectrics²⁸, photodetection²⁹, solar cells¹⁷, phase change memory³⁰, and gas sensing³¹. It possesses an indirect bandgap of approximately 0.98 eV and a direct bandgap of approximately 1.43 eV.³²

Our interest in PtSe₂ stems from its intriguing photonic, physical, and chemical properties³³ and finds potential applications in field-effect transistors³⁴, photodetectors³⁵, and gas sensor³⁶. Exfoliation of PtSe₂ enables the manipulation of its electronic structure, resulting in a tunable bandgap. When exfoliated to less than three layers, PtSe₂ undergoes a transition from a semimetal to a semiconductor, exhibiting a bandgap of 1.17 eV for monolayers.³⁷

Liquid Phase Exfoliation (LPE) was employed as it is a versatile, scalable, and sustainable technique that facilitates processes otherwise impractical, and it is compatible with printing techniques.²

1.2 Exfoliation techniques

There are many exfoliation techniques to obtain 2D nanosheets (Figure 1), and these can be divided into top-down and bottom-up methods. Top-down synthesis methods use either a physical or chemical procedure to produce nanosheets. A physical top-down method is, for example, the use of ultrasonic waves; a chemical method depends on chemical reactions caused by ion exchange, heat, etc. Bottom-up methods, instead, are: physical aggregation, chemical reactions or the use of templates to manipulate the assembly of the basic building blocks, leading to the formation of nanostructures.³⁸

A first and well established top-down method is the micromechanical cleavage exfoliation, which consists in the application of a mechanical force by the use of a Scotch tape to break the van der Waals forces between the planes of the layered material, and therefore obtaining a 2D material.³⁹ This technique, employed by Novoselov and Geim, was the first used to exfoliate graphite to obtain 2D monolayered graphene.⁴⁰

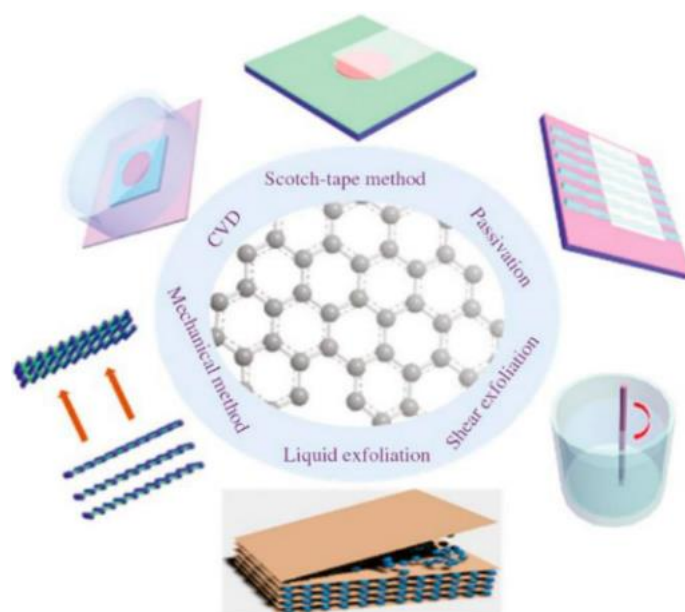


Figure 1. Different exfoliation techniques to produce 2D nanomaterials. Picture credit: Reference 38.

The graphite flakes are firstly placed on the scotch tape, which is then folded in half several times. After repeating the process more times, the graphite flakes get thinner and thinner, and subsequently, the graphite flakes are pressed on a silicon wafer. Finally, 2D monolayer graphene is obtained by the removal of the tape. The scotch tape method has two main shortcomings. The first is the low yield considering the amount of effort this technique requires, the second is that it produces monolayers which are severely broken up so very small monolayers.⁴¹

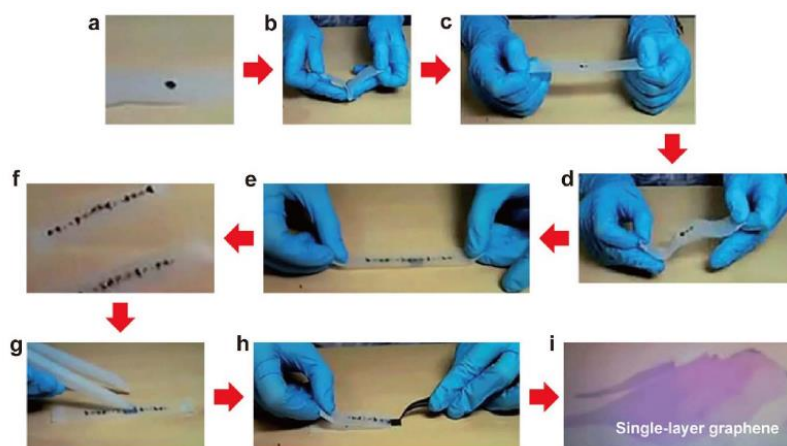


Figure 2. Steps of scotch-tape exfoliation of graphene. (a) Placing bulk graphite on the scotch tape. (b)-(f) Folding scotch tape in half. (g) Pressing graphite flakes onto the substrate. (h) Removing scotch tape. (i) Micrograph of exfoliated graphene. Picture credit: Reference 41.

Mechanical exfoliation (Figure 2), though, is not limited to just scotch-tape exfoliation, despite the latter being the best known. Graphene exfoliation via three-roll mill has been demonstrated

⁴² and implementation of scotch-tape exfoliation with home-built machines is also a good way to obtain few- or mono-layer flakes.⁴³

Shear exfoliation is exfoliation in a solution using rotor-stator high shear mixing or even simple kitchen mixers. The graphene nanosheet exfoliated with this method is of similar size and quality to the ones obtained by ultrasonication exfoliation and, most importantly, the main advantage of this method is that it is easy to scale up ⁴⁴ When scaling up the shear exfoliation for graphene, it was observed that there is the need for a shear minimum rate for the exfoliation to take place. This shear minimum is defined as a function of the energy cost of exfoliation;

$$\dot{\gamma}_{min} = \frac{[\sqrt{E_{S,G}} - \sqrt{E_{S,L}}]^2}{\eta L}$$

Where $\dot{\gamma}_{min}$ is shear min, η is the liquid viscosity, L the minimum exfoliable platelet length and $E_{S,G}$, $E_{S,L}$ are the material and liquid surface energy respectively.⁴⁵

Another example of exfoliation in a liquid medium is the ion intercalation exfoliation. Lithium is the most obvious choice because of the well-known intercalation of the Li^+ ions exploited in lithium batteries since the 1970s. The Li intercalation process is monitored until the full reach of the insertion. Afterwards, Li metal is used as the anode and source of Li ions, while the layered materials are incorporated into the cathode of the battery test cell. Once the insertion is complete, the cell is disassembled and the material is sonicated in water, during which the formation of $\text{Li}(\text{OH})$ and hydrogen gas facilitates the separation and isolation of the 2D nanosheets, as shown in Figure 3.⁴⁶

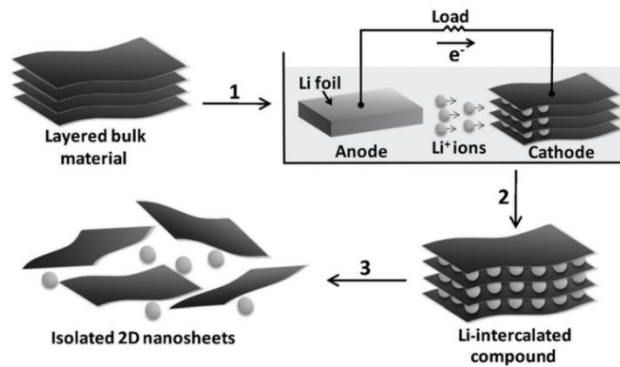


Figure 3. Schematics of ion intercalation exfoliation. Electrochemical lithiation process for the fabrication of 2D nanosheets of the layered bulk material. Picture credit: Reference 46.

This technique has also been employed for SnSe, utilising a hydrothermal method to intercalate lithium ions into the layered SnSe. Subsequently, this hybrid was introduced into water, triggering a vigorous reaction to separate the sheets. Finally, sonication was conducted to disperse the nanosheets.⁴⁷

Another interesting method is the ion exchange, which takes advantage of the fact that layered double hydroxides (LDHs), clays, and some metal oxides, contain an exchangeable interlayer of cationic counterions. Such ions can be exchanged for protons by soaking in acidic solutions. The protons can then be exchanged for bulky organic ions, leading to substantial swelling, as shown in Figure 4.⁴⁸

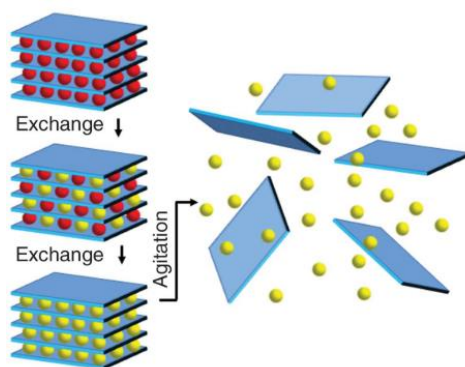


Figure 4. Schematics of ion exchange exfoliation. Some layered compounds contain ions between the layers to balance the surface charge on the layers. These ions (red) can be exchanged in a liquid environment for other, larger ions (yellow). Agitation results in an exfoliated dispersion. Picture credit: Reference 48.

Bottom-up methods of synthesising nanosheets comprise chemical vapour deposition (CVD). This is a promising approach to obtain graphene monolayers because it is inexpensive, transferable and it can produce high quality and large-area graphene films. The growth process involves the thermal decomposition of a hydrocarbon source of a heated substrate and, depending on the substrate, it can be catalytically enhanced. During the reaction, the metal substrate not only works as a catalyst, but also determines the graphene deposition mechanism. In the case of metals having high carbon solubility (Ni, Fe), the carbon will diffuse/dissolve into a heated substrate according to the solubility of the carbon. As the substrate cools down, the dissolved carbon will segregate to the surface to form graphene sheets.¹¹

1.2.4 Liquid Phase exfoliation

Despite the advantages of the bottom-up methods described in the previous paragraph, top-down methods are cost-effective and easily scalable, more suited to industrial applications². The choice of the solvent is crucial because if the surface energy of the solvent is similar to the one of the layered material, the energy difference between exfoliated and reaggregated states will be minimized, therefore the driving force for reaggregation will be removed, as shown in Figure 5.⁴⁸

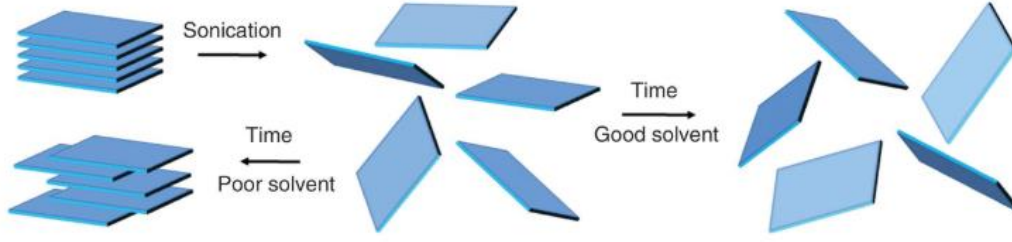


Figure 5. Schematic of the liquid phase exfoliation. The layered crystal is sonicated in a solvent, resulting in exfoliation and nanosheet formation. In good solvents, those with appropriate surface energy, the exfoliated nanosheets do not reaggregate. In bad solvents, reaggregation and sedimentation will occur. Picture credit: Reference 48.

In this thesis, LPE is the chosen exfoliation technique. LPE, though, does not produce only delaminated crystals, but also multi-layered micro- and nanoparticles of all sizes and thicknesses, which means that the ink production must encompass a size selection process to remove the non-exfoliated material. In particular, sonication-assisted exfoliation starts with the dispersion of the bulk material in a solvent, followed by material exfoliation by ultrasonic energy and removal of the non-exfoliated material by centrifugation. Exfoliation is induced by alternating expansive and compressive ultrasonic waves travelling through the solvent, which leads to cavitation events involving gasses or microscopic voids present in the liquid. As the bubbles expand, their inner pressure considerably decreases, such that after they reach their maximum size they undergo a violent collapse.²

The dispersions, to be stable, must have the enthalpy of mixing, ΔH_m , minimized:

$$\Delta H_m \approx \phi(1 - \phi)[(\delta_{S,D} - \delta_{F,D})^2 + (\delta_{S,P} - \delta_{F,P})^2 + (\delta_{S,H} - \delta_{F,H})^2]$$

Where ϕ is the dispersion's flake fraction, $\delta_{S,D}$, $\delta_{S,P}$ and $\delta_{S,H}$ are the dispersion (δ_D) polar (δ_P) and hydrogen (δ_H) solubility parameters of the solvent, and $\delta_{F,D}$, $\delta_{F,P}$ and $\delta_{F,H}$ those of the flake. ΔH_m can be minimized by matching as closely as possible the solubility parameters of the solvent and the flake.²

Minimal energy cost of exfoliation is expected for solvents whose surface energy matches that of the layered material. For compatible solvents, this ratio must be close to zero.⁴⁹

Respecting the minimum enthalpy condition, it is possible to exfoliate several materials such as graphene, with a concentration of up to 30 mg/ml, which is promising for all the range of applications where good electrical performance is required. Besides graphene, LPE has been used to exfoliate materials such as h-BN and a range of TMDs; the latter are important because they can find applications as composite fillers and energy storage. Other materials to be exfoliated with this technique are oxide nanosheets, which are most often wide-bandgap semiconductors, making them good candidates for applications in photocatalysis and high-

dielectric constant materials.⁴⁸ The last two mentioned applications are indeed the most important for this project, and to understand why semiconductors, among which SnSe and PtSe₂, can find applications as components of photoelectronic devices, it is necessary to explain the concept of *band structure*. The band structure of a compound is determined by its crystal structure, in which a is the lattice spacing, meaning the unit cell in one dimension, and k is an index of the irreducible representation of the translation group Ψ . The wave function corresponding to $k = 0$ is the most bonding one, the one for $k = \pi/a$ the top of the band; k also counts nodes, meaning that the larger the absolute value of k , the more nodes one has in the wavefunction. The range $-\pi/a \leq k \leq \pi/a$, or $|k| \leq \pi/a$, is called the first Brillouin zone, which is the range of unique k . There is an energy level for each value of k , which is also a wave vector, and it measures momentum; it is quantized, and there is a finite, but large, number of levels. Graphs of $E(k)$ vs k are called band structures: an example of this graph is shown in Figure 6.

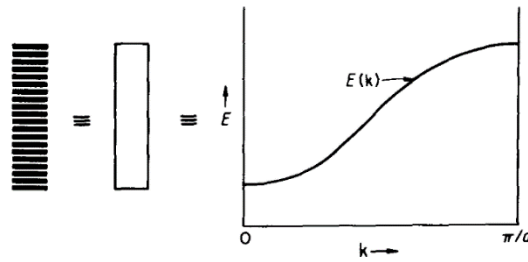


Figure 6. Band structures, $E(k)$ vs k . Picture credits: Reference 50.

Bandwidth is the difference in energy between the highest and lowest levels in the band. It depends on the overlap between the interacting orbitals: the greater the overlap between neighbours, the greater the bandwidth. The energy of the orbital at the centre of the zone $E(k = 0)$ is less than the one at the edge $E(k = \pi/a)$. In the case of two dimensions (or more) k is treated as a vector, with components in reciprocal space, and the Brillouin zone is a two- or three-dimensional area (or volume) and a square lattice is defined by the translation vectors $\vec{a}_1$ and $\vec{a}_2$. The wavelength is inversely proportional to the magnitude of that vector. The space of k is defined by two vectors $\vec{b}_1$ and $\vec{b}_2$ and the range of allowed k (the Brillouin zone) is a square. Certain values of k are given names: $\Gamma = (0,0)$ is the zone center, $X = (\pi/a, 0) = (0, \pi/a)$, $M = (\pi/a, \pi/a)$.⁵⁰

1.3 Applications ultimately sought by this project

As stated previously, the LPE exfoliated 2D SnSe and PtSe₂ will be used for the development of optoelectronic devices. In specific, solar cells and water-splitting photocatalytic heterostructured devices were the applications sought in the project. Below, the background theory of these two types of devices is elucidated.

1.3.1 Principles of solar cells

Solar cells are important because they are the most deployed solar electric technology today; they are fuelled by sunlight and can operate near ambient temperature with no moving parts, and they enable distribution of energy at any scale, thus making them a good renewable source. Solar cells are of two types: the first type, wafer-based solar cells, are fabricated on semiconducting wafers and can be handled without an additional substrate. The most mature photovoltaic technology is crystalline silicon (c-Si) solar cells⁵¹, since the first invention of solar cells in 1954 by Bell Laboratories⁵², which have the fundamental limitation of the indirect bandgap. This leads to weak light absorption and require wafers with the thickness on the order of 100 μm in the absence of advanced light-trapping strategies.⁵¹

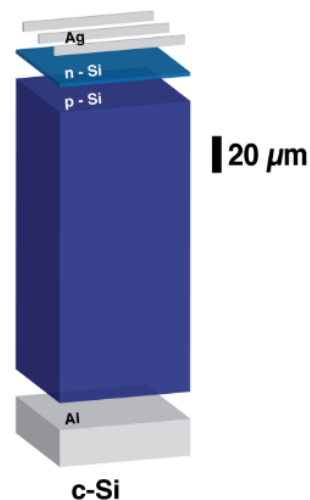


Figure 7. c-Si wafer solar cell structure. The primary absorber is labelled in white. Picture credits: Reference 51.

In Figure 7, a c-Si wafer solar cell is shown. Aluminium is as a substrate, while the main absorbers of light are *p*-Si and *n*-Si. In the end, silver transports the current generated from this cell.⁵¹

The second type of solar cells is the thin-film cells, which consist of semiconducting films deposited onto a glass, plastic, or metal substrate.⁵¹ The development of this kind of cell started in the 70s, with the CdS/CdTe solar cell by Bonnet.⁵³ An example of flexible perovskite

photovoltaic device (PSC) is shown in Figure 8. A low-temperature solution process prepared the PSC on an indium tin oxide (ITO) electrode and subsequently fabricated the device with the graphene electrodes by coating a two-layer graphene with different polymer substrate films such as P3HT (poly-3-hexylthiophene) to serve as hole transport layer.⁵⁴

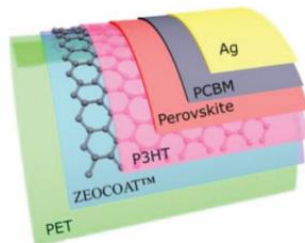


Figure 8. Schematic representation of flexible PSC. Picture credit: Reference 54.

The development of thin film solar cells is driven by the way of producing photovoltaic modules more cheaply than ever before to meet the sustainable green energy demand. The material for these thin film-based cells must be cheap, non-toxic and earth-abundant, it should have an optimal bandgap, high absorption coefficient, high quantum yield for excited carriers, long carrier diffusion length and precise controllability of stoichiometry to yield high quantum efficiency. Tin selenide (SnSe) is a material that satisfies these conditions since it has a near optical band gap of 1.3 eV with a high optical absorption and coefficient of 10^5 cm^{-1} , which indicates that a thin layer of 300 nm thickness is sufficient to absorb the most useful part of the solar spectrum.⁵⁵ As for SnSe, indeed, a heterojunction FTO/SnSe has already been built and it is shown in Figure 9. FTO films are prepared on glass, and an ultrathin layer of Se is deposited prior to SnSe to maintain the stoichiometry of SnSe film. SnSe is evaporated onto the FTO-coated glass slides, and then a silver layer is grown on the SnSe film for electrical contact and backfield reflectance.⁵⁶

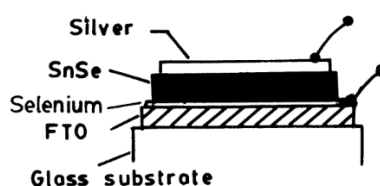
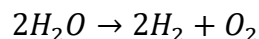


Figure 9. Schematics of FTO/SnSe heterojunction. Picture credit: Reference 56.

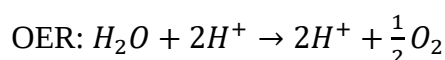
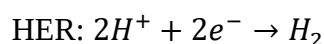
1.3.2 Principles of heterostructure for water splitting photocatalysis

A heterostructure is defined as a composite structure that couples different solid-state materials with interfacial interaction. The heterostructured composites not only preserve the intrinsic characteristic of both components, but also serve to produce novel or enhanced performance,

which can be attributed to the synergistic effects arising from the heterointerface.⁵⁷ Water is the most extensive resource on earth as one of the most important H-containing compounds. Electrochemical water splitting is a very mature technology, in theory.⁵⁸ Water-splitting is an endothermic reaction in which water is broken down into oxygen and hydrogen:



Splitting water into hydrogen is an uphill chemical process with a corresponding rise in Gibbs free energy.⁵⁹ In theory, only two half-reactions are involved: oxygen evolution reaction (OER) on the anode and hydrogen evolution reaction (HER) on the cathode.⁵⁸



In these reactions, significant potential losses are expected, resulting from entropy contributions of electrons and potential interfacial barriers caused by poor alignment.⁵⁹ In order to have these reactions working, a large potential is needed to drive these reactions due to the sluggish electrochemical kinetics, since nowadays the energy conversion efficiency of water-splitting is only 56-73% and only 5% hydrogen is produced by this technology. It is therefore necessary to develop efficient catalysts to accelerate the reaction rate of HER and OER.⁵⁸

Photocatalytic materials usually comprise metal oxide semiconductors and efficiently absorb visible light irradiation up to a wavelength of 520 nm. Such semiconductors must meet the thermodynamic conditions for driving water breakdown in H_2 and O_2 . A photon with energy higher than the bandgap excites an electron from a filled valence band state to an empty conduction band. After photoexcitation, the ability of a photoexcited electron (e^-) and hole (h^+) to reduce and oxidize is then determined by the bottom of conduction band (CB) and the top of valence band (VB) in the band structure. Those carried charges should be thermally relaxed to the bottom of the CB and the top of the VB. At the bottom of CB, the conditions for a photocatalytic reaction should be higher (more positive) than the reactant's reduction potential (P_{red}) (Figure 10).⁵⁹

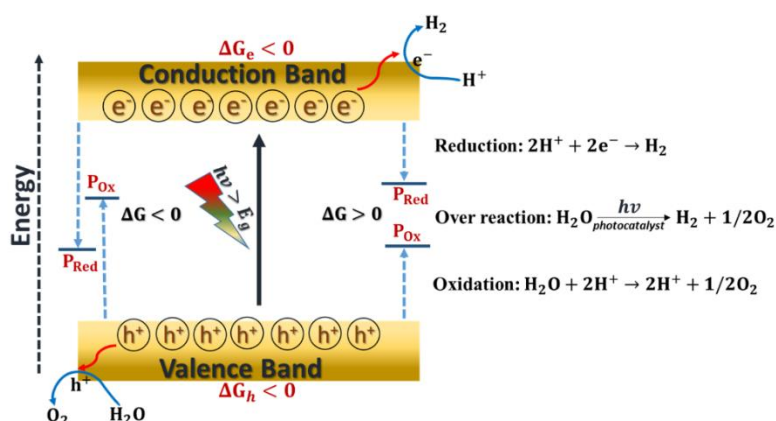


Figure 10. A schematic diagram of the band alignment of a semiconductor photocatalyst. Picture credit: Reference 59.

Photocatalytic splitting has received more attention due to its characteristic of using sunlight to split water without producing contaminated by-products. The electronic reaction is the main bottleneck restricting the efficiency of water splitting due to its kinetic sluggishness.⁶⁰ The production and migration of electron-hole pairs within the surface and recombination of electron-hole pairs followed by the oxidation and reduction reaction with reactants take place on the surface of photocatalyst materials.⁶⁰

The most urgent task is to design and develop a low-cost, effective, and stable under acidic conditions photocatalyst, reduce the kinetic obstacles in the OER reaction process and improve the separation efficiency of electrons and holes, thereby increasing the photoelectrocatalytic activity. PtSe₂ has both properties of semiconductors and of metals excellent photoelectronic properties, high carrier mobility and layer-dependant band structure. In order to construct heterojunction and obtain good photoelectrocatalysis performance, LPE exfoliated hBN can be chosen as substrate. As a 2D material, hBN has a wide band gap and can better tune the bandgap of heterojunctions. hBN possesses strong hardness and a flat surface, which is not easy to deform. It has both physical and chemical inertia, and it can play a protective role, and therefore it is a good substrate for carrying other 2D materials. PtSe₂ and hBN can be used together to build a type-II heterojunction so that the electrons and holes can be separated in space.⁶⁰

1.4 Objective of this work

2D materials exhibit distinctive properties that become pronounced when the thickness approaches near-atomic levels². Hence, the primary objective of this project is to optimize the parameters for the Liquid Phase Exfoliation (LPE) of SnSe and PtSe₂. The adoption of LPE is justified by its scalability and the ability to produce substantial quantities of dispersed nanosheets⁴⁸, rendering it suitable for potential industrial applications.

The selection of SnSe and PtSe₂ stems from their distinct characteristics. SnSe is chosen for being an earth-abundant material with non-toxic properties and cost-effectiveness, as documented in literature⁶¹. Conversely, PtSe₂ has garnered attention due to its noteworthy photonic, physical, and chemical attributes⁶².

Following the verification of exfoliation quality through scanning electron microscopy (SEM), transmission electron microscopy (TEM), and atomic force microscopy (AFM), the resultant inks will undergo printing. Initial depositions will be executed on paper due to its remarkably low cost, biodegradability, and potential for facilitating the manufacture of flexible and foldable electronic devices.⁶³ Subsequently, the SnSe and PtSe₂ inks will be applied to Si/SiO and polycarbonate substrates to investigate the impact of different substrates.

2. Experimental techniques

In this section, the main characterization techniques employed in this work will be discussed. These comprise Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Atomic Force Microscopy (AFM), and the LiteScopeTM system that integrates both SEM and AFM. Other techniques discussed here include inkjet printing and aerosol jet printing.

2.1 Transmission Electron Microscopy

Transmission Electron Microscopy (TEM) is an effective technique that is widely utilized for analyzing the structural and chemical properties of materials. The transmission of electrons through a specimen causes an image to be cast on a fluorescent screen or detected by a charge-coupled device (CCD) camera.⁶⁴ Magnetic lenses are responsible for controlling the electron beam through their magnetic field, and the specimen must be transparent to electrons (Figure 11).⁶⁵

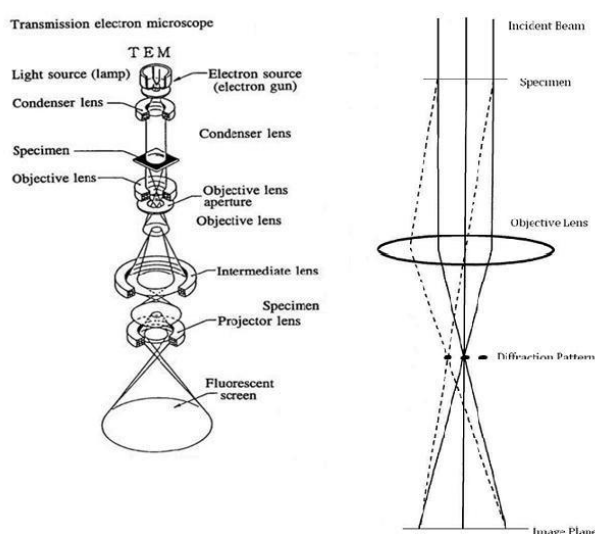


Fig 1

Fig 2

Figure 11. Schematics of TEM. On the left, TEM in image mode. On the right, TEM in diffraction mode. Picture credit: <https://warwick.ac.uk/fac/sci/physics/current/postgraduate/regs/mpagswarwick/ex5/techniques/structural/tem/>

TEM can be used either in image mode, in which resolution is determined by Rayleigh criterion and a detailed image is projected onto the viewing screen/CCD, or diffraction mode, where it is possible to see the diffraction pattern projected onto the viewing screen/CCD.⁶⁵

2.2 Scanning Electron Microscopy

The Scanning Electron Microscope (SEM) is an advanced microscopy technique that uses an electron beam focused by electromagnetic lenses on a sample in an ultra-high vacuum (10^{-6} mbar). From the interaction between the electrons and the samples, multiple signals (such as backscattered and secondary electrons) are collected by the sensors. Secondary electrons are generated by inelastic scattering (>50 eV) of the electrons with the samples. The origin of these low-energy electrons lies within nanometers of the sample's surface and is crucial for examining surface morphology. The elastic interaction between the beam and the sample causes backscattered electrons to be generated. Information about the material's composition is given by these interactions that occur within the sample (Figure 12).⁶⁶

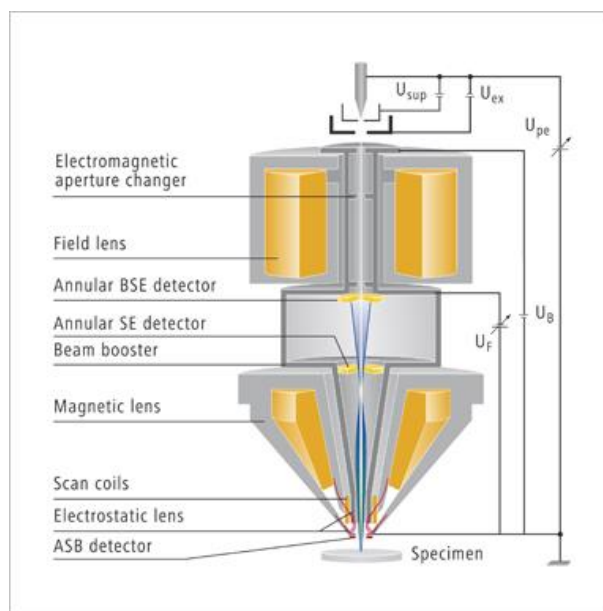


Figure 12. Schematics of SEM microscope. The SEM is comprised of an electron gun, anode, a series of lenses to focus the electron beam and scan coils to raster the beam on the material to image them. Picture credit: Zeiss SEM Manual.

2.3 Atomic Force Microscopy (AFM)

Atom force microscopy (AFM) is a useful tool when analysing micron-to-nano-sized structures. AFM permits both surface imaging and interaction with surfaces of interest to assist researchers in explaining the crystal lattice structure and chemical and mechanical properties at the nanoscale.²⁴ The principle of the AFM is to raster scan a sample in close vicinity to a probing tip that is mounted to a free end of a cantilever; the deflection of this cantilever can be measured with subnanometer precision. A feedback controller tracks the probing force by varying the position of the sample in the vertical direction (Figure 13).⁶⁷

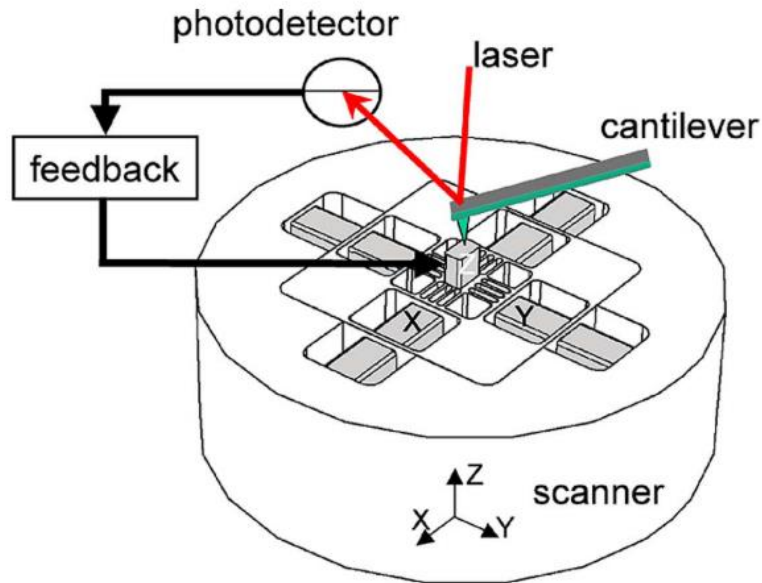


Figure 13. Schematics of AFM. Picture credit: Reference 67.

LiteScope™ (AFM+SEM system)

Atomic force microscopy (AFM) and scanning electron microscopy (SEM) Are two of the most used techniques for sample nanoscale analysis. To keep the pace with the market, Nenovision has developed a unique AFM designed to be integrated into the SEM, the LiteScope™ (Figure 14). Efficient and complex in situ characterization can be achieved with this hybrid system, and it introduces new possibilities for advanced correlative imaging, allowing sample analysis in a way that would be impossible with separate AFM and SEM.⁶⁸

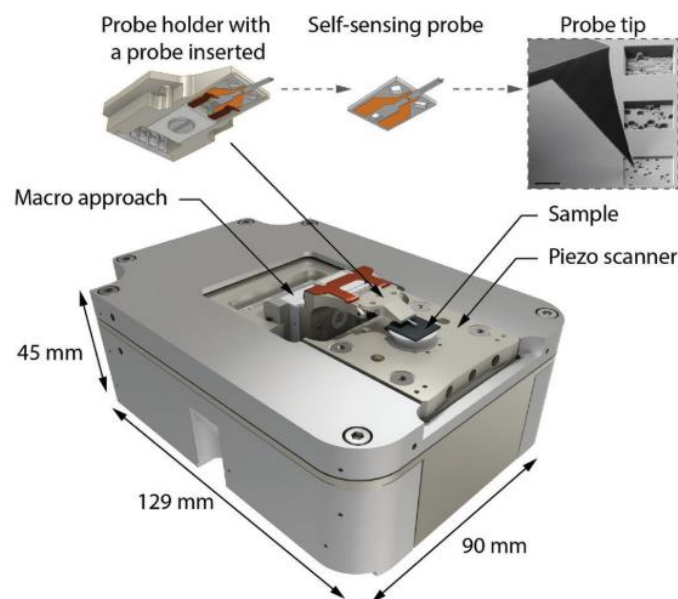


Figure 14. Schematics of LiteScope™. The image shows the macro motor to move the probe holder close to the sample holder and zooms on the probe holder and the probe. Picture credit: Reference 68.

A 2D SEM image provides a great material contrast and a large depth of focus with resolution up to 1 nm; by using an AFM with a sharp tip, the surface is scanned and the attractive and repulsive surfaces that emerge between the tip and the sample are measured, providing sub-nanometer resolution along with information on topography, mechanical properties, and electrical properties. Integrating AFM inside a SEM microscope combines the capabilities of both imaging techniques.⁶⁸

2.4 UV-VIS

The energy from electromagnetic radiation can be described by $E = h\nu$, where E is energy (joules) h is Planck's constant and ν is the frequency of the photon in hertz. The interaction between matter and electromagnetic radiation is studied through spectroscopy, which measures absorbance when measuring the UV-Vis spectrum. The difference between incident radiation (I_0) and transmitted radiation (I) determines how much light is absorbed when light passes through or is reflected from a sample. The amount of light absorbed can be defined as $A = -\log T$.⁶⁹ and light transmittance is defined as $T = I/I_0$

The Lambert-Beer law states that:

$$A = \varepsilon cd$$

Where A is the absorbance, ε is the molar absorption coefficient, c is the concentration of the solution, d is the optical path length of the sample.⁷⁰

For this work, the UV-Vis spectra were taken with a PerkinElmer UV-Vis with an integrating sphere to calculate the absorbance without the scattering contribution.⁷¹

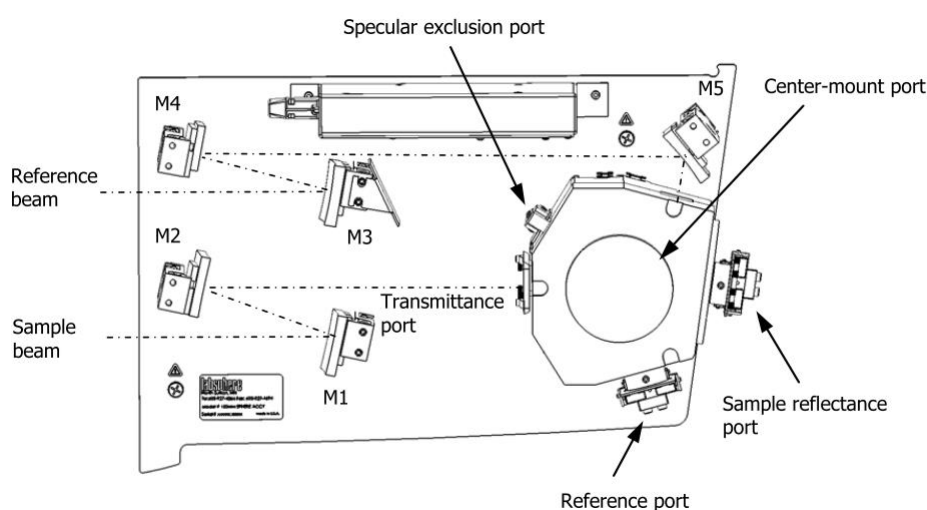


Figure 15. Schematics of UV-VIS. Picture credit: Reference 71.

2.5 Inkjet printing

Inkjet printing is a technique for depositing and patterning materials in the liquid phase.⁷² This technique has the following advantages: low material waste, low cost, and scalability to a large area of manufacturing⁷³ and the flexibility of changing patterns is an advantage concerning other deposition methods⁷⁴. This method is suitable for printing inexpensive and single-use devices.⁷³

The inks are composed of a dissolved or dispersed material in a solvent⁷³, But the ink design is complex. The “first drop problem”, also known as clogging of partially dried ink on the nozzle, is a major concern in inkjet printing; it is likewise important to match the ink properties to the characteristics of each printer.⁷⁵

The printing process consists of ejecting a fixed quantity of ink into a chamber from a nozzle and passing through a sudden quasi-adiabatic reduction chamber via piezoelectric action.⁷³

Inkjet printing can be divided into two main classes: continuous inkjet (CIJ) and drop-on-demand (DOD). An external electrical field is needed for CIJ to induct an electrical charge on a liquid by ejecting a jet of conductive ink in a region. The jet's isolated droplets will be charged and used to deflect them into the substrate or the ink collection system.. In DOD, instead, droplets are only formed when required. Thermal and piezoelectric DOD are two different types of DOD. Thermal DOD involves creating droplets by heating the ink chamber wall and creating vapour bubbles that eject them through a nozzle orifice. In the latter, a pressure wave is generated in the ink chamber by applying a voltage pulse to a piezoelectric stack or plate, thus forming droplets at the nozzles (Figure 16).⁷²

With this technique, it is possible to print polymer light-emitting diodes (PLED)⁷⁶, organic transistors⁷⁵, thin-film transistors⁷³, LEDs^{73,75}, ceramics⁷⁵, solar cells⁷³, magnetic data storage applications⁷³, sensors, detectors⁷³, and biopolymer arrays⁷⁵.

The occurrence of the 'coffee-ring effect' is one of the main problems with inkjet printing, where the deposit is thicker at the edges and significantly thinner at the center.⁷⁷

This work utilizes inkjet printing as it can accurately deposit inks through digitally controlled ejection to form patterns in a material-conserving manner. The deposition process is largely influenced by ink parameters and printing conditions, making it challenging to achieve high-quality inkjet printing. The printability of inks for ink-jet printing is usually predicted by a dimensionless inverse Ohnesorge (Oh) number (Z):

$$Z = \frac{1}{Oh} = \frac{\sqrt{\gamma \rho a}}{\eta}$$

Where γ , ρ , and η are the viscosity, density, and surface tension of the ink respectively, and a is the nozzle diameter. To be suitable for the printing process, inks should have low viscosity, but during the drying, the inner solvent flows to the edges to replenish the evaporated solvent, resulting in the accumulation of deposited material on the periphery. Optimizing drop frequency, substrate temperature, and printing speed is necessary to achieve uniform patterns with smooth lines and even edges.⁷⁸

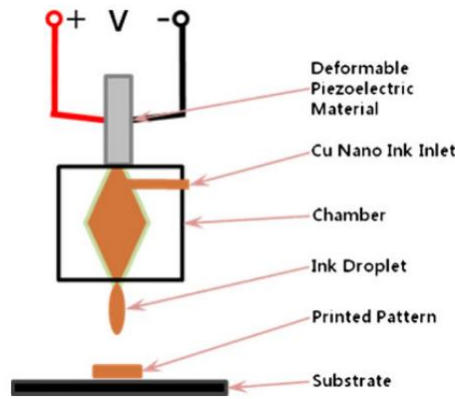


Figure 16. Schematics drop-on-demand in inkjet printing systems. Picture credit: Reference 74.

2.6 Aerosol jet printing

Aerosol jet printing (AJP) uses a directed aerosol stream to provide consistent deposition at nozzle-substrate offsets of 1-5 mm. This approach enables the patterning of more complex surfaces.⁷⁹ AJP can print on orthogonal surfaces with sharp angles between planes, generate multi-layered circuitry without utilizing common 2D approaches, such as multilayer substrates with plate-mask-etch methods, attach discrete components, and directly print conformal sensors and antenna on 3D surfaces.⁸⁰ In theory, any material can be suspended in aerosol compatible to be printed via AJ printing.⁷⁹

To generate an aerosol, the ink must go through an ultrasonic atomic process to generate droplets of active ink; due to the micron-scale size of the droplets, solvent evaporation occurs rapidly, resulting in a reduction in droplet size. The droplets are transported to the deposition head by the carrier gas (aerosol gas). Losses can be caused by two mechanisms during transit: gravitational settling and impingement on tube walls by diffusion. The beam is collimated in the deposition head by a sheath gas surrounding the aerosol gas. When the deposition nozzle passes through the narrow, converging nozzle, inertial effects in the narrow, converging nozzle

can divert droplets from their flow stream, resulting in aerodynamic focusing. In the end, the impinging jet directs the droplets towards the substrate.⁸¹

Optomec claims that their AJ printers (Figure 17) can print noncontact and conformal patterning of sizes as small as 10 μm on various substrates; the company also claims that the maximum printing distance for these resolutions is 5 mm, enabling consistent deposition of inks on 3D substrates.⁸²

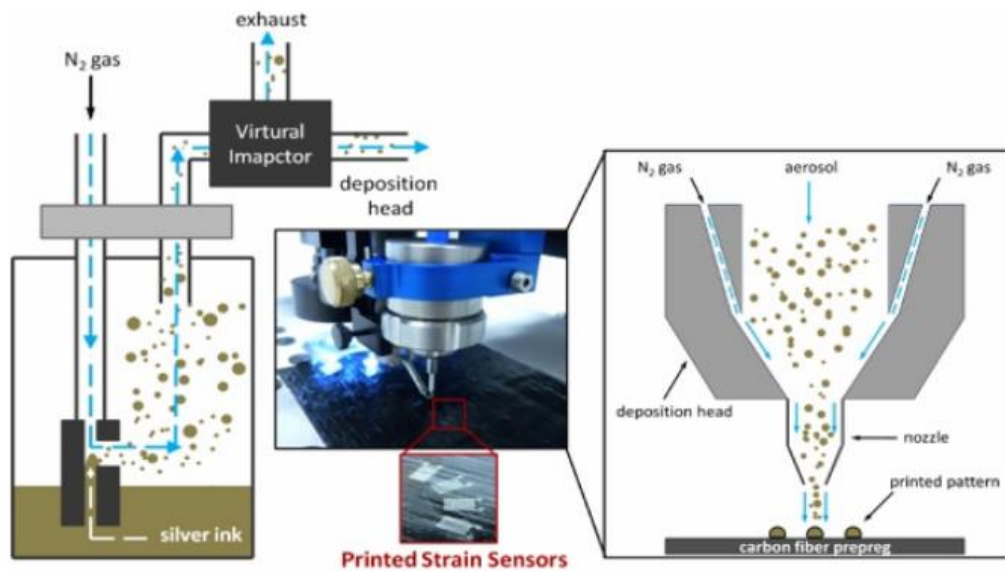


Figure 17. Schematics of Optomec AJ300. Picture credit: Reference 82.

3. SnSe, exfoliation and characterization

3.1 Introduction

Mono-chalcogenides IV-VI semiconductors hold significant importance across a range of optoelectronic applications^{32,83}. They have attracted considerable interest owing to their unique physical and chemical properties. These materials, characterized by narrow bandgaps and the chemical formula unit MX (M = Pb, Cd, Sn & X = S, Se, Te), are particularly valuable for their potential applications in photovoltaic cells^{51,54,84}, near-infrared detectors (such as night vision and IR sensors)⁸⁵, and even biological imaging agents⁸⁶. Lead and cadmium chalcogenides, owing to their encouraging bandgap and electronic structures, have found widespread use in various optoelectronic devices, demonstrating enhanced performance and conversion efficiencies. However, the primary challenge associated with the utilization of these chalcogenide materials lies in the toxicity of Cd and Pb elements⁸⁷.

Within the IV-VI semiconductor family, orthorhombic Tin mono-selenide (α -SnSe) has garnered significant attention from researchers due to its promising optoelectronic properties⁸⁸, natural abundance, chemical stability, moderate toxicity^{61,89}, and potential for applications in energy storage and conversion^{90,91,92}.

α -SnSe (Figure 11) has an orthorhombic P_{nma} structure: Se atoms are bonded to 3 adjacent Sn atoms to form a puckered honeycomb network on the y-z plane.⁹³ This material possesses strong anisotropy and can be easily exfoliated due to its weak interactions between the layers⁹⁴ that lead to easy exfoliation along the x direction⁹³.

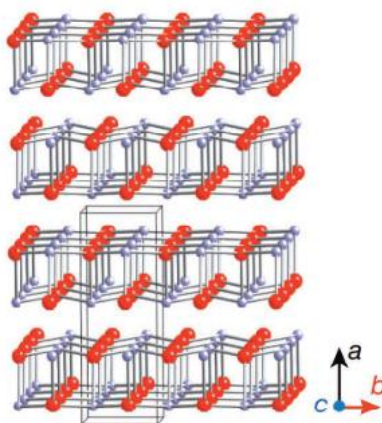


Figure 18. Orthorhombic structure of tin selenide. The red atoms are selenium, and the grey ones are tin. Picture credit: Reference 61.

Due to its indirect band gap of 0.9 eV, SnSe is considered a semiconductor. The band gap increases when the thickness of the material decreases, due to the quantum confinement effect⁹⁴. SnSe can find applications in solar cells, energy storage and thermoelectric applications⁹⁵, photovoltaic cells and near-infrared detectors.⁹⁶ These properties are granted by ultralow thermal conductivity, ultrahigh hole mobility, power factor and outstanding electrothermic compatibility.⁹⁷ SnSe indeed shows an absorbance peak in the near-IR region, about 1450 nm wavelength.⁹⁸

Due to its high storage capacity and its lithiation kinetics, this material can be used as an anode in LIBs and reducing the material to nanosheets can be a useful way to enhance its properties since increasing the surface area can lead to an enhanced capacity and cycling performance.⁹⁷

3.2 Materials and Methods

During this project 3 different LPE routes were investigated; ultrasonic bath sonication, ultrasonic tip sonication to make dispersions and liquid cascade centrifugation so size-select the material dispersions. Details of these experimental procedures are given below.

Ultrasonic bath

SnSe (120 g, powder, Alfa Aesar) was dispersed in IPA (40 ml, 2-Propanol for spectroscopy Uvasol®, Supelco) and immersed in a sonic bath (FisherBrand 11207) for 7 hours, 37 kHz frequency and 80% power. The dispersions were left resting overnight, and the supernatant was collected.

Sonic tip

SnSe (120 g, powder, Alfa Aesar) was dispersed in IPA (40 ml, 2-Propanol for spectroscopy Uvasol®, Supelco) and the solution was dispersed using a sonic tip (Fisherbrand Ultrasonic Disseminator) for 9.5 hours with a 3.2 mm tip at an amplitude of 30%, 6 seconds on and 2 seconds off. The obtained dispersion was then left to rest overnight.

Liquid cascade centrifugation

The obtained SnSe dispersion was centrifuged (Heraeus Multifuge x1 Centrifuge) for 30 minutes at 1500 rpm. The supernatant was collected, and the deposit was redispersed to obtain **I**. Then **I** was centrifuged for 30 minutes at 1500 rpm, the supernatant collected and the deposit

redispersed to obtain **II**. The supernatant of **II** was centrifuged for 30 minutes at 3500 rpm, and the deposit was redispersed to obtain **III**.

3.3 Results

3.3.1 Analysis of SnSe exfoliated with sonic bath

As previously discussed, SnSe was dispersed in IPA and the resulting dispersion was ultrasonicated in a bath for 7 hours. Dispersibility in IPA is a great advantage from a processability point of view. This solvent is widely available, cheap and nontoxic; importantly, it is very compatible with printers. Afterwards, the liquid cascade centrifugation (LCC) was performed at three different speeds, 1500, 2500 and 3500 rpm and the deposits redispersed each time in IPA in sequence. From now on reference to dispersions **I**, **II** and **III** will be as follows; **I** is the dispersion obtained at the lowest centrifugation speed (1500 rpm), which is the fraction which should consist of bigger chunks of non-entirely exfoliated material; **II** is the fraction obtained after centrifuging at medium speed (2500 rpm); and **III** is the fraction obtained after centrifuging the dispersion at the highest speed (3500 rpm). This last dispersion should therefore consist of the smallest flakes. An image of these three fractions is presented in Figure 19.

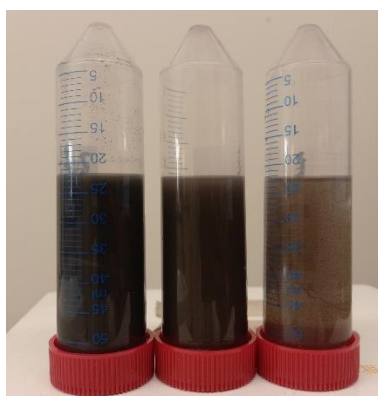


Figure 19. Dispersion of SnSe after the LCC. From left to right: **I** (1500 rpm), **II** (2500 rpm) and **III** (3500 rpm).

The colour of the dispersions gives a first indication that the LCC successfully achieved separation of different size-fractions of the material. This was later confirmed by SEM and TEM characterisation. UV-Vis was also performed on all fractions to characterise their optical behaviour.

Structural and morphological analysis

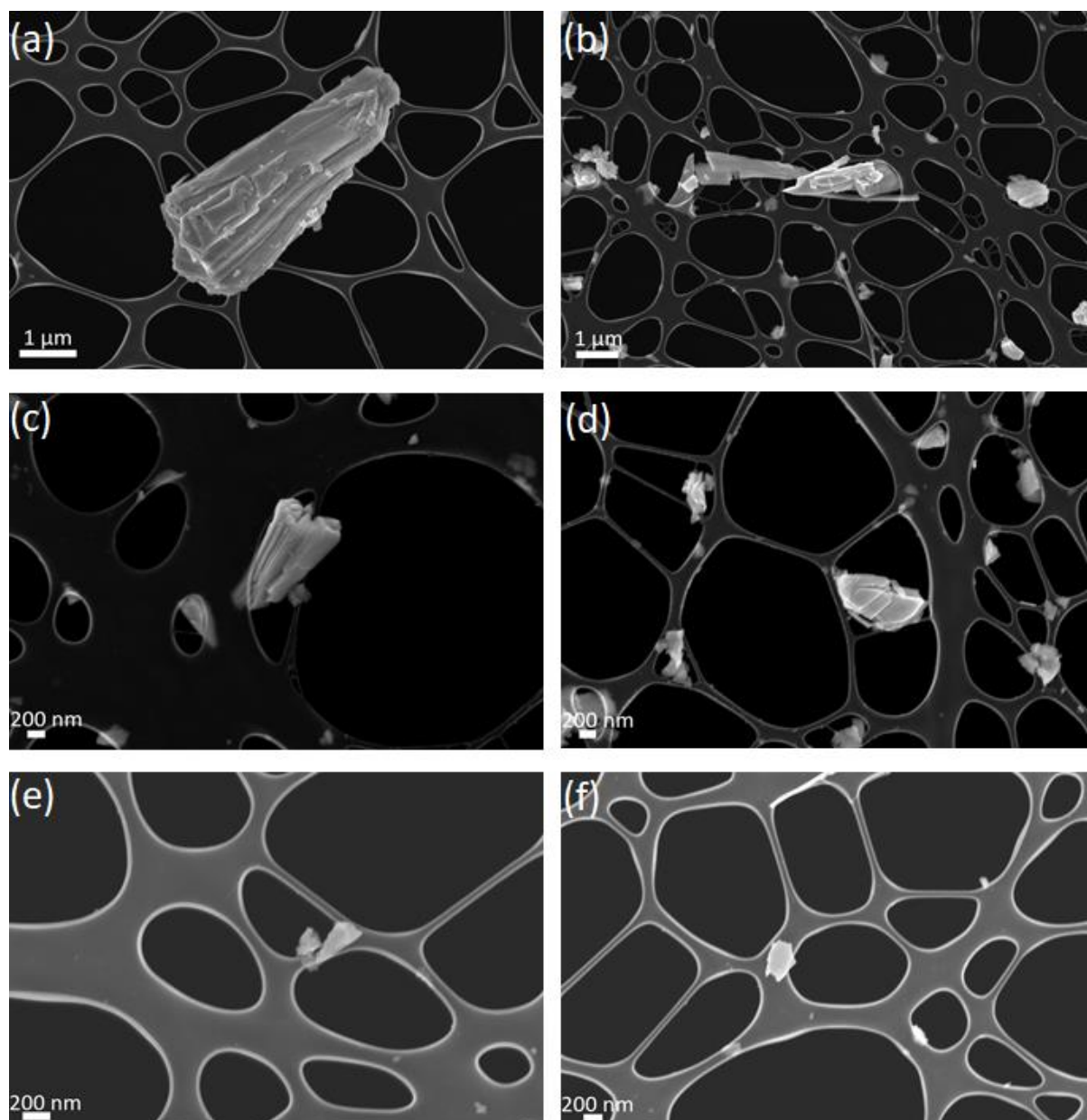


Figure 20. Representative SEM images of the following fractions: (a, b) I. (c, d) II. (e, f) III.

As shown in Figure 20 (a, b), SEM characterisation demonstrated that fraction **I** indeed contained the bigger chunks of SnSe, with dimensions up to several microns; importantly, the layered morphology of the material is clearly visible. This fraction clearly contains the un-exfoliated or non-entirely exfoliated material, demonstrating that LPE cannot exfoliate all the bulk in the same way. SEM images of fraction **II** (Figure 20, c, d) demonstrated that this dispersion consisted of smaller SnSe chunks, arriving up to 1 μm in size. The layered nature of the material is still clearly visible. However, the material appears visibly thinner than fraction **I**. The layers are much less visible, meaning that in this dispersion there are chunks for which

the exfoliation had worked much better. Representative SEM images of fraction **III** are displayed in Figure 20 (e, f). Being this the fraction obtained at the highest centrifugation speed, it contains the smallest flakes of tin selenide. As Figure 20 (e, f) show, the flakes are up to 200 nm in lateral size and there are as many visible layers as in the 2 previous fractions obtained at lower centrifugation speed. This result is in accordance with what was expected. TEM characterisation was also performed on the three fractions to gather more information about the thickness and the structure of the blocks.

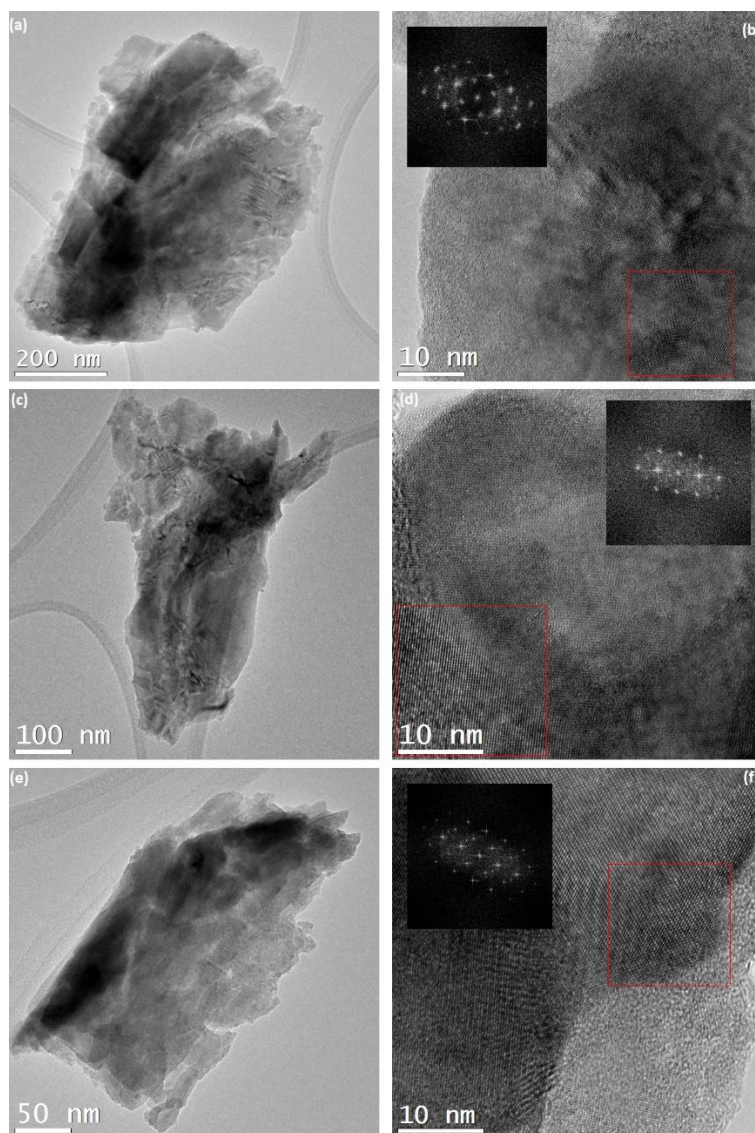


Figure 21. Representative TEM images of the following dispersions (a, b) **I**, (c, d) **II**, (e, f) **III**.

Representative TEM images of the three fractions are displayed respectively in Figure 21: (a, b) for dispersion **I**, (c, d) for dispersion **II**, and (e, f) for dispersion **III**. Images displayed in Figure 21 (a, c, e) show decreasing thickness, which is in accordance with the fact that they are respective flakes from fractions **I**, **II** and **III**. Figure 21 (b, d, f) instead show the crystalline

structure of the flakes, which is orthorhombic, and it is shown from the diffraction pattern. Images contrast, moreover, show that all fractions consist of multi-layered material. All this is in accordance with what was already seen in SEM, where **I** showed to have bigger chunks of material and **III** had the smaller. This is an important confirmation of what was observed with other analysis meaning that not only the lateral size is bigger, but it confirms that the thickness is larger in dispersion **I**, whilst fraction **III** consists of thinner flakes. With both these confirmations, it was then possible to move on to the optical characterisation of the three fractions.

A Nenovision LiteScope was used to obtain nanometer precise in-time AFM and SEM correlative analysis of the exfoliated material's thickness.

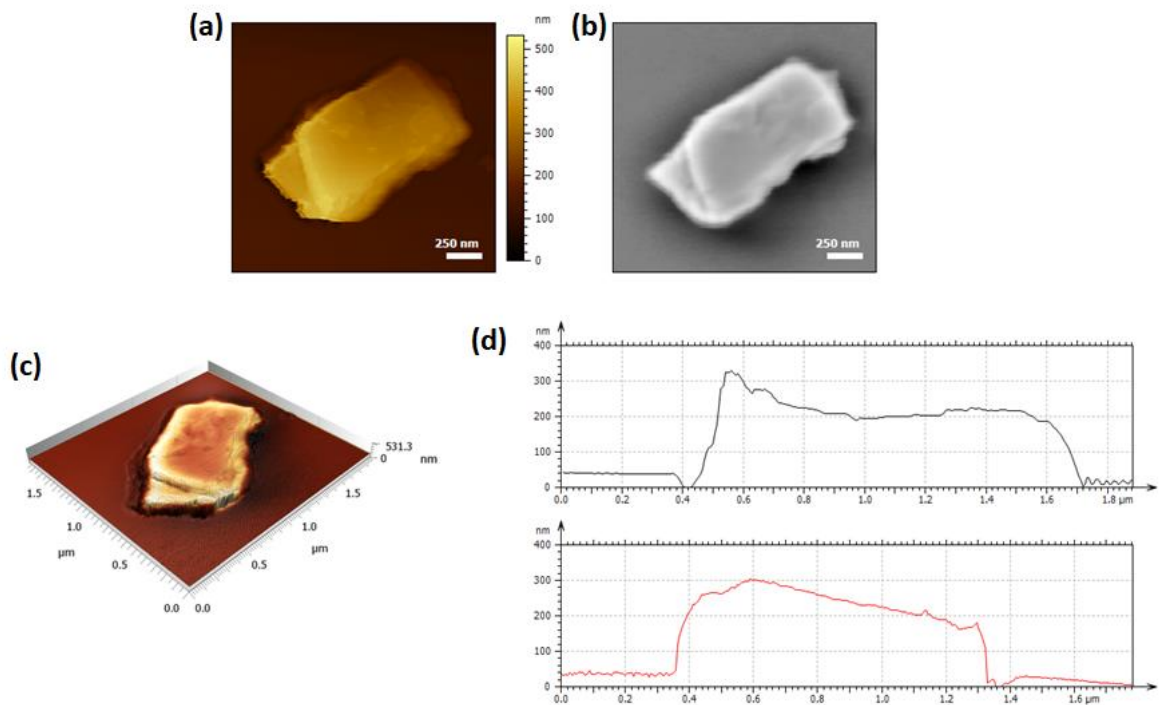


Figure 22. (a) AFM of fraction **I**. (b) SEM of fraction **I**. (c) AFM+SEM of fraction **I**. (d) Profile analysis of fraction **I** along two different directions.

Figure 22 shows (a) the AFM and (b) the SEM of the same flake in fraction **I**. (c) The CPEM obtained overlapping and processing the AFM and (d) the profile analysis. Figure 22 (a) shows that the flake chosen navigating the sample surface with SEM (b) is thinner than 500 nm, confirmed also by the overlap of these two images shown in (c). The profile analysis (d) confirms that the thickness of this representative flake is less than 400 nm measuring in two different directions.

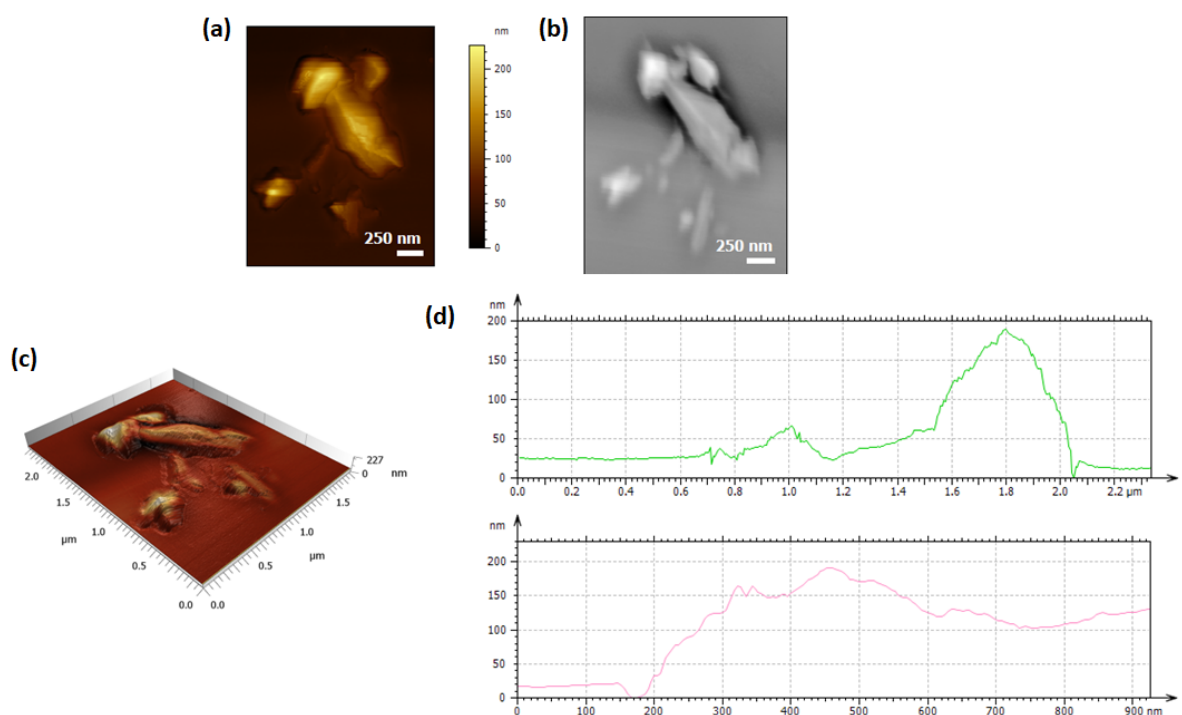


Figure 23. (a) AFM of fraction II. (b) SEM of fraction II. (c) AFM+SEM of fraction II. (d) Profile analysis of fraction II along two different directions.

Figure 23 (a) shows that the flake chosen navigating the sample surface with SEM (b) is thinner than 200 nm, confirmed also by the overlap of these two images shown in (c). The profile analysis (d) confirms that the thickness of this representative flake is less than 200 nm measuring in two different directions.

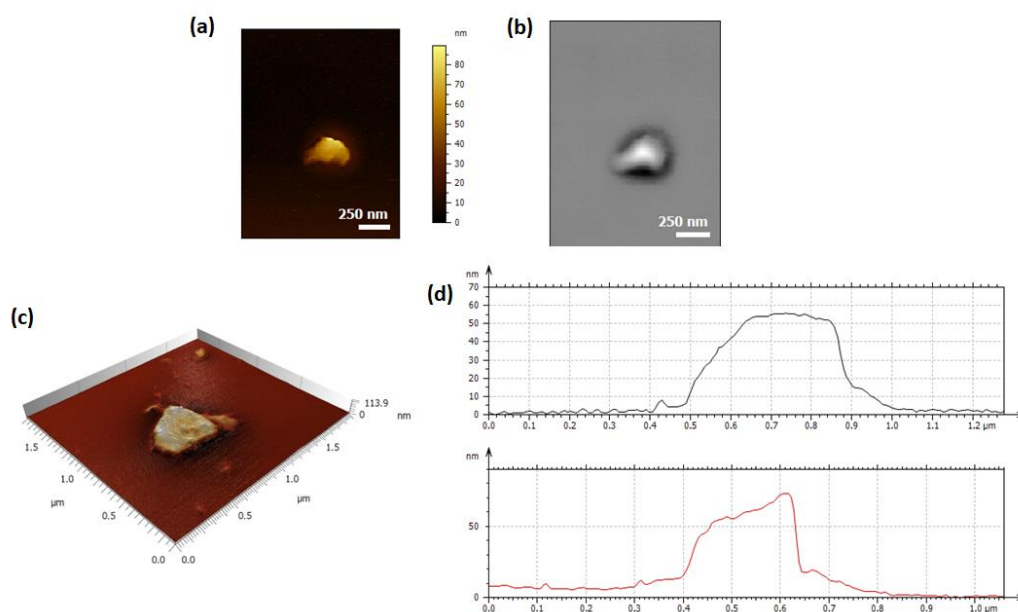


Figure 24. (a) AFM of fraction III. (b) SEM of fraction III. (c) AFM+SEM of fraction III. (d) Profile analysis of fraction III along two different directions.

Figure 24 shows (a) the AFM and (b) the SEM of the same flake in fraction III. (c) The CPEM obtained overlapping and processing the AFM and (d) the profile analysis. Figure 24 (a) shows that the flake chosen navigating the sample surface with SEM (b) is thinner than 100 nm, confirmed also by the overlap of these two images shown in (c). The profile analysis (d) confirms that the thickness of this representative flake is less than 100 nm when measuring in two different directions.

These confronted analyses confirm that the size and thickness of the flakes decrease from fraction **I** to fraction **III**.

Optical analysis

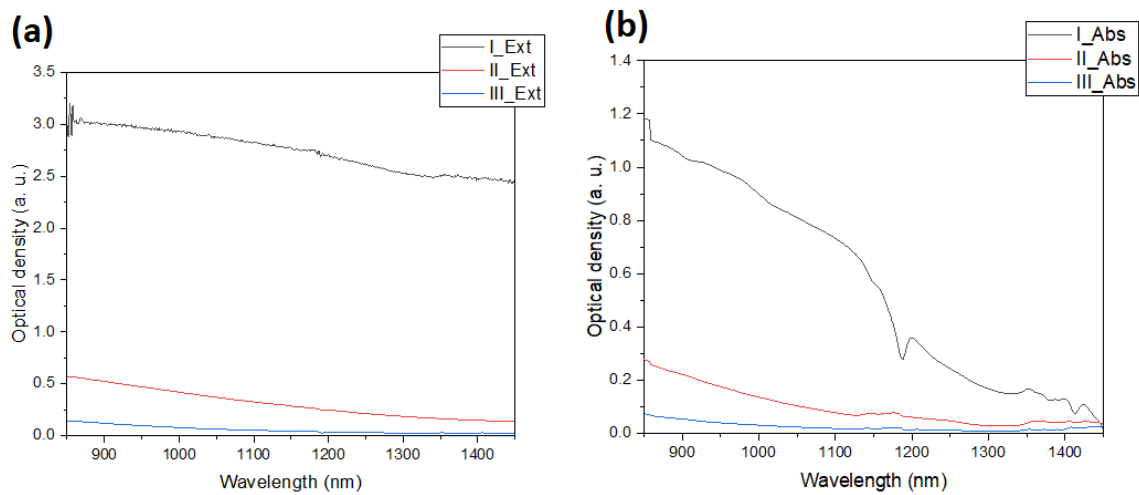


Figure 25. (a) Extinction UV-VIS of the dispersions **I**, **II** and **III**. (b) Absorbance UV-VIS of the dispersions **I**, **II** and **III**.

Figure 25 shows the extinction (a) and the absorbance (b) spectra of the three fractions. These are indeed in accordance with the concentration of the dispersions, where the fraction at higher concentration (**I**) has the most intense spectra. This trend can be already seen in Figure 16 (a), where the extinction spectra shows that fraction **I** has the highest optical density, whilst fraction **III** instead has the lowest, even considering the scattering contribution. Figure 25 (b), instead, only shows the absorbance contribution and it confirms what it was observed in the extinction spectra. In particular, the absorbance has peaks at about 1400 nm (zoomed in spectra in Figure 26).

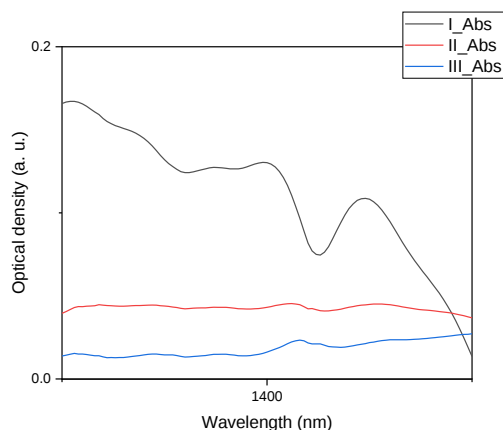


Figure 26. Zoom of the spectra in Figure 25 (b) from 1350 nm to 1450 nm.

The peaks at about 1400 nm are pronounced for dispersion **III**, and only slightly present in dispersion **II**. Dispersion **I** display broad peaks, which are blue-shifted; this can be explained by the difference in the flakes' size. Smaller flakes therefore cause a red shift in the spectra.

3.3.2 Analysis of SnSe exfoliated by sonic tip

For comparison to the exfoliation obtained by ultrasonic bath, a sonic tip was also used for the exfoliation of tin selenide. We started from an initial concentration of 3 mg/ml and IPA as solvent. The ultrasonic tip amplitude was set at 30%, on a pulsed setting (pulse on 6 seconds and pulse off 2 seconds), with a total sonication time of 9.5 hours. These settings were selected on the basis of our know-how on LPE of other 2D materials.

The solicited dispersion was allowed to rest overnight. The colour of the rested solution (shown in Figure 27) was promising since it was the same as the one ultrasonicated with the sonic bath. Achieving exfoliation by sonic tip was a major goal in terms of processibility as it does not require periodic and constant changes of water, having its own cooling system.



Figure 27. Photograph of a SnSe dispersion obtained by tip ultrasonication.

SEM, TEM and optical characterisation were therefore performed to verify whether the tip sonication resulted in some sort of flake damage or not.

Structural and morphological analysis

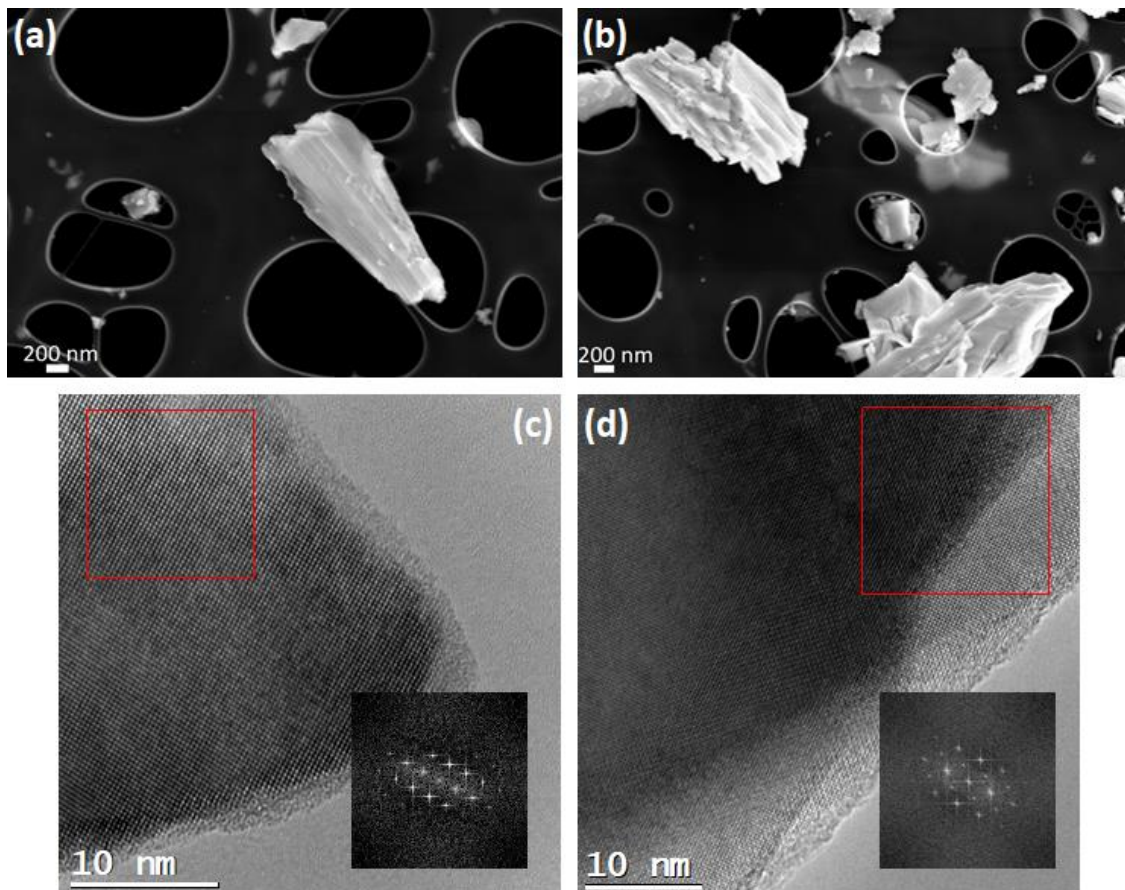


Figure 28. (a,b) Representative SEM images of SnSe exfoliated by the sonic tip. (c,d) Representative TEM images of SnSe exfoliated by sonic tip.

The SEM images shown in Figure 28 (a, b) show that the exfoliation had worked properly. Some flakes are up to 1 μm in lateral size. Figure 28 (c, d) in the diffraction pattern show the orthorhombic structure of SnSe, meaning that the sample has not been damaged. TEM also shows an interesting detail, which is that the layers that protrude are very thin, an important observation to keep in mind for the project as it will allow for atomic resolution imaging and study of defects at a later stage.

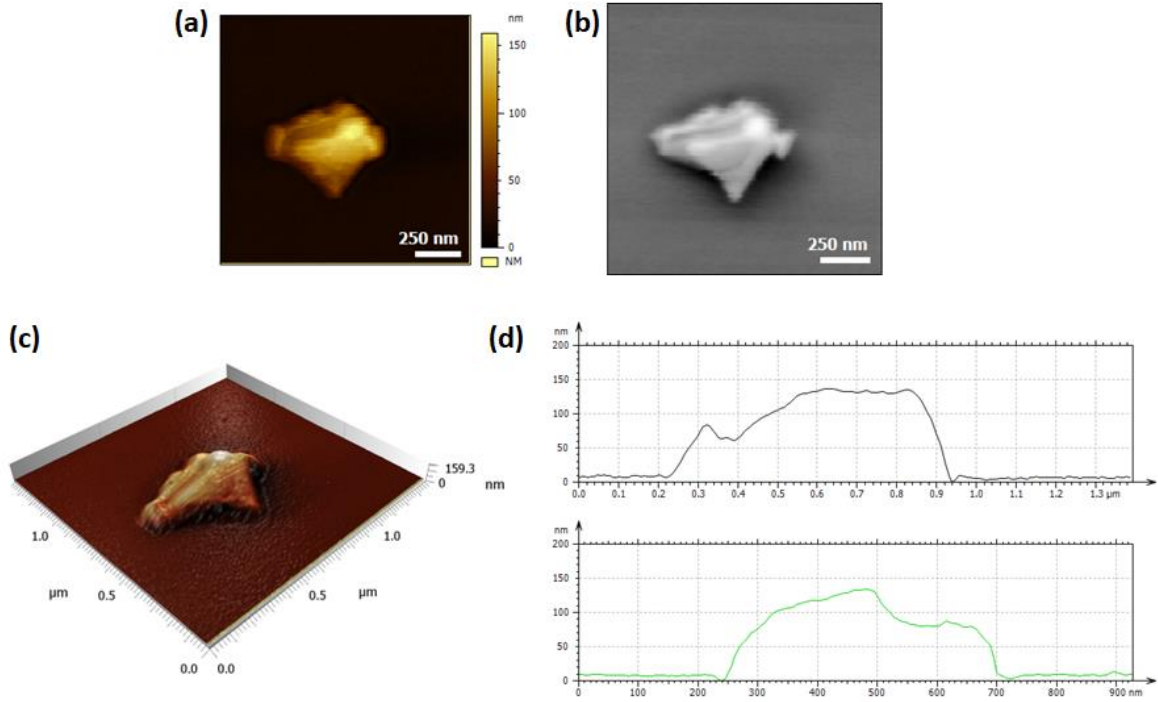


Figure 29. (a) AFM of SnSe exfoliated with sonic tip. (b) SEM of SnSe exfoliated with sonic tip. (c) AFM+SEM of SnSe exfoliated with sonic tip. (d) Profile analysis of SnSe exfoliated with sonic tip.

Figure 29 (a) shows that the flake chosen navigating the sample surface with SEM (b) is thinner than 100 nm, confirmed also by the overlap of these two images shown in (c). The profile analysis (d) confirms that the thickness of this representative flake is less than 100 nm measuring in two different directions. This analysis confirmed that the LPE with sonic tip is an efficient technique.

Optical analysis

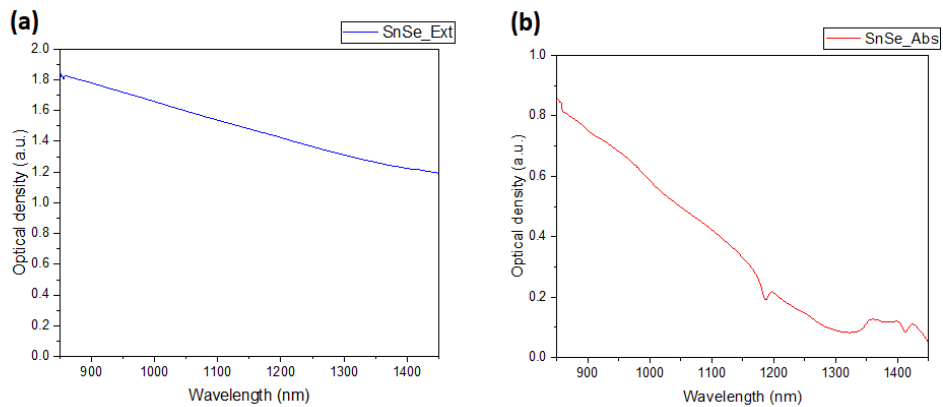


Figure 30. (a) Extinction spectrum of SnSe sonicated with sonic tip. (b) Absorbance spectrum of SnSe sonicated with sonic tip.

The Extinction spectrum shown in Figure 30 (a, b) shows that the UV-Vis are in accordance with the spectra found in the previous section of this work for bath sonicated materials. This is important information, meaning that SnSe can be successfully exfoliated in IPA, both by bath ultrasonication and tip ultrasonication, resulting in good quality dispersion in both cases and without causing important changes.

3.4 Conclusions

The conditions for the exfoliation of SnSe in IPA were used and successful exfoliation was demonstrated both for sonic bath and tip sonications. Microscopy characterisation for flakes thinner than 1 μm , and even thinner than 100 nm in the case of the solutions treated with LCC. The optical properties show peaks in the near-IR region that make SnSe a candidate for optoelectronic studies.

These results led the research to print SnSe with different techniques (inkjet printing, deposition via pen plotter and film deposition) on several substrates to study the optoelectrical properties of the thus obtained devices.

4. PtSe₂, exfoliation and characterization

4.1 Introduction

Platinum selenide (PtSe₂) is a novel compound, which attracted our attention due to its photonic, physical, and chemical properties^{37,99}. Its structure comprises three atomic layers stacking in the order of Se-Pt-Se, which are held together by weak Van Der Waals forces (Figure 31). PtSe₂ has also chemical properties like high charge-carrier mobilities and long-term air stability.³³ This compound exhibits a bandgap of 1.2 eV for monolayer PtSe₂. Moreover, the carrier mobility of monolayer PtSe₂ is the highest and comparable with black phosphorus and the absorption spectra depend on the thickness of the flakes. The first peak around 450 nm is without shift, whilst the second peak redshifts as the number of layers is increased. This second peak decreases as the wavelength increases from 800 to 2200 nm.⁶² This shift could be explained by the fact that PtSe₂ transits from semiconductor to semimetal when thickness increases.¹⁰⁰

PtSe₂ is a layered material with a thickness-dependent electronic structure¹⁰¹ PtSe₂ crystal possesses a typical 1T-type hexagonal crystal structure with P-3m1 space group.⁹⁹

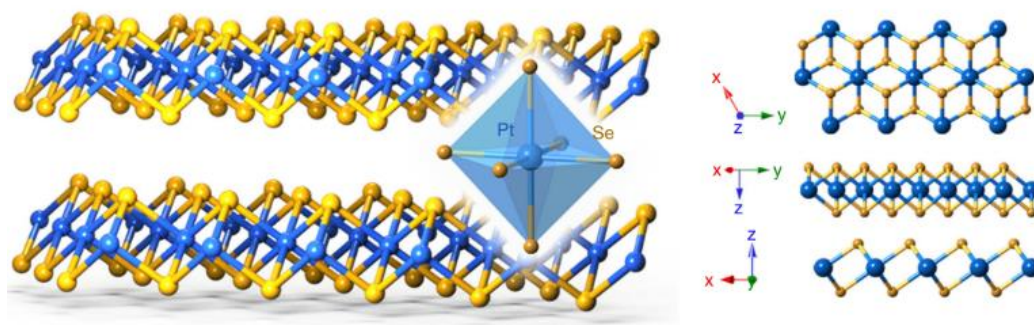


Figure 31. Atomic structure of PtSe₂. Picture credits to Reference 99.

Exfoliation of PtSe₂ allows the modulation of the electronic structure, resulting in a tuneable bandgap, a transition from semimetal to semiconductor when exfoliated to less than three layers.¹⁰²

4.2 Materials and methods

During my project, I investigated 2 different LPE routes, ultrasonic bath sonication and ultrasonic tip sonication. Details of these experimental procedures are given below.

Ultrasonic bath

PtSe₂ (40 g, powder, synthesised by Professor Zdenek Sofer) was dispersed in NMP (40 ml, Acros Organics) and immersed in a sonic bath for 7.5 hours, 37 kHz frequency and 100% power. The dispersions were left resting overnight, and the supernatant was collected.

Sonic tip

PtSe₂ (120 g, powder, synthesised by Professor Zdenek Sofer) was dispersed in IPA (40 ml, 2-Propanol for spectroscopy Uvasol®, Supelco) and the solution was dispersed using a sonic tip (Fisherbrand Ultrasonic Dissembrator) for 5.5 hours with a 3.2 mm tip at an amplitude of 50%, 6 seconds on and 2 seconds off. The obtained dispersion was then left to rest overnight and the supernatant was collected.

4.3 Results

4.3.1 Analysis of PtSe₂ exfoliated with sonic bath

PtSe₂ was exfoliated using the sonic bath. The solvent initially chosen was NMP, starting at a concentration of 1 mg/ml, 37 kHz frequency, 100% power and allowing the sonication to go for 7.5 hours. The dispersion was then left to rest overnight, and the dark brown colour of the dispersion resembled the one of the SnSe in IPA, as shown in Figure 32.

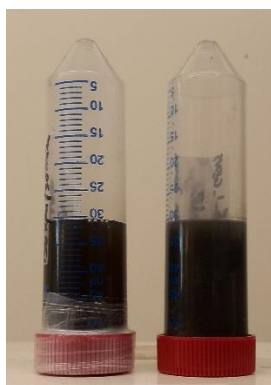


Figure 32. Photograph of the dispersions. On the left, PtSe₂ dispersed in NMP. On the right, SnSe is dispersed in IPA. The colour is very similar, and therefore we decided to proceed with further characterization.

Structural and morphological analysis

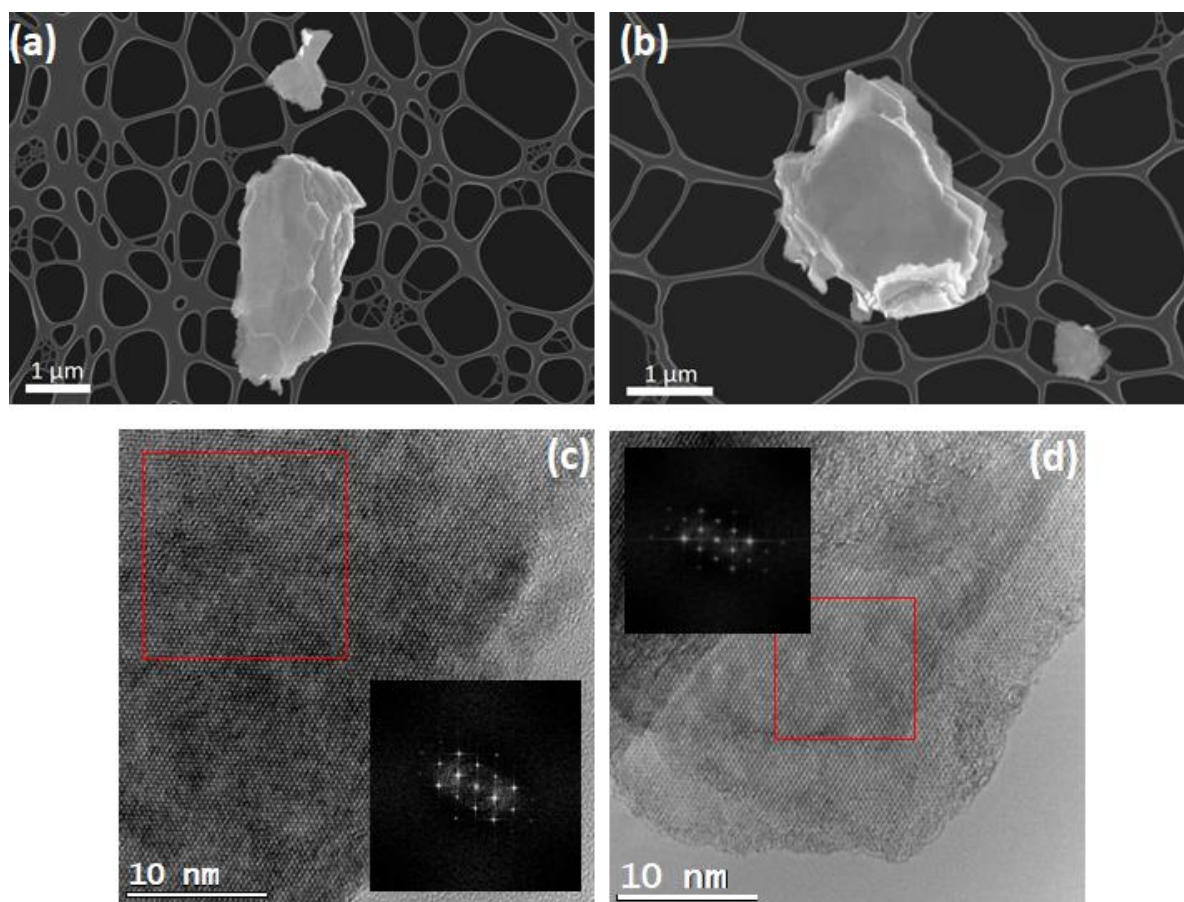


Figure 33. (a, b) Representative SEM images of LPE PtSe₂. (c, d) Representative TEM images of PtSe₂.

These images show flakes consisting of many layers, as well as also very thin layers protruding on the sides. Since with the optimization of the LPE, very thin nanoflakes can be obtained in future, the opportunity to further optimise the bandgap of the material with a more optimised exfoliation can be reached. The flakes in this dispersion have dimensions up to 1 μm in lateral size, meaning that the exfoliation must be optimised. The representative TEM images are shown in Figure 33 (c, d). The image contrast indicates the presence of multilayers, even though much thinner ones when compared to the ones shown in the SEMs in Figure 33 (a, b). Figure 33 (d), in particular, shows a very thin flake, thus meaning that probably scattered around the grid there are some flakes too thin to be seen in SEM. The fact that the material can maintain the crystallinity after the exfoliation means that PtSe₂ can be used as a candidate for printing for building optoelectronic devices.

This first exfoliation approach can be further improved and optimised in future. This will be discussed in the Conclusions section of this thesis.

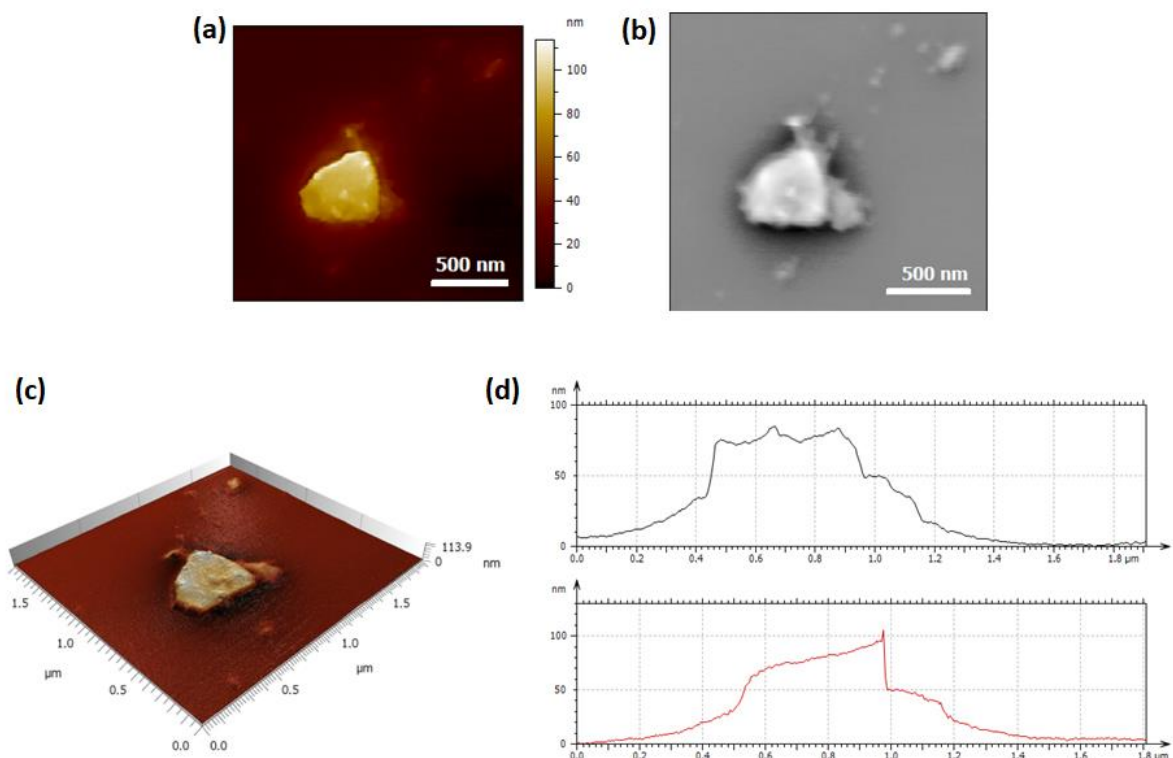


Figure 34. (a) AFM of PtSe₂. (b) SEM of PtSe₂. (c) AFM+SEM of PtSe₂. (d) Profile analysis of PtSe₂ along two different directions.

These pictures show how the flakes are thinner than 100 nm. Figure 34 (a) shows that the flake chosen navigating the sample surface with SEM (b) is thinner than 100 nm, confirmed also by the overlap of these two images shown in (c). The profile analysis (d) confirms that the thickness of this representative flake is less than 100 nm when measuring in two different directions.

Optical analysis

Figure 35 (a) and Figure 35 (b) show the extinction and absorbance spectra of the PtSe₂ dispersion in NMP, respectively. Essentially there is a very small difference caused by the scattering, because the peak is in both graphs at around 450 nm, as stated in literature⁶². The second peak, the one that is between 800 and 2200 nm, is not visible, and that is probably due to the thickness of the flakes.

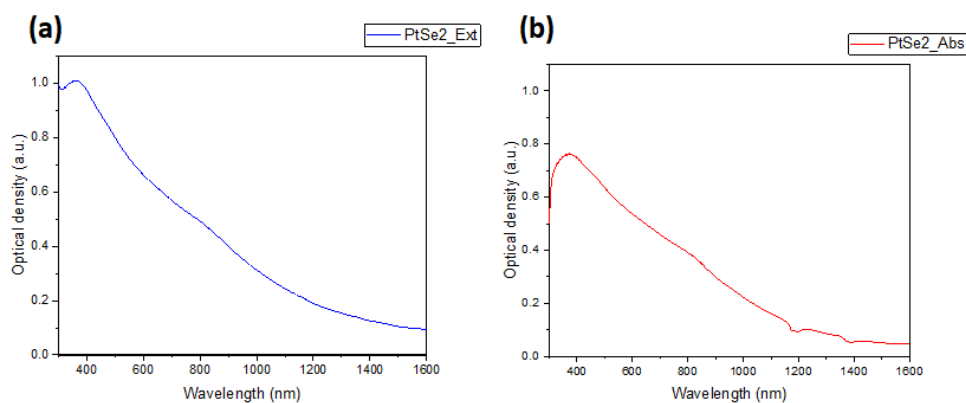


Figure 35. (a) Extinction spectrum of PtSe₂ sonicated in NMP by sonic tip. (b) Absorbance spectrum of PtSe₂ in NMP sonicated by sonic tip.

4.4 Conclusions

The conditions for the exfoliation of PtSe₂ were studied and microscopy characterisation demonstrates efficient exfoliation. Images show flakes thinner than 100 nm in the case of the solutions treated with LCC. The optical properties show peaks in the near-IR region that make PtSe₂ a candidate for optoelectronic studies.

These results led the research to print SnSe with different techniques (inkjet printing, deposition via pen plotter and film deposition) on several substrates to study the optoelectrical properties of the thus obtained devices.

5. Devices

5.1 Deposition devices

Paper is an extremely cheap substrate and biodegradable and potentially allows the fabrication of flexible and foldable electronic devices. It is possible to draw semiconductor devices with the abrasion technique.⁶³ To print on paper, it is necessary to use a low-cost, robust, and easy technique. For this reason, a pen plotter was chosen, since it is a cost-effective, high-throughput fabrication strategy for paper-based substrates. Pen-plotted films are mainly used as conductive tracks and very limited functionality was demonstrated as shown in Figure 36.¹⁰³



Figure 36. Pen plotter to draw the pattern of the 2D Foundry on paper. Picture credit: Reference 103.

Firstly, the inks are made by exfoliating the chosen compound via LPE with the sonic tip, and then the inks are loaded into empty markers with a pipette. The software Inkscape is used to choose the pattern to print, and the marker is positioned into the plotter as shown in Figure 36. Then, the printing is started, and the plotter traces the chosen pattern.

5.1.1 Results with SnSe

The first device printed was SnSe in IPA (Figure 31). Figure 37 shows the first device deposited on paper. The grey area is the deposited solutions of SnSe dispersed in IPA (12 mg/ml), the darker lines are the graphite ink electrodes 1 mm apart.

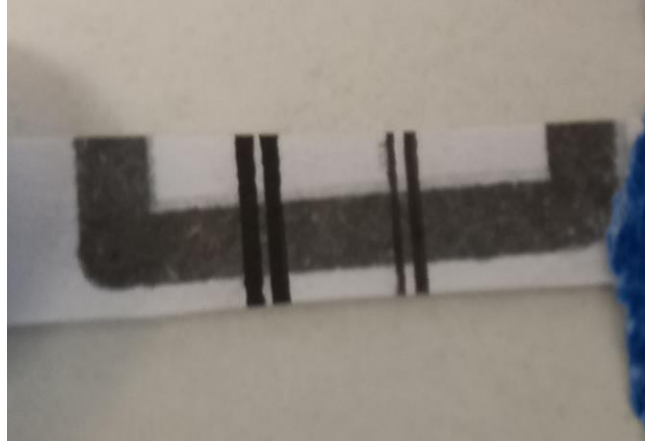


Figure 37. Printing of SnSe 12 mg/ml on paper (grey). The electrodes of ink graphite are 1 mm apart (black).

The obtained device was then studied while illuminated with LEDs at several wavelengths (385, 420, 470, 530, 595, 617, 660, 780 and 850 nm) while different analysis was performed.

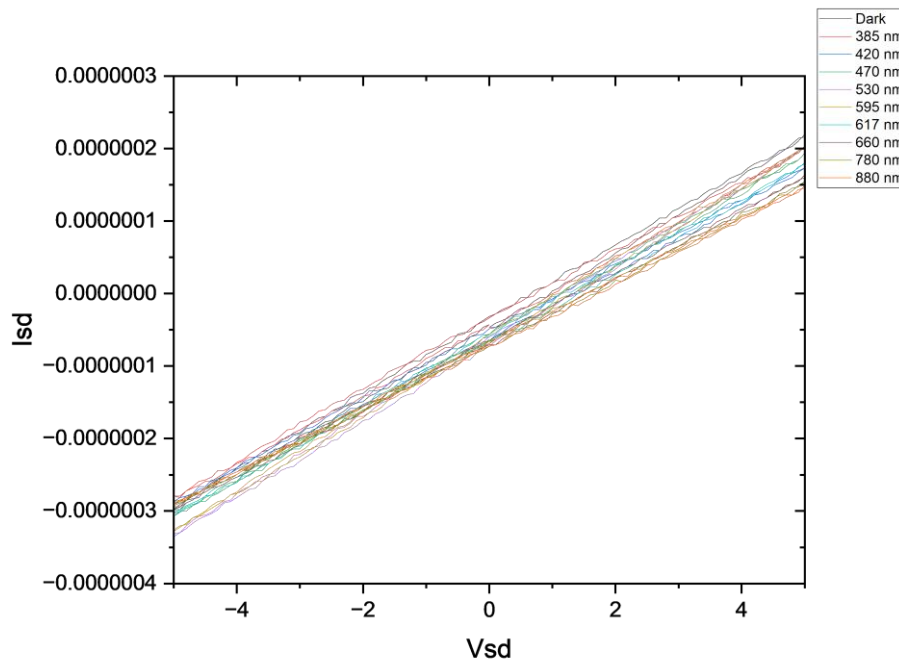


Figure 38. Current vs power of the device under different wavelength illumination.

The first analysis shown in Figure 38 is the measure of current while applying a voltage of 5V. It was verified the presence of current in the 10^{-7} A range, as shown in the graph, and afterwards, photoresponse measurement started.

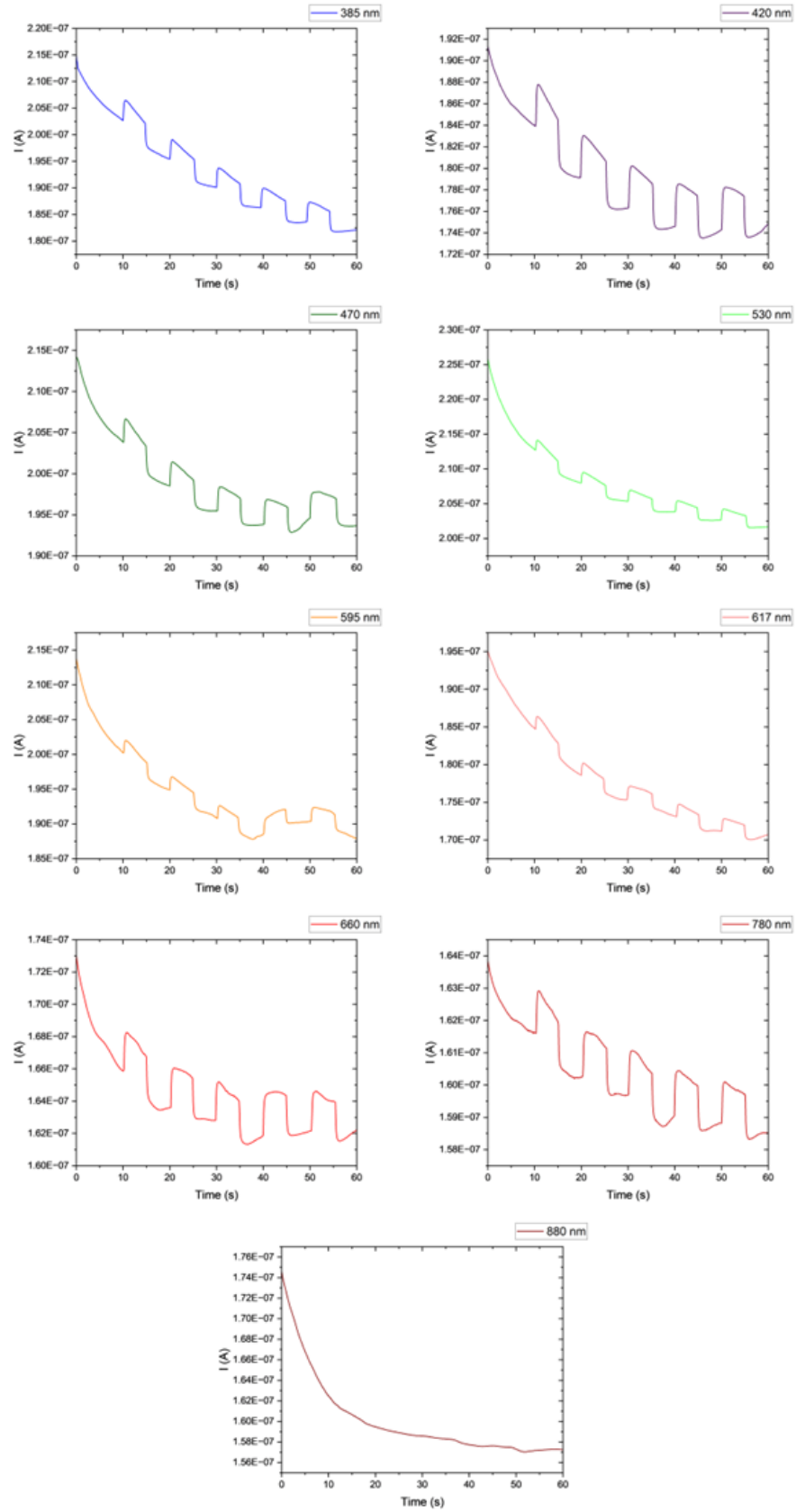


Figure 39. Photoresponse at different wavelengths. The device was kept in the dark for 10 seconds, then illuminated for 5 seconds with a LED and afterwards the LED was turned off for 5 seconds, repeating until 60 seconds. This procedure was reiterated for 385, 420, 470, 530, 595, 617, 660, 780 and 880 nm LED.

Figure 39 shows the photoresponse study; the device was kept in the dark for 10 seconds, then illuminated for 5 seconds and in the dark again for 5 seconds and the graph obtained shows steps for each interval where the LED was on. The procedure was repeated for all the wavelengths until 880 nm did not show any response.

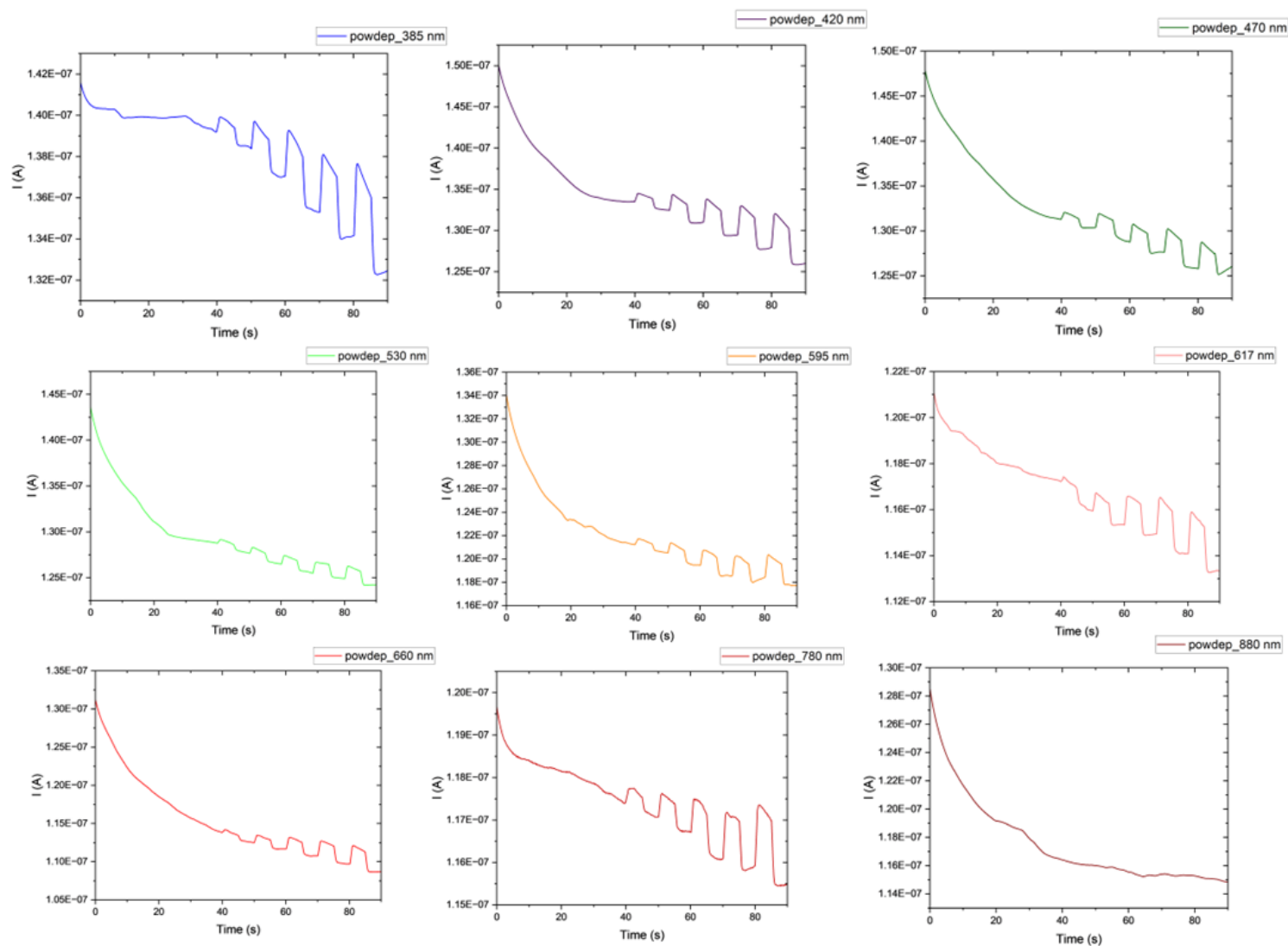


Figure 40. Power dependence at several wavelengths. The device is kept in the dark for 40 seconds, then a voltage of 1 V is applied for 5 seconds and illuminated with the LED at the same time, then the LED is turned off and the voltage applied increased by one; this was repeated until the voltage applied was 5 V. This procedure was reiterated for 385, 420, 470, 530, 595, 617, 660, 780 and 880 nm LED.

The device is kept in the dark for 40 seconds, then illuminated for 5 seconds with the LED and turned off for 5 seconds. Each time the LED is on, a different power is applied to the device; 1V, 2V, 3V, 4V and 5V. The graph shows that the step increases with the increasing of the power, which is to be expected.

Lastly, it was decided to calculate the photoresponse vs power, since this parameter can help us understand the efficiency of the device (Figure 41).

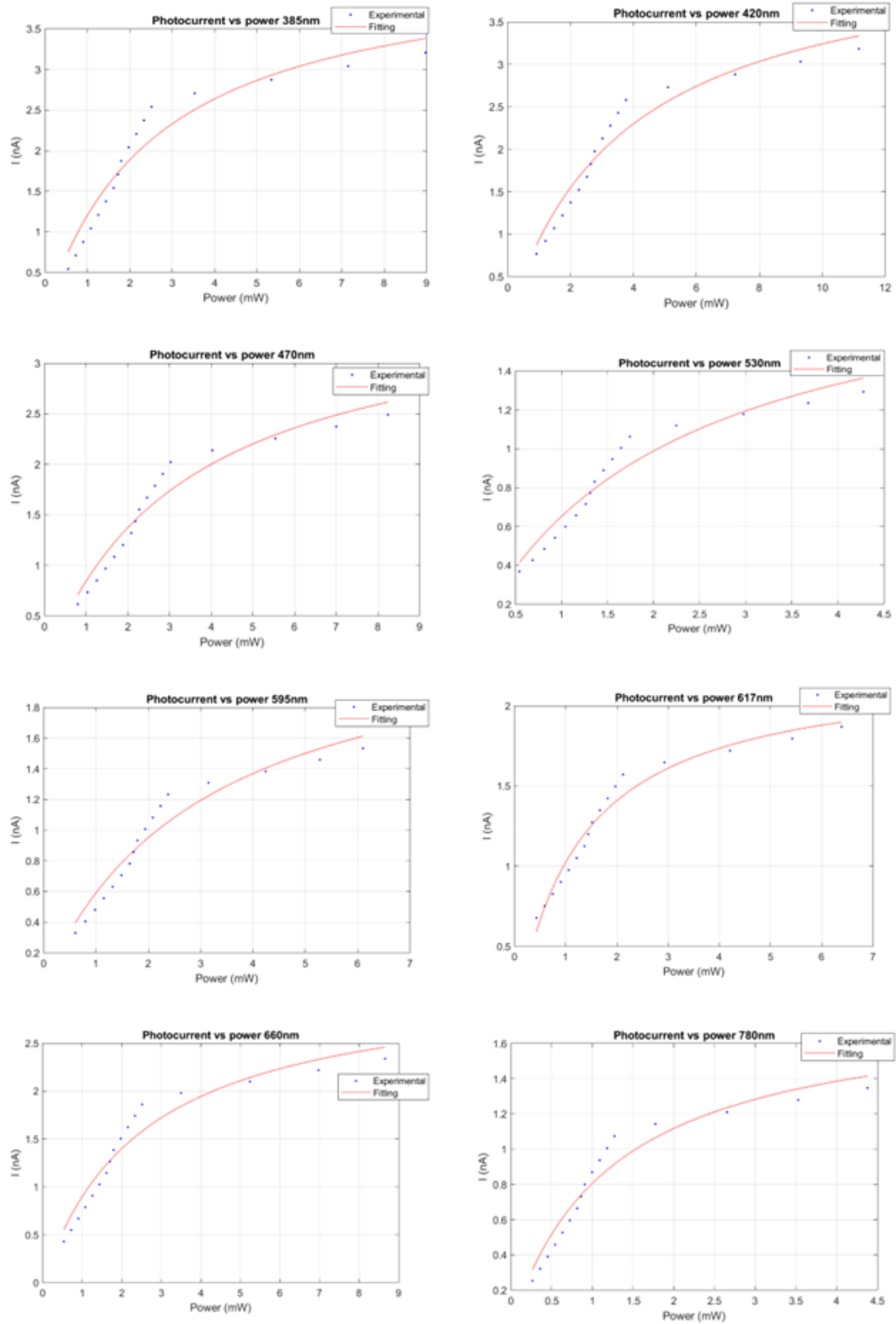


Figure 41. Photocurrent vs power at different wavelengths. These values have been extrapolated from the photoresponse and calculated then with MatLAB.

Figure 41 shows the plot of the photocurrent extrapolated from Figure 40 vs power applied to the device. By interpolating with previously known data, the power was calculated and then divided by the light spot's area to determine the power density, which was then multiplied by the device's area. All the calculations have been made with MatLAB.

The second device was obtained by deposition of SnSe dispersed in IPA, but this time with the graphite ink electrodes being 2 mm apart to test if the feedback is related to the electrode distance (Figure 42).



Figure 42. Printing of SnSe 12 mg/ml on paper (grey). The electrodes of graphite ink are 2 mm apart (black).

The lighter grey part is the deposited dispersion of SnSe in IPA (12 mg/ml), and the darker vertical lines are the graphite ink electrodes. The so obtained device was then studied while illuminated with LEDs at several wavelengths (385, 420, 470, 530, 595, 617, 660, 780 and 850 nm) while different analysis were performed.

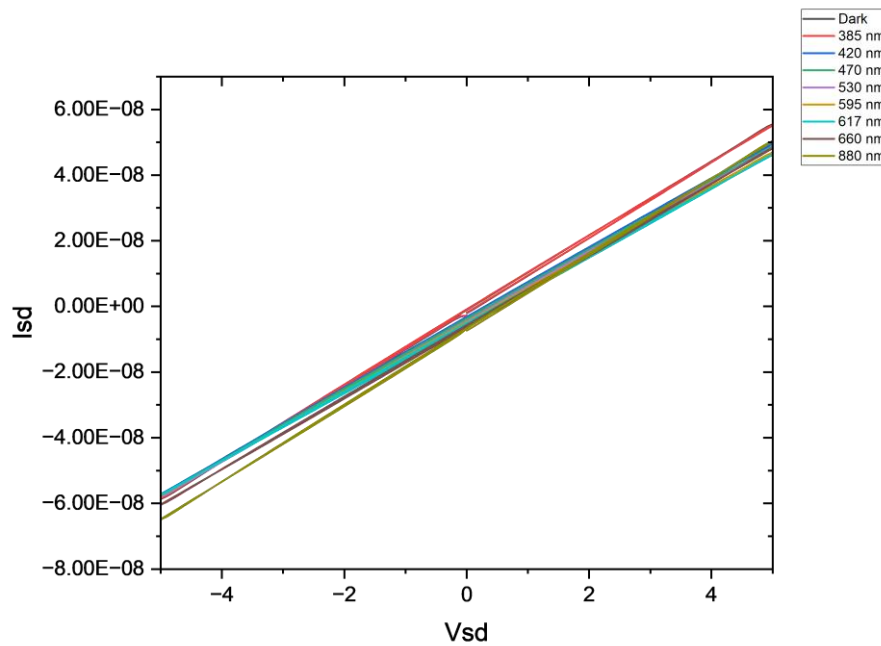


Figure 43. Current vs Volt of the device under different wavelength illumination.

The first analysis shown in Figure 43 is the measure of current while applying a voltage of 5V. It was verified the presence of current in the 10^{-8} A range, as shown in the graph, and afterwards, the photoresponse measurement started.

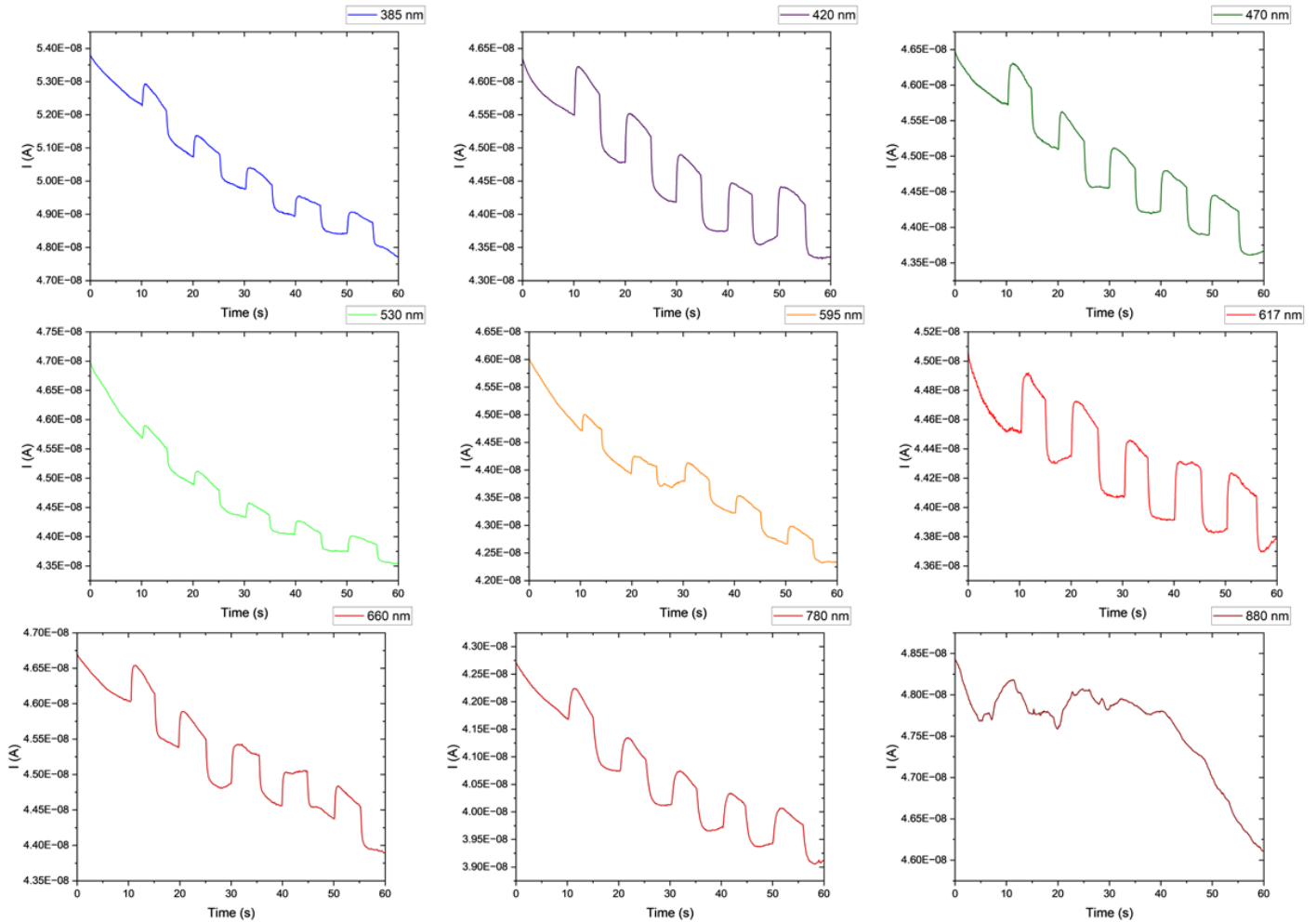


Figure 44. Photoresponse at different wavelengths. The device was kept in the dark for 10 s, then illuminated for 5 seconds with a LED and afterwards the led was turned off for 5 seconds, repeating until 60 seconds. This procedure was reiterated for 385, 420, 470, 530, 595, 617, 660, 780 and 880 nm LED.

Figure 44 shows the photoresponse study: the device was kept in the dark for 10 seconds, then illuminated for 5 seconds and in the dark again for 5 seconds and the graph obtained shows steps for each interval where the LED was on. The procedure was repeated for all the wavelengths until 880 nm did not show any response.

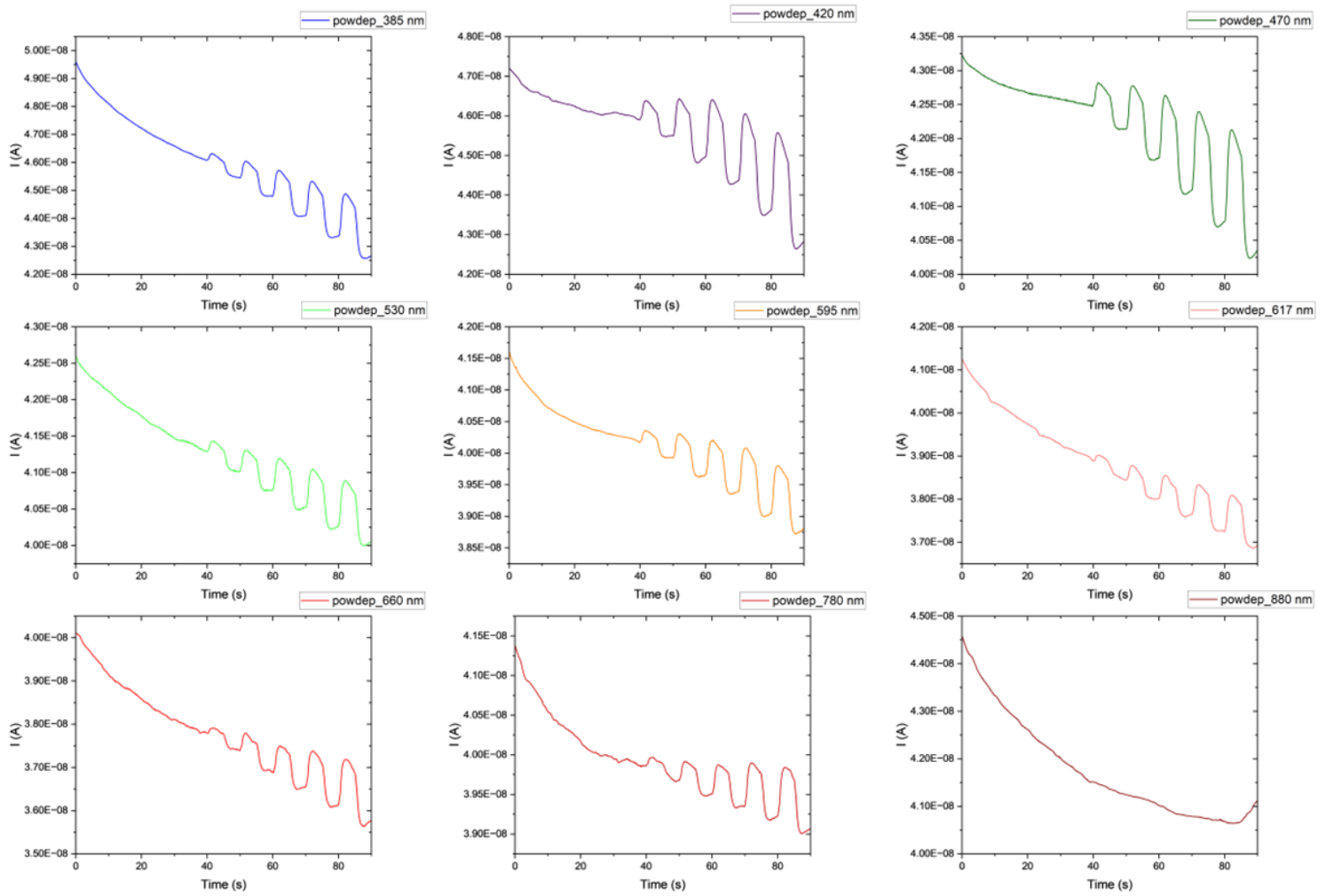


Figure 45. Power dependence at several wavelengths. The device is kept in the dark for 40 seconds, then a voltage of 1 V is applied for 5 seconds and illuminated with the LED at the same time, then the LED is turned off and the voltage applied increased by one; this was repeated until the voltage applied was 5 V. This procedure was reiterated for 385, 420, 470, 530, 595, 617, 660, 780 and 880 nm LED.

Figure 45 shows how the power dependence changes the height of the step. The device is kept in the dark for 40 seconds, then illuminated for 5 seconds with the LED and turned off for 5 seconds. Each time the LED is on, a different power is applied to the device, respectively 1V, 2V, 3V, 4V and 5V. As shown already before step increases with the increasing of the power. This is due to the increase in voltage which caused increased photoresponse at every step.

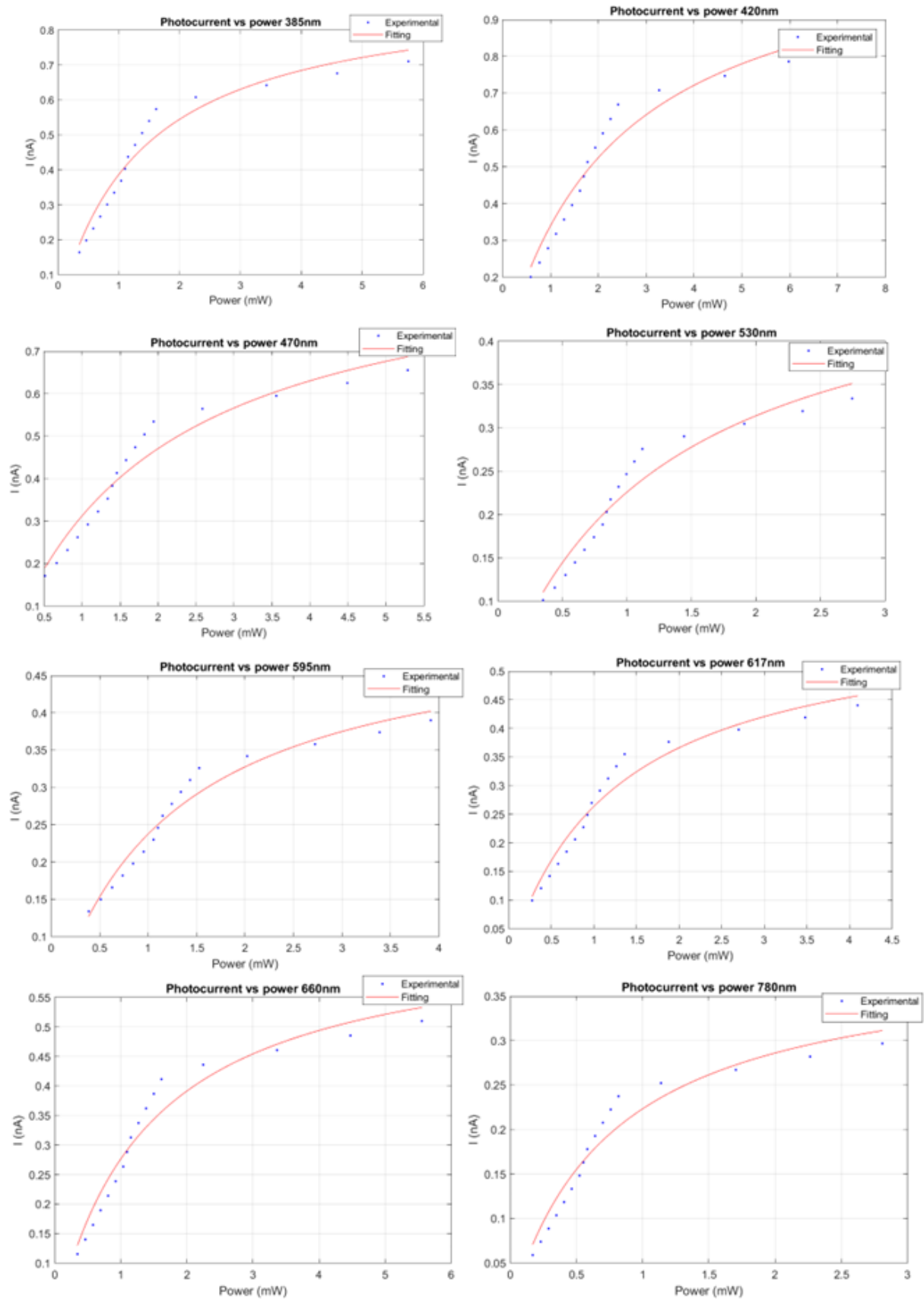


Figure 46. Photoresponse vs power at different wavelengths. These values have been extrapolated from the photoresponse and calculated then with MatLAB.

Figure 46 shows the plot of the photocurrent extrapolated from Figure 40 vs power applied to the device. By interpolating with previously known data, the power was calculated and then divided by the light spot's area to determine the power density, which was then multiplied by the device's area. All the calculations have been made with MatLAB.

To compare the exfoliated devices, a fraction of bulk SnSe was also deposited via abrasion on a paper and the current vs power was measured, followed by photoresponse via the same method shown before.

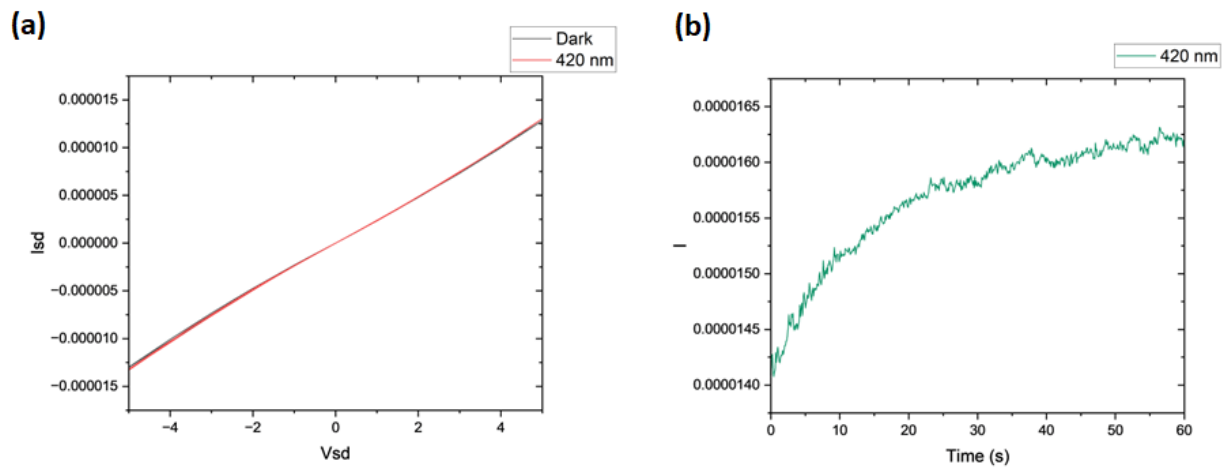


Figure 47. (a) Current vs power of bulk SnSe deposited via abrasion. (b) Photoresponse of bulk SnSe deposited via abrasion with a LED at 420 nm. Photoresponse was studied by keeping the device in the dark for 10 seconds, turning on the LED for 5 seconds and turning it off for another 5 seconds. This procedure was repeated for 60 seconds.

Figure 47 shows that, despite the bulk SnSe shows some current in the 10^{-7} A range, there is no photoresponse. This means that exfoliating SnSe enhances its photoresponse and, consequently, that it is power dependant.

5.1.2. Results with PtSe₂

The last paper device was made with PtSe₂.



Figure 48. Printing of PtSe₂ 16 mg/ml on paper (grey). The electrodes of ink graphite are 2 mm apart (black).

Figure 48 shows the first device deposited on paper. The lighter grey part is the deposited solutions of SnSe dispersed in IPA (12 mg/ml), the black lines are the graphite ink electrodes 2 mm apart. The so-obtained device was then studied while illuminated with LEDs at several wavelengths (385, 420, 470, 530, 595, 617, 660, 780 and 850 nm) while different analysis were performed.

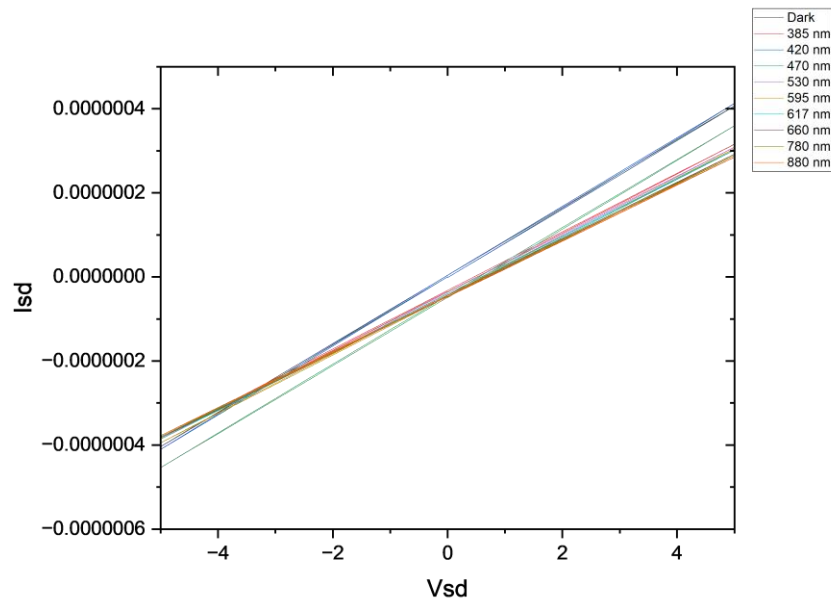


Figure 49. Current vs power of the device under different wavelength illumination.

The first analysis shown in Figure 49 is the measure of current while applying a voltage of 5V. It was verified the presence of current in the 10^{-8} A, as shown in the graph, and afterwards photoresponse measurement started.

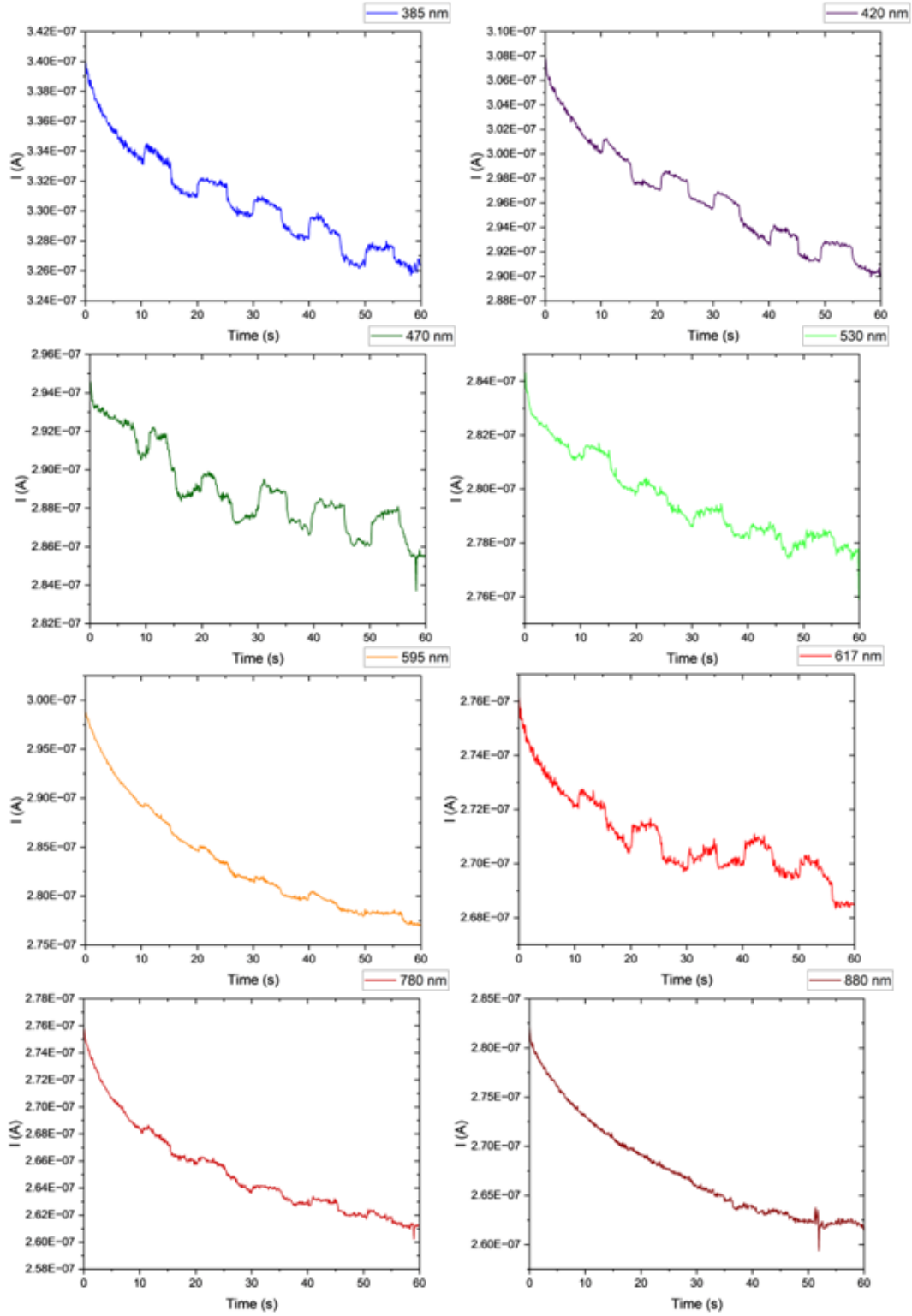


Figure 50. Photoresponse at different wavelengths. The device was kept in the dark for 10 seconds, then illuminated for 5 seconds with a LED and afterwards the LED was turned off for 5 seconds, repeating until 60 seconds. This procedure was reiterated for 385, 420, 470, 530, 595, 617, 780 and 880 nm LED.

Figure 50 shows the photoresponse study: the device was kept in the dark for 10 seconds, then illuminated for 5 seconds and in the dark again for 5 seconds and the graph obtained shows

steps for each interval where the LED was on. The procedure was repeated for all the wavelengths until 880 nm did not show any kind of response.

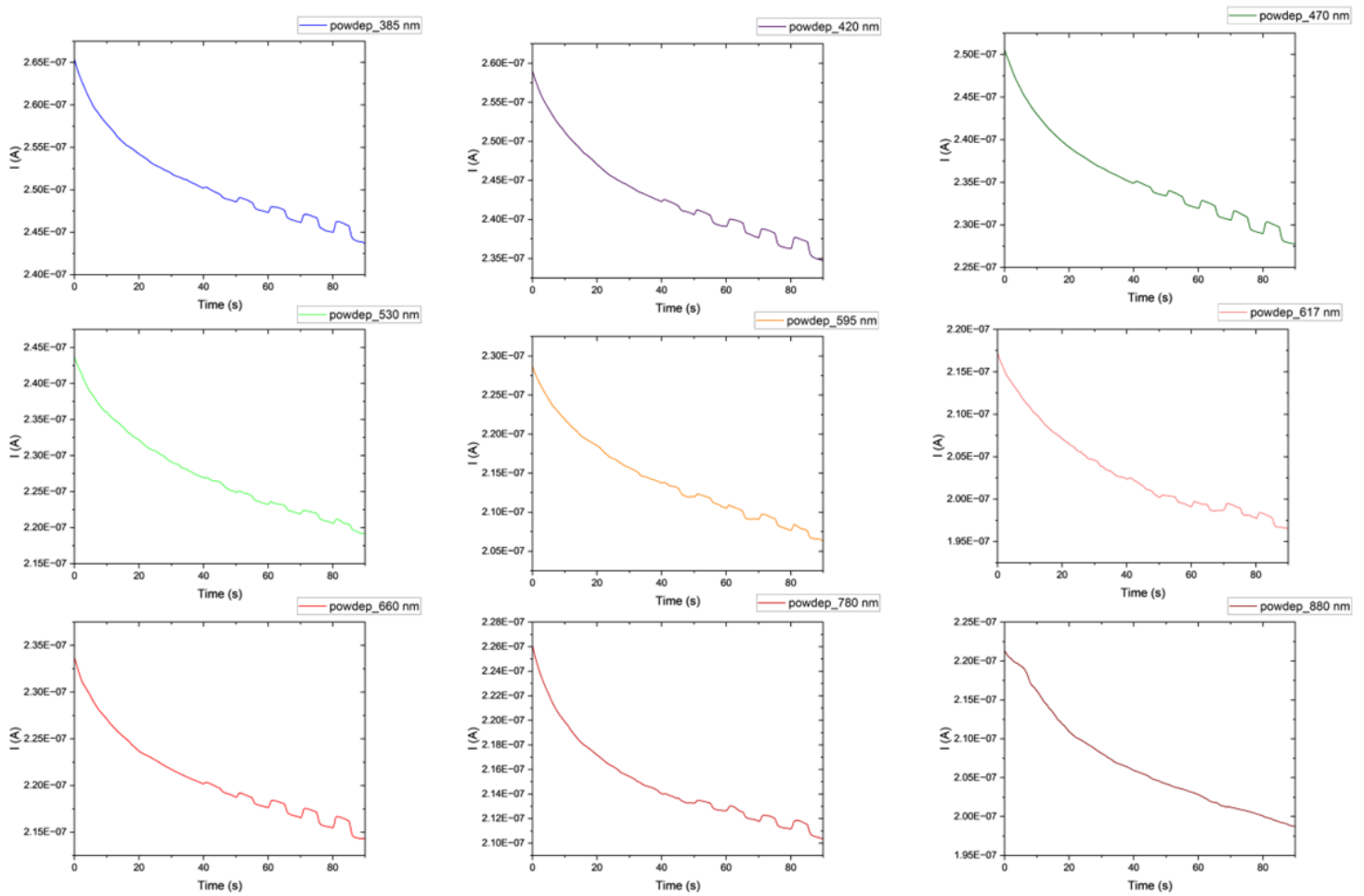


Figure 51. Power dependence at several wavelengths. The device is kept in the dark for 40 seconds, then a voltage of 1 V is applied for 5 seconds and illuminated with the LED at the same time, then the LED is turned off and the voltage applied increased by one; this was repeated until the voltage applied was 5 V. This procedure was reiterated for 385, 420, 470, 530, 595, 617, 660, 780 and 880 nm LED.

Figure 51 shows how the power dependence changes the height of the step. The device is kept in the dark for 40 seconds, then illuminated for 5 seconds with the LED and turned off for 5 seconds. Each time the LED is on, a different power is applied to the device, respectively 1V, 2V, 3V, 4V and 5V. The graph shows that the step increases with the increase of the power, which is to be expected.

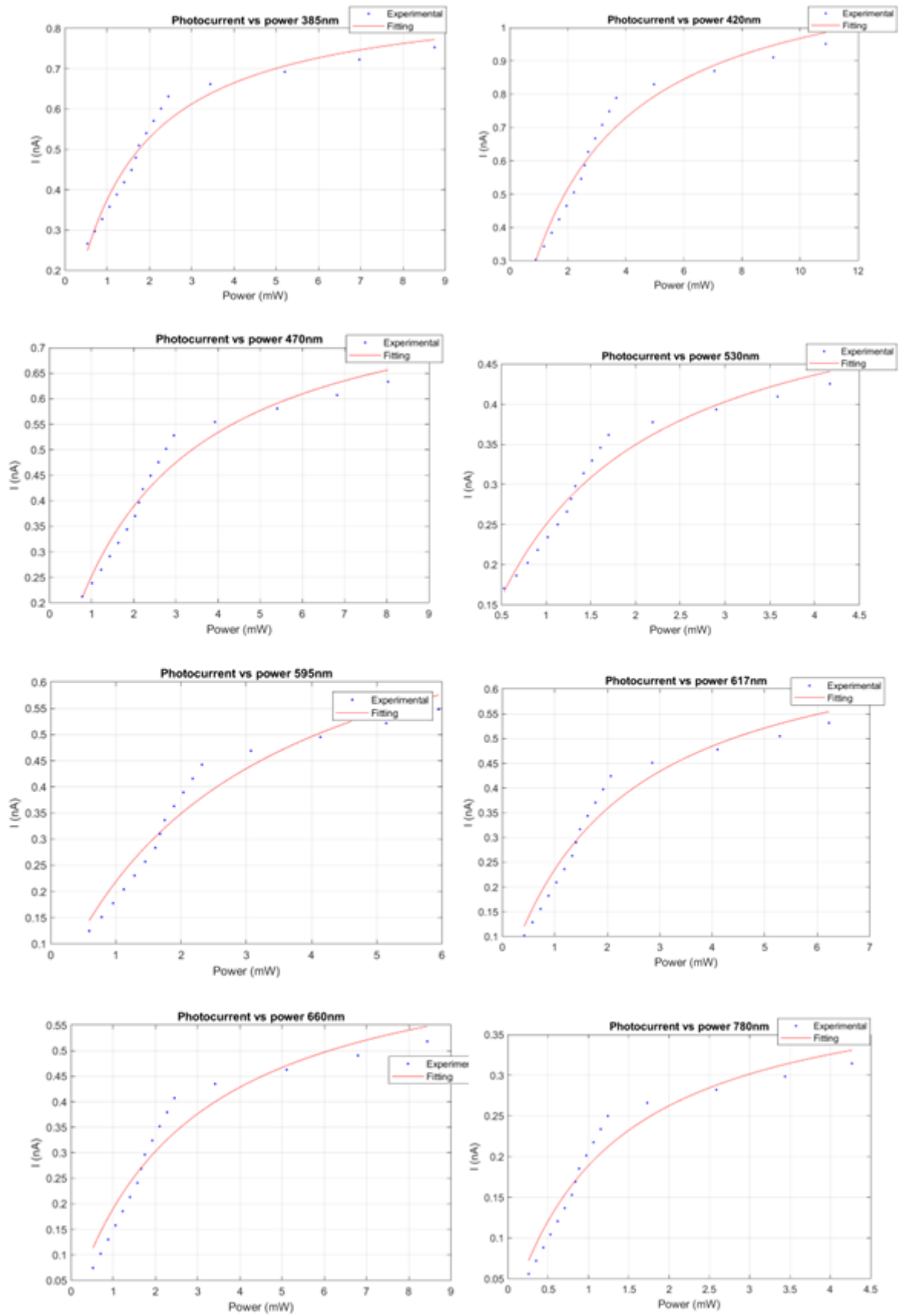


Figure 52. Photoresponse vs power at different wavelengths. These values have been extrapolated from the photoresponse and calculated then with MatLAB.

Figure 52 shows a photoresponse vs power fitting extrapolated from Figure 51. By interpolating with previously known data, the power was calculated and then divided by the light spot's area to determine the power density, which was then multiplied by the device's area. All the calculations have been made with MatLAB.

To have a confrontation, a fraction of bulk PtSe₂ was deposited on paper via abrasion and the current vs power was measured.

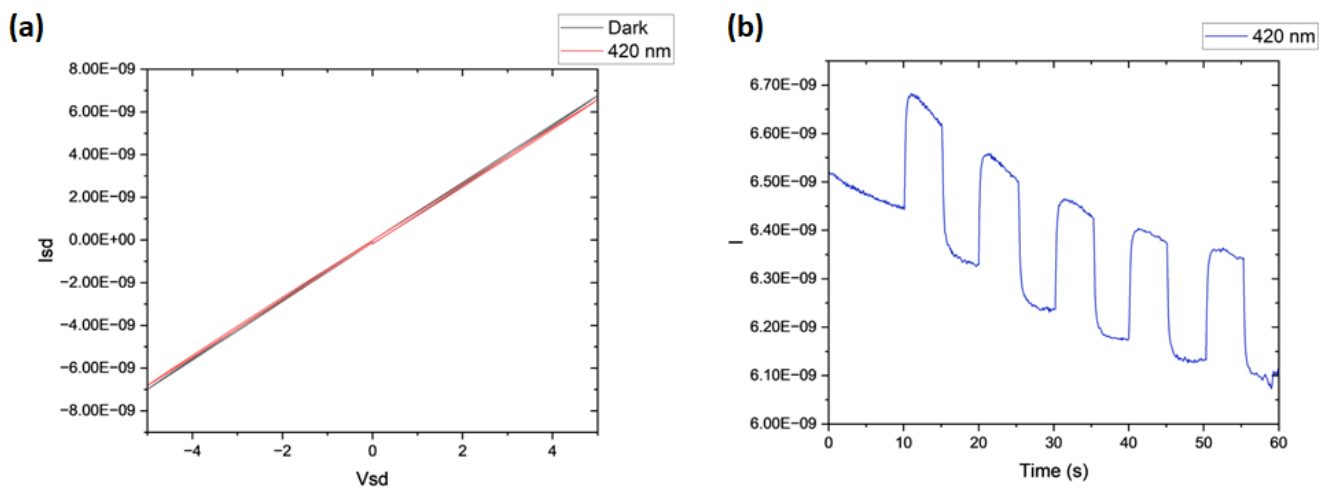


Figure 53. (a) Current vs power of bulk PtSe₂ deposited via abrasion. (b) Photoresponse of bulk PtSe₂ deposited via abrasion with a LED at 420 nm. Photoresponse was studied by keeping the device in the dark for 10 seconds, turning on the LED for 5 seconds and turning it off for another 5 seconds. This procedure was repeated for 60 seconds.

Figure 53 shows that, despite the bulk PtSe₂ exhibiting some current vs power feedback, the photoresponse is two orders smaller than its exfoliated counterpart. This is evidence of the fact that the exfoliation enhances the photoresponse, and therefore the power-dependence, of PtSe₂.

5.2 Printed devices

Devices were also printed with Dimatix and Optomec printers. the Dimatix is an ink-jet printer, providing less freedom of pattern printing, while the Optomec is an aerosol-jet printer compatible with AutoCAD, which offers more printing freedom and higher spatial resolution.

5.2.1 Printing of SnSe dispersions

The first printing was made using a Dimatix inkjet printer and glass was chosen as a substrate. The pattern is a translation along the X-axis by a printhead with 16 nozzles. For this part of the experiment, 100 and 150 layers of the solution in the shape of a box were printed, to verify if

the sample can maintain a certain shape when printed. The printing was performed at 60°C, to let the IPA dry between the printing of one layer and the other, and the glass was therefore left to dry overnight at room temperature. IPA is not the most compatible solvent with the printer, therefore not all the nozzles work at once. Despite this, the printed boxes are very dark (meaning that the material was depositing well), consistent in shape and easily visible on glass.

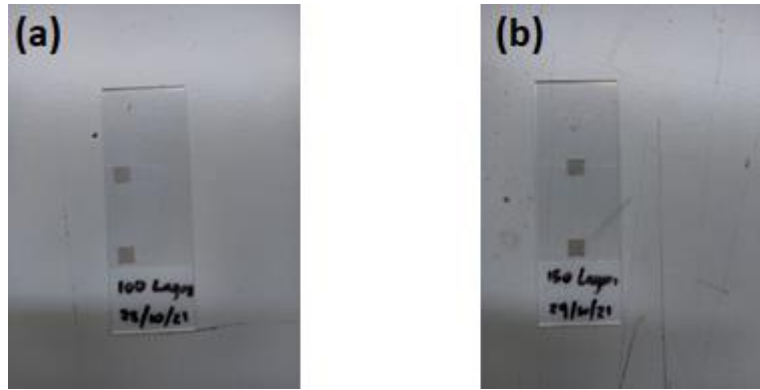


Figure 54. (a) 100 layers of SnSe printed on glass. (b) 150 layers of SnSe printed on glass.

Figure 54 shows photographs of the SnSe IPA dispersions printed on glass: 100 printing layers in (a) and 150 in (b). In both cases, the print is stable and dry and it maintains the shape that it was initially set. Because inkjet printing with IPA is time-consuming, it was decided to move onto aerosol jet printing next, using our Optomec AJ3000 instead. At the time of this work, only boxes have been printed to verify the stability and fidelity of the printed devices. The shape and the pattern of the box have been defined with the software AutoCAD, and the parameters chosen with the software of the Optomec. Using a 300 nm nozzle at room temperature, the SnSe box was printed on glass and analysed with the optical microscope.

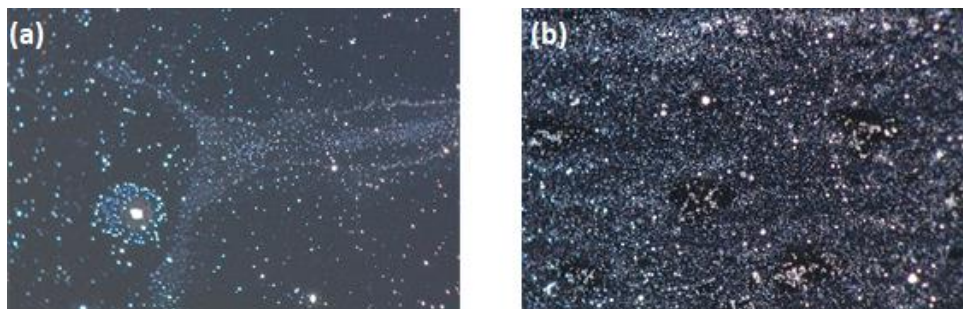


Figure 55. Dark-field optical microscope images of: (a) the bare glass substrate. (b) the SnSe dispersion printed by aerosol-jet printing on glass.

Figure 55 shows the dark field optical microscope images of the bare glass substrate (a), and the SnSe dispersion printed on glass by aerosol-jet printing (b). It can be seen that the SnSe layer is uniform, and this is crucial for printing devices because they must not have gaps within.

The whole box is observed, and it is shown that it is uniformly printed along the whole structure.



Figure 56. Optical image of the printed SnSe box.

Figure 56 shows the optical image of the whole box. SnSe maintains the printed shape very well. The printed material maintains most of its uniformity, the box has no gaps or missing pieces, and the lines are straight.

5.2.2 Printing of PtSe₂ dispersions

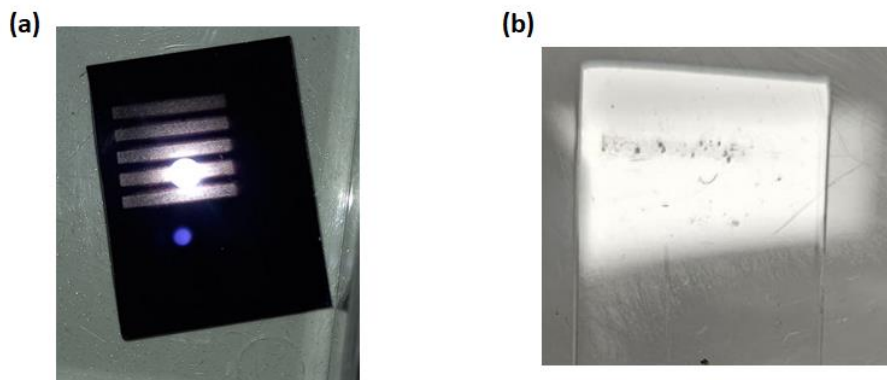


Figure 57. (a) Printing of PtSe₂ on Si/SiO, 200 layers. (b) Printing on PtSe₂ on polycarbonate, 400 layers.

Figure 57 shows the printed PtSe₂ is barely visible both on the Si/SiO and even less on polycarbonate. The Dimatix faced many problems, like the clogging of nozzles and motor problems and this could also explain why the PtSe₂ printing is barely visible.

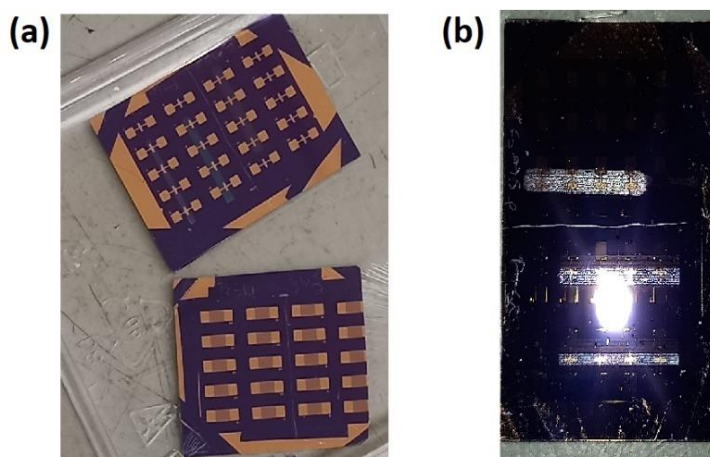


Figure 58. (a) PtSe₂ printed on Si/SiO substrate with gold electrode pattern. (b) The substrate is illuminated to highlight the PtSe₂ printed.

Figure 58 shows other substrates on which the Dimatix printer was used. The substrate is Si/SiO 250 nm with gold circuit patterns evaporated on it. The printing was made on the neighbouring gold electrodes to close the circuit and therefore allow the current exchange, but the printing is not uniform, and this is confirmed by the optical microscope.

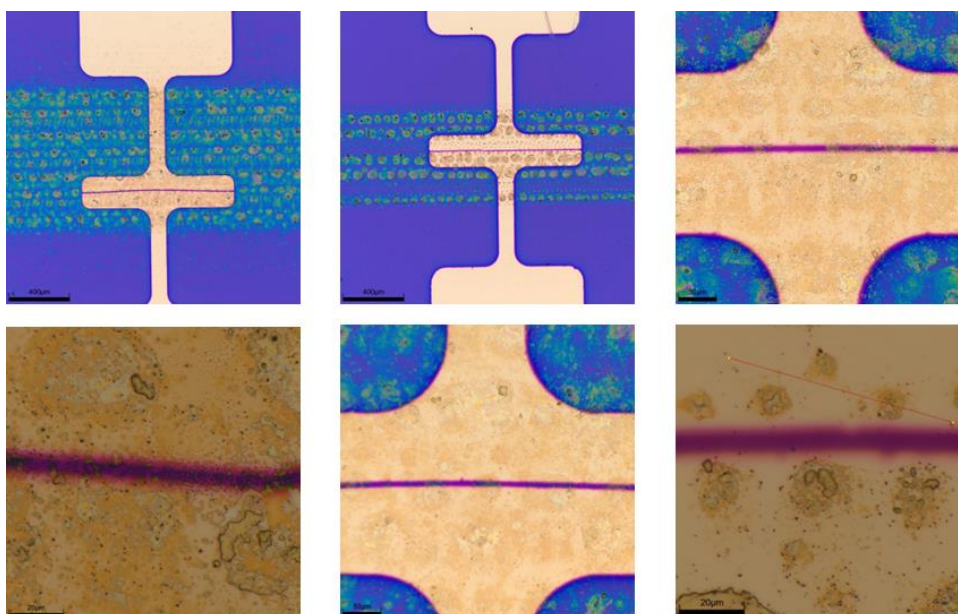


Figure 59. Microscope images of printed PtSe₂ on the circuit. It can be seen that PtSe₂ flakes do not close the circuit.

Figure 59 shows clearly that the printing is not uniform and the flakes do not bridge the two gold pieces to close the circuit. Since in this case the printing is suitable for our aim, a new deposition technique was used.

5.3 Film deposition

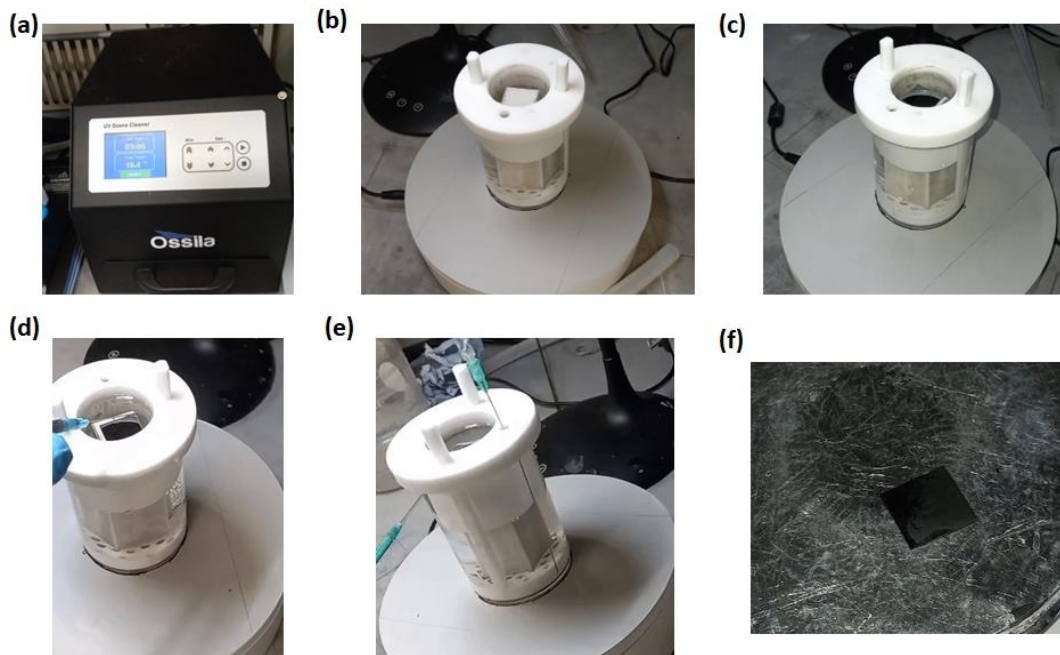


Figure 60. (a) UV Ozone cleaning for 3 minutes. (b) The system filled with water. (c) The substrate is in the system and there is an interface of H_2O /hexane. (d) Drop addition to create a film in the interface. (e) Removal of water from the system and adhesion of the film to the substrate. (f) Annealing on the hot plate at 50 C for 15 minutes.

Figure 60 shows the film deposition technique: firstly, (a) the substrate is pretreated with UV Ozone cleaning for 3 minutes, while (b) the system is filled with water. (c) The substrate is then positioned on the system, where it is added hexane, and (d) the ink is added drop by drop to create a film at the interface. Lastly, (e) the water is removed with a pump leaving a film adhering to the substrate (f). The obtained device (f) is annealed at 50 degrees for 15 minutes.

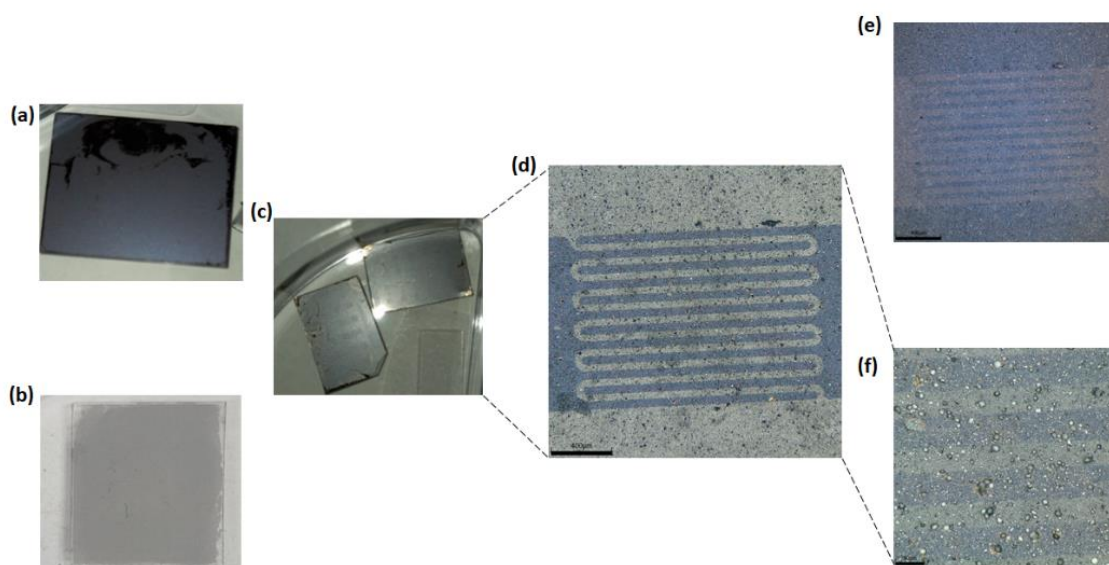


Figure 61. $PtSe_2$ films. (2) Si/SiO 250 nm. (b) Polycarbonate. (c) Polycarbonate with Au devices. (d) Optical microscope bright field. (e) Dark-field. (f) Bright field zoom.

We can see from Figure 61 (a, b, c) that the deposition of PtSe₂ is uniform, and the microscope images also confirm the uniformity of the printing and that the flakes bridge between the circuit electrodes (Figure 61 (c, d, e)).

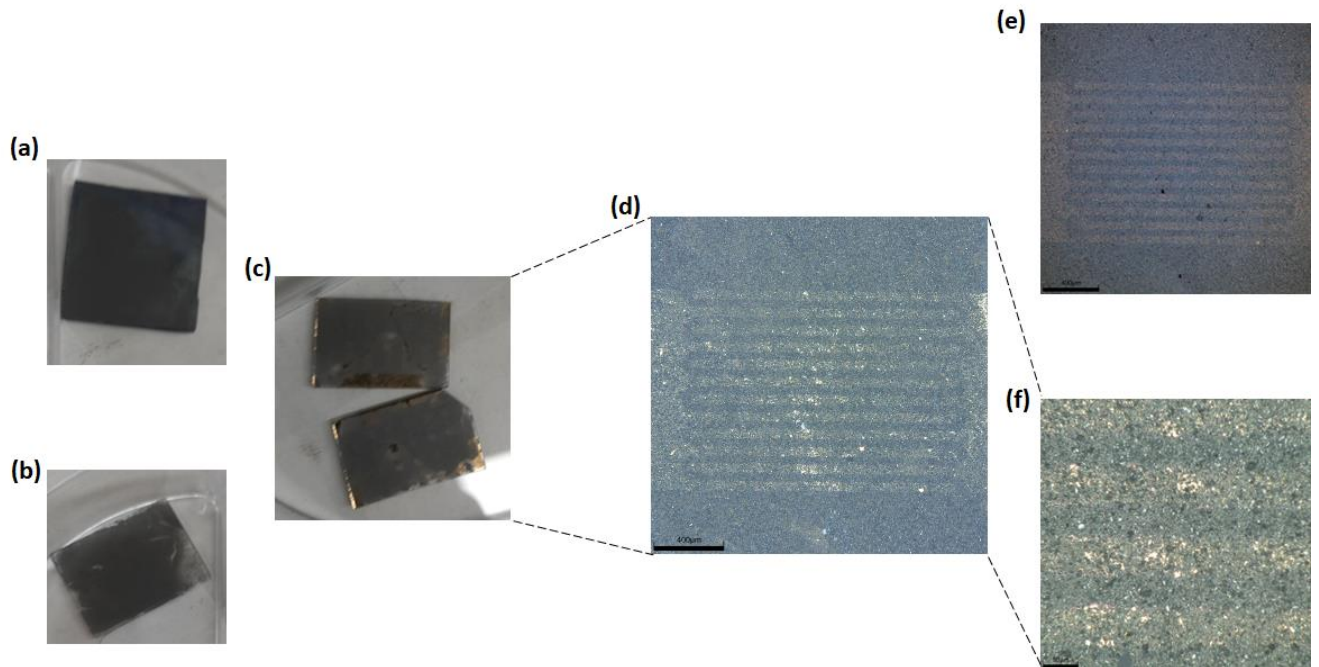


Figure 62. SnSe films. (a) Si/SiO₂ 500 nm. (b) Polycarbonate. (c) Polycarbonate with Au devices. (d) Optical microscope bright field. (e) Dark field. (f) Bright field zoom.

It was possible to see from Figure 62 (a, b, c) that the deposition of SnSe is uniform, and the microscope images also confirm the uniformity of the printing and that the flakes bridge between the circuit electrodes (Figure 62 (c, d, e)).

5.4 Conclusions

Several techniques of printing and deposition have been tested and characterized, starting with Dimatix and Optomec printing which revealed to have many problems such as clogging of the nozzles, and low printing rate (with some of the printing patterns barely visible). Optical microscopy also confirmed that the flakes do not bridge the golden electrodes.

Film deposition seems to be the most promising together with the pen plotter, also because it allows the flakes to bridge between the gold pattern and close the circuit. Further studies about these devices will be made to confirm their optoelectronic properties.

6. Conclusions and future work

This thesis successfully explores the liquid phase exfoliation of SnSe in IPA by use of a sonic bath. With this method, we were able to produce nanoflakes up to < 200 nm in size, yielding nanoflakes with sizes below 200 nm. Additionally, we achieved successful exfoliation of SnSe in IPA with a pulsed sonic tip, showcasing the versatility of the method. The size selection of SnSe was effectively accomplished through liquid cascade centrifugation (LCC), separating a fraction comprising thinner and smaller flakes.

PtSe₂ was another material investigated, with successful exfoliation in N-methyl-2-pyrrolidone (NMP) via bath ultrasonication. Although microscopy characterization indicated successful exfoliation for all dispersions, further optimization is planned for PtSe₂ to address potential restacking phenomena.

Optical characterisation with the UV-Vis revealed peaks at approximately 1400 nm for SnSe and at 450 nm for PtSe₂, which are in agreement with what was reported in literature^{98,62}. SnSe can have applications in near-IR sensors, while PtSe₂ can have applications in visible-light sensors. Both the inkjet printer and the Aerojet printer are compatible with the achieved dispersions, and the deposition of the SnSe ink on glass has been proved successful. The boxes printed on glass maintained their shape fidelity and uniformity, thus showing that it would be possible to print other shapes. We will also move to other substrates, such as Si/SiO₂.

For future work, LCC will be performed on SnSe exfoliated with the sonic tip, and the resulting fractions compared to the ones obtained by LCC on bath ultrasonication. Moreover, LCC will be performed on the PtSe₂ dispersions, along with the characterization of each fraction. We will also optimise starting concentration and sonication parameters in NMP and other more volatile solvents (such as IPA), to improve processibility.

Comparative AFM and SEM studies confirmed the thickness of SnSe flakes to be < 500 nm for fraction I, < 200 nm for fraction II, and < 100 nm for fraction III. The sample exfoliated with the sonic tip displayed < 100 nm thickness. PtSe₂ also exhibited < 100 nm thickness, as corroborated by profile analysis.

Devices printed on paper with SnSe demonstrated a photoresponse in the range of 10^{-7} A to 10^{-8} A for electrodes spaced 1 mm and 2 mm apart, respectively, surpassing the zero photoresponse of the bulk material. PtSe₂ devices on paper displayed a photoresponse in the range of 10^{-7} A for electrodes spaced 2 mm apart, outperforming the bulk photoresponse in the order of 10^{-8} A.

Furthermore, PtSe₂ and SnSe inks were successfully printed on Si/SiO with 250 nm and 500 nm thickness, as well as on polycarbonate. The homogeneity of deposition was verified using an optical microscope. Future endeavours include measuring the thickness and photoresponse of these printed devices on Si/SiO and polycarbonate to conduct a comprehensive comparative study and assess their conductivity.

7. References

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