

NANOMETRIC THIN ORGANIC AND INORGANIC LAYERS AND THEIR USE IN PEROVSKITE SOLAR CELLS AND ELASTOMERS

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**NANOMETRSKO TANKE ORGANSKE IN
ANORGANSKE PLASTI TER NJIHOVA UPORABA V
PEROVSKITNIH SONČNIH CELICAH IN
ELASTOMERIH**

Doktorska disertacija

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To my close family

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Abstract

Organometal halide perovskites are a class of semiconducting compounds which marked the research in the photovoltaic field by their excellent optical and electronic properties convenient for light harvesting applications. In a 7-year period of research and their application in solar cells, power conversion efficiencies surged to over 21%, which was only a decade ago unimaginable for mainly solution-processed solar cells. Albeit the high power conversion efficiency, there are several issues that need to be addressed before the technology becomes mature for industrial scale production. Solution processing of organolead halide perovskites is typically performed by using toxic, high boiling point solvents. In addition, the occurrence of other structural phases as nonstoichiometric residues during the film formation is directly connected to the atmospheric conditions during crystallization. In order to overcome these problems I introduce a straightforward, scalable and environmentally friendly synthesis of submicron sized stoichiometric perovskite particles, which can be afterwards deposited in the form of an ink on large area substrates. Synthesized particles are applied in a photoconductor in which the dominant photoconducting charge type is revealed.

Currently the most efficient perovskite solar cell structures implement metal oxide electron transporting layers which require complex processing with high-temperature sintering, are unstable under ultraviolet (UV) light irradiation and cause interface charge build up which results in electrical instabilities in the form of hysteresis. Here I present a novel approach of using self-assembled siloxane functionalized fullerenes on an optically transparent conductive oxide electrode as an effective electron extracting layer in perovskite solar cells. It is demonstrated that a 1.5 nm thick monolayer, formed by a low temperature dip coating method, is enough to obtain a UV stable charge selective interface.

Transition metal dichalcogenides, particularly MoS_2 and WS_2 belong to a large family of layered, quasi 2D materials which have a common feature – anisotropic layered-like growth with characteristic weak interlayer interactions. This property allows one to isolate individual sheets from the parent crystal by means of exfoliation techniques. As band gap tunable semiconductors with rich surface chemistry they have proven to be promising materials for numerous thin film opto-electronic devices. As a proof of concept, I present exfoliated WS_2 applied as an inorganic hole transporting layer in perovskite solar cells, which resulted in a 6% of stabilized solar cell power output. Furthermore I propose perovskite- WS_2 band alignment supported by an indirect indication of charge transfer over the perovskite- WS_2 interface.

Lastly, specific surface functionalization applied on chemically exfoliated MoS_2 is presented by decorating MoS_2 nanosheets with gold nanoparticles directly in a colloidal suspension. This led to their homogeneous incorporation into an elastomer by virtue of strong gold-thiol interaction. Together with the possibility of induced metal to semiconducting phase transformation in MoS_2 we produced a matrix of metallic and semiconducting parts by a laser-induced phase transition.

Povzetek

Polprevodniški organokovinski halogenidi s perovskitno strukturo so s svojimi izjemnimi optičnimi in elektronskimi lastnostmi zadnja leta zaznamovali področje raziskav sončnih celic. V 7-letnem obdobju od začetka prve uporabe organosvinčevih halogenidov v sončnih celicah, se je izkoristek pretvorbe sončne energije v električno naglo povečeval in danes presega 21 %. Kljub hitremu napredku in visokim izkoristkom pa področje organosvinčevih perovskitov potrebuje nadaljnje raziskave in nove pristope k sintezi in procesiranju, s katerimi bi razrešili težave, ki preprečujejo prehod v industrijsko proizvodnjo. Trenutna priprava prekursorjev organosvinčevih perovskitov bazira na osnovi zdravju škodljivih topil z visoko temperaturo vrelišča, ki je nadalje otežena s potrebno popolno kontrolo nad atmosfero ter prisotnostjo par topil med formacijo perovskitnega filma. V nasprotnem primeru se v tankoplastnem filmu pojavijo nestoichiometrične faze, ki zavirajo optimalno delovanje fotoaktivne plasti. V izogib tem težavam predstavljam enostavno, nizkotemperaturno ter okolju prijaznejšo sintezo podmikronskih organosvinčevih perovskitnih delcev, ki je prilagodljiva na večjo proizvodnjo in nadomesti celoten postopek priprave perovskitnih plasti s pomočjo prekursorjev. Tako sintetizirane delce sem nadalje uporabil v enostavnem fotoprevodniku, s pomočjo katerega sem določil večinske nosilce naboja v perovskitni plasti.

Trenutno se v najbolj učinkovitih perovskitnih sončnih celicah z izkoristki nad 20 % za elektronsko prevodno plast uporablja kovinske okside, na primer titanov dioksid, ki potrebuje visokotemperaturno sintranje, je nestabilen pri izpostavitvi ultravijolični svetlobi ter povzroča nabiranje negativnega naboja na meji z aktivno plastjo. V disertaciji predstavljam samourejanje monoplasti funkcionaliziranega fulerena na optično transparentnih prevodnih elektrodah za uporabo v perovskitnih sončnih celicah. Tanka plast, nanešena s pomočjo enostavne metode s potapljanjem (ang. dip coating), se izvaja z nizkotemperaturnim procesiranjem in je prilagodljiva za nanos na večje površine. Izkaže se, da je 1,5 nm tanka organska plast dovolj za selektiven prenos nosilcev naboja, hkrati pa je obstojna na visokotemperaturno procesiranje in ultravijolično obsevanje.

Dihalkogenidi prehodnih kovin, na primer MoS_2 in WS_2 , spadajo v družino plastovitih kristalov, v katerih šibka interakcija med sosednjimi plastmi omogoča njihovo razslojevanje. Na osnovi raznolikih elektronskih in optičnih lastnosti, izvirajoč iz njihove kemične sestave ter stopnje razslojenosti, so bili plastoviti kristali uporabljeni v mnogih tankoplastnih opto-elektronskih napravah. Tu predstavljam uporabo razslojenega wolframovega disulfida (WS_2) kot selektivno plast za vrzeli v perovskitnih sončnih celicah s stabilnim 6 % izkoristkom. Nadalje s pomočjo karakterizacije pasovne strukture določim energijsko poravnavo med perovskitno plastjo ter WS_2 .

Nazadnje predstavljam funkcionalizacijo površine MoS_2 , ki sem jo izvedel v raztopini s pritrditvijo zlatih nanodelcev na površino MoS_2 . Tako pripravljene nanoplasti smo s pomočjo močne interakcije med zlatimi delci, pritrjenimi na površino MoS_2 , in monomeri homogeno vgradili v elastomer. V tako pripravljenem elastomernem filmu smo s pomočjo laserske svetlobe inducirali fazni prehod med kovinsko in polprevodniško fazo MoS_2 .

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Abbreviations

ACN	...	Acetonitrile
ALD	...	Atomic layer deposition
AM	...	Air mass
BWD	...	Backward
CBM	...	Conduction band minimum
CCD	...	Charge-coupled device
CIGS	...	Copper indium gallium selenide
CPE	...	Constant phase element
cTiO ₂	...	Compact titanium dioxide
CV	...	Cyclic voltammetry
CVD	...	Chemical vapor deposition
DFT	...	Density functional theory
DMF	...	<i>N,N</i> -Dimethylformamide
DMSO	...	Dimethyl sulfoxide
DNA	...	Deoxyribonucleic acid
DSSC	...	Dye-sensitized solar cell
EIS	...	Electrochemical impedance spectroscopy
EQE	...	External quantum efficiency
ETL	...	Electron transporting layer
FA	...	Formamidinium
FAI	...	Formamidinium iodide
FF	...	Fill factor
FFT	...	Fast Fourier transform
FRA	...	Frequency response analyzer
FTO	...	Fluorine doped tin oxide
FTPS	...	Fourier-transform photocurrent spectroscopy
FWD	...	Forward
GBL	...	<i>Gamma</i> -Butyrolactone
GNP	...	Gold nanoparticles
HR-TEM	...	High-resolution transmission electron microscope
HTL	...	Hole transporting layer
ITO	...	Indium tin oxide
Li-TFSI	...	Bis(trifluoromethane)sulfonimide
MA	...	Methylammonium
MAI	...	Methylammonium iodide
MBE	...	Molecular beam epitaxy
MPP	...	Maximum power point
n-BuLi	...	<i>N</i> -Butyllithium
NMP	...	<i>N</i> -Methyl-2-pyrrolidone
OMHP	...	Organometal halide perovskite
PCBM	...	Phenyl-C61-butyric acid methyl ester

PCE	...	Power conversion efficiency
PDS	...	Photothermal deflection spectroscopy
PL	...	Photoluminescence
PLD	...	Pulsed laser deposition
PMMS	...	Poly[(mercaptopropyl)methylsiloxane]
PSC	...	Perovskite solar cell
SAM	...	Self-assembled monolayer
SEM	...	Scanning electron microscope
Sil-C60	...	<i>N</i> -[3-(triethoxysilyl)propyl]-2-carbomethoxy-3,4-fulleropyrrolidine
Spiro	...	2,2',7,7'-Tetrakis[<i>N,N</i> -di(4-methoxyphenyl)amino]-9,9'-spirobifluorene
STEM	...	Scanning transmission electron microscope
TBAFTB	...	Tetrabutylammonium tetrafluoroborate
tBP	...	4-tert-Butylpyridine
TCO	...	Transparent conductive oxide
TEM	...	Transmission electron microscope
TMD	...	Transition metal dichalcogenide
UPS	...	Ultraviolet photoelectron spectroscopy
UV	...	Ultraviolet
VBM	...	Valence band maximum
XPS	...	X-ray photoelectron spectroscopy
XRD	...	X-ray diffraction

Symbols

h . . . Planck constant
 c . . . Speed of light
 q . . . Elementary charge

Chapter 1

Introduction

1.1 Motivation

This doctoral dissertation encompasses the work done in the fields of two distinct types of materials, namely organometal halide perovskites (OMHPs) and layered transition metal dichalcogenides (TMDs). Rapid increase in the scientific interest for both materials started with the pioneering discoveries of graphene and the first use of organometal halide perovskites in solar cells. Since then these two young, but very prospective scientific fields are in need of novel synthetic approaches, advanced knowledge of the material and their application in various devices. Specifically for organometal halide perovskites the main motivation is to drive the research in a direction of developing long-term stable OMHP compounds suitable for photovoltaic applications. This technology has expressed great potential as an alternative to silicon solar cells as less energy demanding in production while being competitively efficient in light to electricity conversion in comparison to other highly efficient photovoltaic technologies. In an ideal case, perovskite solar cells (PSCs) can come out as an unmatched low-cost renewable source of energy which could find its application in consumer markets supplying energy for low-power electronic devices, in medium-scale electricity production for buildings (wall integrated or as rooftops) and ultimately in large-scale electricity production (solar power plants). Especially in developing countries with high levels of annual solar irradiance, low-cost OMHPs could cover the energy needs for residential areas, increasing the overall quality of living. Reaching the state of transition to industrial scale production requires this technology to be long-term environmentally stable achieving low energy payback times (i.e. the time in which the solar cell produces the amount of electrical energy required for its manufacture) and even more importantly it should be safe and harmless to the environment. Only recently, when the performance increase of perovskite solar cells has slowed down converging to its limits, these aspects are taken a lot more into consideration when developing novel compounds or cell structures.

On the other hand inorganic layered materials with their two-dimensional structure, particularly TMDs, show intriguing properties that stem from nanometric thin films. They express unique behavior at the nanoscale which already led to discoveries that either improved the performance of various opto-electronic devices or that were used in an innovative way where conventional three-dimensional materials do not suffice. The main motivation behind the studies of TMDs presented in this thesis are the predispositions of semiconducting layered materials, as an example the large aspect ratio of 2D nanosheets and rich surface chemistry, which call for a combination with other organic or inorganic materials forming novel functional composites and heterostructures.

1.2 Hypothesis and Goals

The initial hypothesis was based on the intrinsic property of TMDs – their layered growth. If one can achieve control over the degree of exfoliation, provide a deposition technique for conformal and homogeneous films of TMDs, they could be used in thin film-based opto-electronic devices. Specific low dimensional growth can provide significant reduction of the film thickness and consequently reduction of the series electrical resistance of the functional layer in comparison to other conventional three-dimensional materials. Additionally, these materials offer tuning of optical and electronic properties when thinned down to nanometric scale and external tuning of these properties by various doping procedures. The major goal related to the initial hypothesis was to exfoliate the most abundant TMDs by various methods and apply them in thin film photovoltaic technologies. They carry a potential to replace other solution-processed charge-selective layers in solar cells offering high tunability, environmental stability being resistant to oxidation and cheap and abundant starting materials.

Due to changes in the research program during my PhD period research goals were not completely fixed and changed accordingly to the research carried out and promising side results which ultimately led to other research routes.

1.3 Synopsis of the Dissertation

Chapter 2 and Chapter 3 comprise a brief overview of organometal halide perovskites and transition metal dichalcogenides respectively, their crystal structure, synthesis, basic electronic and optical properties and their recognized applications. In Chapter 4 I briefly present the most commonly used experimental methods which led to the results presented in the subsequent chapters. In Chapter 5 I introduce the work on the novel synthesis of methylammonium lead iodide (MAPbI_3) perovskite submicron particles and present their application in a simple photoconductor, revealing the dominant charge carrier responsible for the increased photoconductance. In Chapter 6 I present the work on the self-assembled monolayer of siloxane functionalized fullerene molecules acting as an ultrathin electron transporting layer in perovskite solar cells. Chapter 7 comprises a work which combines both main subjects of this thesis, transition metal dichalcogenides and organolead halide perovskites in a novel solar cell structure by using nanoscale WS_2 layers as a hole transporting layer. Chapter 8 comprises of a published paper on gold-decorated MoS_2 and their self-driven incorporation in elastomers driven through gold-polymer thiol-based interactions.

Chapter 2

Organometal Halide Perovskites

Hybrid organic/inorganic perovskites or alternatively organometal halide perovskites are a specific type of chemical compounds marked by the sudden discovery of their light harvesting properties. The discovery and research led this novel research and technological field of perovskite solar cells to become the fastest growing photovoltaic technology up to this date, while having an immense influence on the research orientation of many scientific centers around the world. Today, the performance of PSCs surpasses or is on par with other, much more mature thin film photovoltaic technologies, such as CdTe, CIGS or amorphous Si, making PSCs a promising choice for the future large-scale production and application as a renewable source of energy.

The light harvesting layer in PSCs is based on hybrid organic/inorganic metal halide compounds with a perovskite crystal structure. These compounds have been known for several decades [1], [2], however their light harvesting properties were revealed for the first time in 2009, when their application was realized as a novel sensitizer in Dye-sensitized solar cells (DSSCs), replacing conventional dye molecules [3]. Although the solar cell with organometal halide perovskite as a sensitizer initially worked sufficiently well, incorporated perovskite nanoparticles turned out to be unstable and rapidly degraded in the liquid-state electrolyte used in a device. A few years later (2012) the first applications of OMHPs appeared in a completely solid state solar cell structure [4], [5]. In a very short time frame of only 5 years lab-scale power conversion efficiencies (PCEs) rose to more than 20% [6]-[8], and are continuously increasing, albeit with a slower trend [9]. The advantage of PSCs in comparison to other established technologies is in the abundance of the materials used [10], apart from the silicon-based solar cells where copious SiO_2 is exploited as the starting material, and the simplicity of the manufacture based on solution processing, very similar to the production of organic solar cells. But most importantly, the origin of OMHPs' impressive energy conversion performance and the processing simplicity lies in the perovskite structure and its optical and electronic properties. Due to these properties, OMHPs found their application in other optoelectronic and electronic devices, as an example in highly efficient light-emitting diodes with emitted photons covering from ultraviolet to near infrared spectral region [11], [12], in optical photodetectors [13], as a lasing material with high lasing quantum yields [14], [15], as a semiconducting channel in field effect transistors [16]-[19], and in water splitting applications [20], [21].

2.1 Crystal Structure

OMHPs form a perovskite crystal structure with a general chemical formula ABX_3 , where A denotes a large cation (usually an organic cation, e.g. methylammonium (MA): CH_3NH_3^+ or formamidinium (FA): $\text{HC}(\text{NH}_2)_2^+$), B is typically occupied by a metal,

doubly charged cation (e.g. Pb^{2+} , Sn^{2+} or Ge^{2+}) and X denotes a halide anion (Cl^- , I^- , Br^-). A cubic perovskite structure unit cell is presented in Figure 2.1a. If we expand the structure beyond the unit cell, we can visualize the perovskite crystal as halide anion octahedra encasing the heavy metal cation centered in the corners of a cube, altogether encircling the organic cation in the center of the unit cell, as presented in Figure 2.1c.

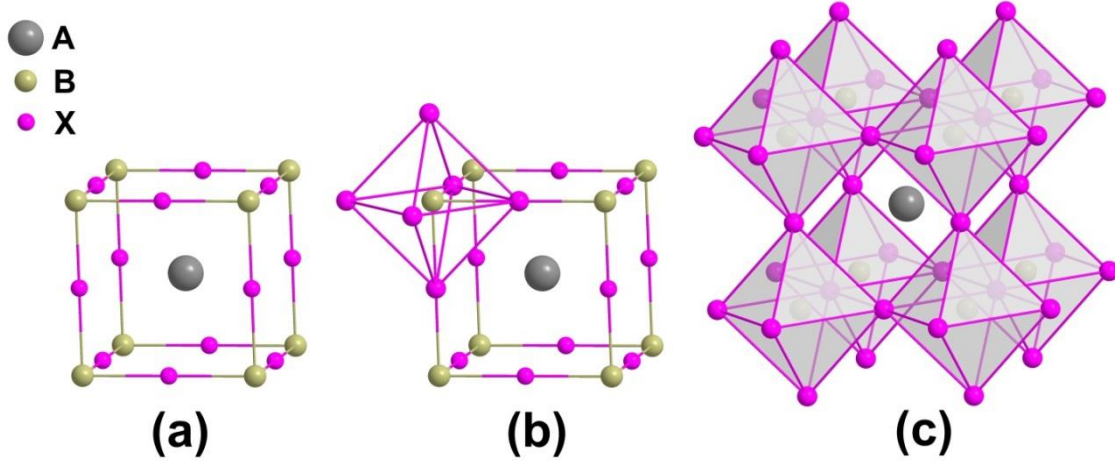


Figure 2.1: ABX_3 perovskite unit cell. a) The unit cell of a perovskite crystal structure. b) Expanded unit cell marking the halide octahedron with a metal cation in its center. c) Intuitive representation of perovskite structure with halide octahedra positioned in the corners of the cubic structure with a large cation in the central compartment amid the octahedra.

The stability and high-symmetry of a perovskite structure are governed by the size of ions comprising the unit cell, as described by V. M. Goldschmidt in 1926 with the geometric Goldschmidt's tolerance factor t :

$$t = \frac{r_A + r_X}{\sqrt{2}(r_B + r_X)}, \quad (2.1)$$

where r_A , r_B and r_X denote A, B and X ionic radii respectively [22]. Derived formula for estimating the tolerance factor takes into account the sizes of all the ions and accordingly predicts the distortion of the perovskite crystal structure. If $t < 0.8$ the crystal takes the shape of an orthorhombic non-perovskite structure, if $0.8 < t < 1$ the ion arrangement forms a stable, predominantly cubic perovskite structure and if $t > 1$ the crystal forms a non-perovskite structure with a face sharing octahedra or a 2D perovskite structure, as in the case of longer organic molecules residing at the A site [23], [24]. The use of the derived tolerance factor is in practice more a rule of thumb, an estimation on which compositions can be stabilized in a perovskite structure and which will form some other configuration. Due to the complexity of the determination of certain ionic radii, especially for ionic molecules, the tolerance factor in specific cases does not provide sufficient prediction and corrections need to be taken into account to successfully predict the stability of the structure [25]. Due to the large halide ionic size, particularly of iodine (I^-), OMHPs are limited in the choice of metal ions where only large doubly charged metal ions satisfy to this restriction [26]. Consequently, in order to obtain a stable cubic perovskite structure, the A site needs to be occupied by a large cation as well, either by an aforementioned molecular cation or by the Cs^+ as the only elemental cation large enough to occupy this site. The perovskite structure is not rigid, it exhibits dynamic

distortions and different structural phases which make these perovskites rich in properties. Methylammonium lead iodide (MAPbI_3), the prototypical example of OMHPs, incorporates large organic methylammonium cations, whose size, shape and charge distribution affect the tilting between the corner sharing octahedra (deviation of the B-X-B angle from 180°) and consequently the band structure [27]. Recently, Lee *et al.* studied the effect of hydrogen bonding between the organic cation and the halide anion and came to the conclusion that this interaction might be even more important for the octahedra tilting away from the ideal structure [28]. A direct consequence of the octahedra tilting are the phase transitions appearing in OMHPs, specifically in MAPbI_3 there is an orthorhombic to tetragonal transition at the temperature of 162 K and from tetragonal to cubic phase at 327 K [29]-[32]. As the tetragonal to cubic phase transitions occurs at operative temperatures typical for solar cells, it is important to know that the phase transition, the associated change in the crystal structure and energy bandgap temperature dependence within this temperature range only marginally affect the solar cell performance [33], [34]. If a specific perovskite composition does not form a stable perovskite structure at solar cell operative temperatures, stabilization of the perovskite structure can be achieved by mixing cations varying in size, effectively tuning the tolerance factor, as in the case of $\text{Cs}_x\text{FA}_y\text{PbI}_3$ perovskite structure where Cs and FA cations are mixed in different ratios [35].

2.2 Electronic and Optical Properties of OMHPs

The successful application in various optoelectronic devices is enabled by the intriguing electronic and optical properties of OMHPs. They are direct band gap semiconductors [36] and thus exhibit a steep absorption edge onset with a large optical absorption coefficient ($\sim 10^5 \text{ cm}^{-1}$) [37], achieving practically complete absorption within the absorbing spectral region in a few hundreds of nanometers thick film. The size of the bandgap in perovskite films can be tuned by the chemical composition. For example in the most typical perovskite structure MAPbI_3 with a band gap of 1.6 eV one can either completely exchange iodine with bromine, creating a 2.2 eV bandgap MAPbBr_3 or make an arbitrary intermixed composition of $\text{MAPbI}_{3-x}\text{Br}_x$ with intermediate bandgap values [38]. Analogously, bromine can be intermixed or completely substituted with chlorine, obtaining MAPbCl_3 with 3.2 eV bandgap [39]. Other strategies for tuning the bandgap include partial or complete replacement of lead (Pb) with tin (Sn) [36], [40]-[42] or germanium (Ge) [43], [44] or introduction of other organic and inorganic A-site cations, such as cesium and formamidinium [35].

Detailed characterization of OMHPs' electronic properties revealed that they are ambipolar semiconductors [45], [46], with electron and hole mobilities on the order of $10 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in polycrystalline films and exceeding $100 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ in a single crystal, depending on the chemical composition and the quality of the crystal structure as well [47], [48]. Upon the photoexcitation, electron-hole pairs are formed with small binding energies of several meV [49]-[51]. The measurements suggest that thermal energy at room temperature is large enough to dissociate most of these excitons, resulting in mostly free charges residing in the light harvesting layer. Photoexcited free charges have long life times and consequently long diffusion lengths up to several micrometers before they recombine, allowing efficient charge extraction at the interfaces between a thin perovskite and adjacent specific charge extracting layers [47], [48], [52]-[54].

2.3 Organometal Halide Perovskites Processing and Synthesis

Due to perovskite's ionic nature, perovskite precursor constituents, such as lead halide compounds (PbI_2 , PbBr_2 or PbCl_2) and organic salts (methylammonium iodide (MAI) or formamidinium iodide (FAI)), can be readily dissolved in polar aprotic solvents (e.g. *N,N*-Dimethylformamide (DMF), Dimethyl sulfoxide (DMSO), *N*-methylpyrrolidone (NMP) or similar) and further processed by either spin coating, or other large-scale deposition technique. The processing starts with the choice of the deposition technique; they can be either fully solution-processed, the processing can be completely based on a thin film evaporation [55] or it is a combination of both methods [56]. Focusing on a complete solution processing, to prepare a lead halide perovskite film a lead halide salt needs to be intermixed with an organic salt and subsequently thermally treated (annealed) to induce the perovskite crystal formation and grain growth. This type of perovskite thin film processing can be roughly divided into techniques distinguished by the number of steps used in the deposition, namely 1-step spin coating [4], 2-step spin coating [57], [58] or a sequential deposition [59], [60]. In the first case both constituents (lead halide and the organic salt) are dissolved in a polar aprotic solvent in the desired stoichiometry and spin coated on a substrate. During the film drying and annealing perovskite grains of the size of several hundreds of nm are formed creating a continuous film over the substrate as sketched in Figure 2.2.

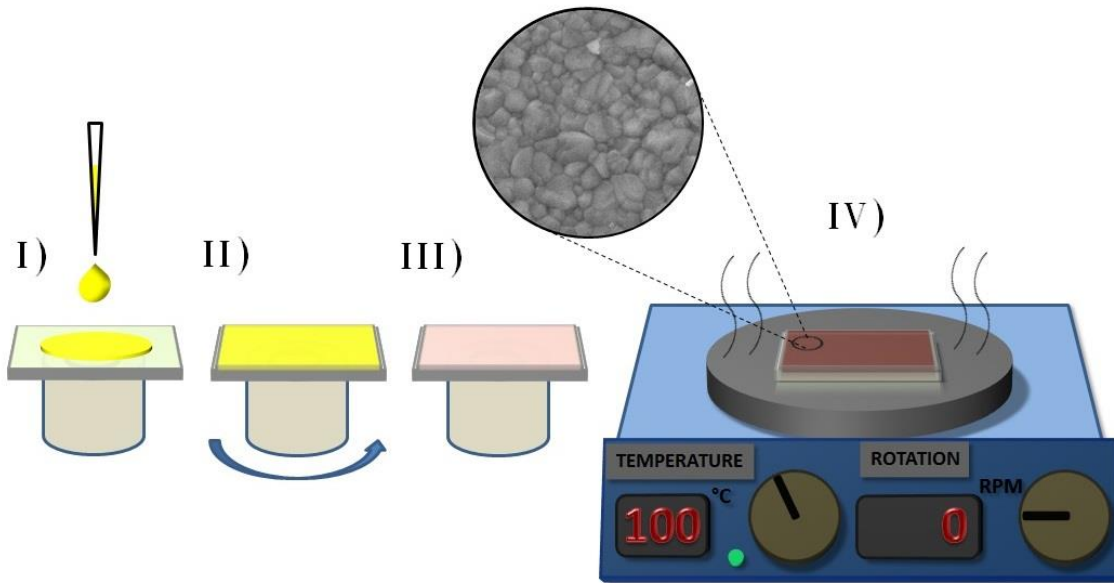


Figure 2.2: Steps involved in a perovskite spin coating procedure. A scheme of typical perovskite spin coating steps, denoting perovskite precursor drop casting onto the substrate (I), high speed rotation of the substrate (II) during which the film loses most of the solvent inside, yielding faint color (III) and finally thermal treatment of the film, during which the perovskite starts to crystallize along the grain growth (IV). The magnified part presents a scanning electron microscope (SEM) image of a typical grainy perovskite thin film structure, with grains of a few hundreds of nanometers in size.

For a 2-step spin coating the inorganic (lead halide) and organic part are dissolved in a polar aprotic solvent and a polar protic solvent (e.g. 2-Propanol) respectively and spin

coated in the same order. The polar protic solvent for the organic part is used as it does not dissolve the lead halide film deposited priorly. In a sequential deposition the lead halide film reacts with the organic part either by dipping it inside an organic salt solution or exposing it to vapors of organic salt [61], [62]. To complete the formation of perovskite film the deposited layer is typically treated on a hotplate at temperatures from 90-150°C for up to an hour. It is worth to note that there are other precursor preparation techniques employing more environmentally friendly low-boiling point solvents, while retaining high efficiency and are all the more suitable for large-scale deposition [63]. Throughout the evolution of perovskite solar cells many parameters governing perovskite crystal growth, affecting morphological, optical and electronic properties and consequently device performance have been investigated. To name only a few, substrate properties [64] and its interaction with the precursor solution reflected in the wettability of the substrate [65], solution concentration [60], stoichiometry and temperature of precursor solution [66], precursor additives retarding the crystallization [8], [67], anti-solvent processing for rapid crystallization [68]-[71], annealing time [72], temperature and atmosphere during the growth [73]-[75], additional post-annealing treatments [76]-[79] and more not mentioned. High quality perovskite films are compact and homogeneous, leaving no pinholes inside (Figure 2.3a), with large single grains protruding from the top to the bottom of the perovskite film.

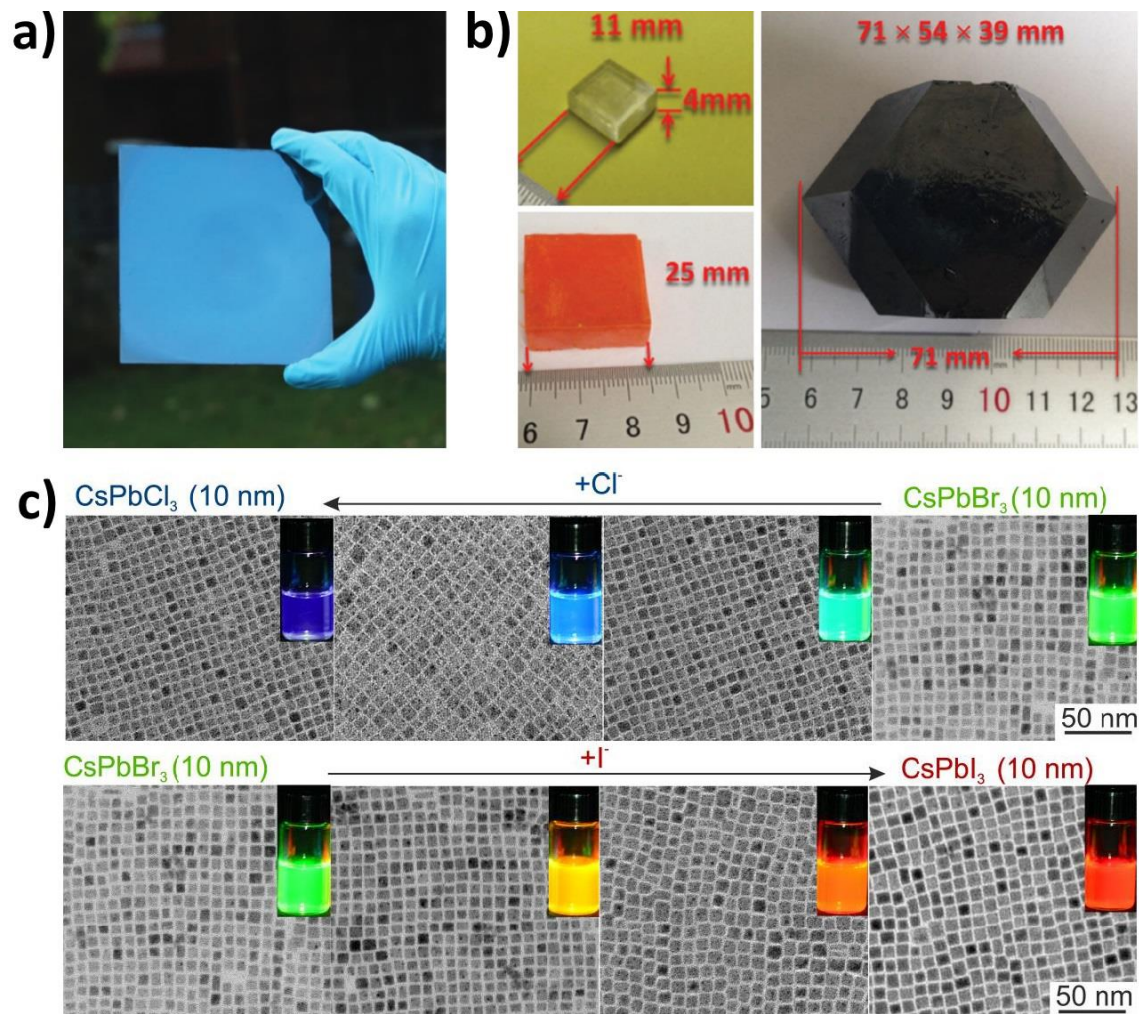


Figure 2.3: Various forms of organolead halide perovskites. a) Highly specular and pinhole free spin-coated thin film of a MAPbI_3 perovskite, processed with

methylamine-saturated acetonitrile. Source: Adapted from [63]. b) Large single crystals of MAPbCl_3 (transparent), MAPbBr_3 (orange) and MAPbI_3 (black) perovskite. Source: Adapted from [80]. c) Various highly emissive perovskite nanocrystals produced by halide ion exchange, fine tuning the composition and emissive properties. Source: Adapted from [81].

For special applications and for basic characterization of material properties, larger single crystals are more suitable due to a more controlled growth, decreasing the amount of structural defects and impurities. In addition, larger bulk crystals have less surface where deviations from intrinsic stoichiometry are present and thus these effects are significantly reduced in this case. Therefore, a lot of research has been devoted to the growth of various compound crystalline perovskites from saturated precursor solutions, yielding single crystals with typical dimensions of up to a few centimeters (Figure 2.3b) [48], [54], [82]-[85]. Instead of processing directly from perovskite precursors, solar cells and other optoelectronic devices can also be prepared from colloidal perovskite suspensions, consisting of nanoparticles with diverse optical properties (Figure 2.3c) [81], [86]-[88].

2.4 Perovskite Solar Cells

2.4.1 Structures and operating mechanisms

Perovskite solar cells can be built in two basic configurations, namely standard and inverted device structure. Essential layers that constitute both are two electrodes (cathode and anode) out of which at least one is highly optically transparent, electron and hole transporting layers (ETL and HTL respectively) and the perovskite layer as the light harvester sandwiched in between the charge selective layers. Standard and inverted structures differ in the type of charge carriers extracted at the side where light is incident on the solar cell. In a standard device structure electrons are extracted at the illuminated side while in the inverted configuration holes are extracted as presented in Figure 2.4.

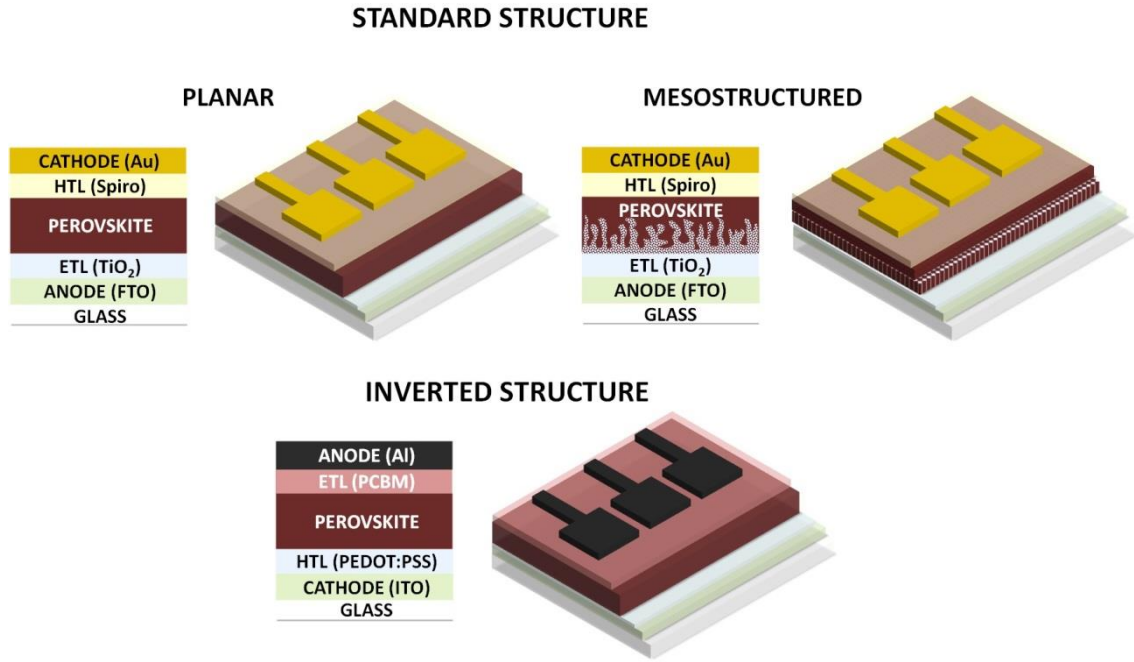


Figure 2.4: Presentation of typical perovskite solar cell structures. Schemes of typical perovskite solar cell structures, standard and inverted discriminated by the type of charge carriers extracted at the illuminated side (glass side). In the cross-section scheme materials conventionally used for specific function are noted in parentheses.

Since all experiments involving solar cells presented in this thesis use the standard device structure, solely this configuration will be discussed in detail. The standard device structure can be further divided into two sub-configurations, planar and mesoporous. The former consists of planar layers with specific functions stacked on top of each other [55], while the latter incorporates a mesoporous, highly porous layer of a wide bandgap metal oxide acting as an electron transporting layer (ETL) [59]. The main function of the mesoporous layer is to increase the interface area between the electron transporting layer and the light harvesting perovskite layer increasing the efficiency of the electron extraction. Important for further discussion, typical components of the state-of-the-art standard perovskite solar cells are fluorine-doped tin oxide (FTO) as a transparent anode, titanium dioxide (TiO₂) or similar wide bandgap metal oxide as an electron extracting layer (planar or mesoporous device), organolead halide perovskite as the light harvesting layer, 2,2',7,7'-Tetrakis-(N,N-di-4-methoxyphenylamino)-9,9'-spirobifluorene (Spiro) as a hole transport layer with a gold or silver cathode on top.

The operating mechanism of the perovskite solar cell is sketched in Figure 2.5. Most of the light incident from the transparent electrode side passes through the electron transporting layer illuminating the perovskite layer. Photons with energies equal or larger than the bandgap energy photoexcite the electrons from the valence to the conduction band, forming weakly bound excitons. Due to their small binding energy most of them quickly dissociate into free charges. In short-circuit conditions, when both electrodes are connected without any load (i.e. no external voltage is applied), the built-in electric field, whose strength is defined by the work function differences of electron and hole extraction layer, causes both carriers to drift towards the respective selective layers. During their path charges can radiatively or non-radiatively recombine. As it has been stated earlier both types of charge carriers have relatively high mobilities, which in combination with a low density of shallow and deep trap states [48] reduces the occurrence of charge

recombination and thus high efficiency of charge extraction can be achieved before any of these recombination pathways become important.

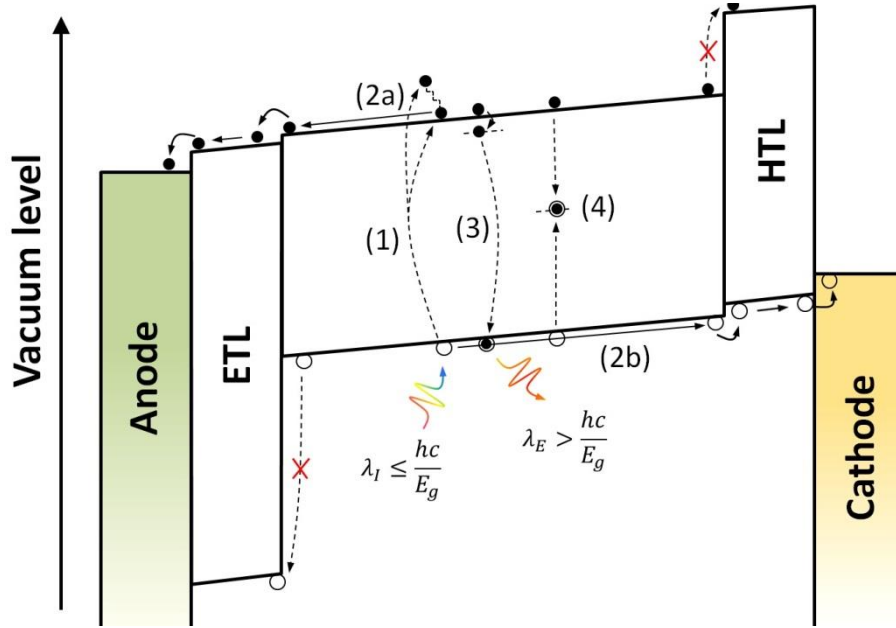


Figure 2.5: Main opto-electronic processes in perovskite solar cells. Simplified scheme of electronic processes and the band alignment in perovskite solar cells. The most common charge involving processes in perovskite solar cells in short-circuit conditions are: 1) Photoexcitation of ground state electrons into the conduction band by photons with the energy equal or larger than the perovskite bandgap (E_g), yielding predominantly free charges. Photons with a larger energy than the bandgap create electrons which rapidly thermalize to the conduction band minimum. 2a) and 2b) Drift of electrons and holes towards the respective charge extracting (and the opposite charge blocking) layers; 3) Radiative recombination of an electron and a hole, followed by an emission of a photon with an energy lower than the E_g ; 4) Non-radiative recombination of electron and hole in deep lying trap states. h -Planck constant, c -speed of light.

Charge selectivity, namely electron extraction (and hole blocking) on one side and hole extraction (and electron blocking) on the other is achieved by an appropriate band alignment between the perovskite layer and adjacent charge selective layers. Electron extraction through the perovskite-ETL interface will follow through the conduction band offset of the respective layers, while the hole extraction at the perovskite-HTL will happen through the valence band offset. Finally, extracted charges at the interface of charge selective layers and the perovskite layer are transported to the respective electrode through contacts with preferentially no potential barriers (Ohmic contacts). Properties of the alignment, i.e. band bending profiles at the interfaces are determined by the type of doping of the layers, consequently the Fermi level position in each charge transporting layers and the quasi Fermi level splitting in the perovskite layer. The parameters affecting the band alignment of perovskite layers with adjacent ones are the type of the perovskite semiconducting nature, i.e. existence of any doping and of which type and associated Fermi level position in thermal equilibrium. These parameters are strongly dependent on the chemical composition and the processing of the perovskite layer. Especially the latter can induce unintentional doping through charged impurities or other structural phases in the bulk or the surface layer of the perovskite, which can

significantly change the properties of the interface's charge extraction and retention. Detailed investigation of local current generation inside a $\text{MAPbI}_{3-x}\text{Cl}_x$ perovskite layer embedded in a standard device structure showed that there are three specific regions, a central intrinsic part with low carrier density and n and p-type regions at the sides associated with efficient charge extraction at respective interfaces with electron and hole transporting layers [89]. On the other hand, Guerrero *et al.* showed that a $\text{MAPbI}_{3-x}\text{Cl}_x$ perovskite layer is p-type doped and forms a p-n junction with the TiO_2 electron transporting layer in the exact same device configuration [90]. From these studies it is suggestive that the band alignment and the junction formed between the perovskite layer and adjacent charge extracting layers can be complex and interpreted in various ways, depending on the electronic properties determined largely by the perovskite processing details.

2.4.2 Solar cell characterization

Solar cells are characterized by exposing them to the light source with the illumination spectrum closely resembling the solar spectrum. The intensity of the illumination is defined with an AM standard. AM denotes the »air mass« and the number that follows presents the light intensity coming from the lamp in comparison to the intensity of solar light attenuated by the atmosphere before illuminating the Earth's surface. For example, an AM1 standard would denote a solar illumination taking the shortest path to the surface of the Earth (1 air mass), which happens at the equator when the sun is at its zenith. AM1.5 would denote a longer light path, attenuated by an effective thickness of 1.5 atmosphere which happens at the Earth's latitude of 48.2° (approx. the latitudes of the central Europe) at the Sun's highest point. The total irradiance of the solar simulator lamp for the AM1.5 standard is 1000 Wm^{-2} (or 100 mWcm^{-2}) and it resembles the spectral irradiance of the Sun on Earth's surface as presented in Figure 2.6a. Together with lenses and filters the light output of a solar simulator closely resembles the spectrum of the Sun.

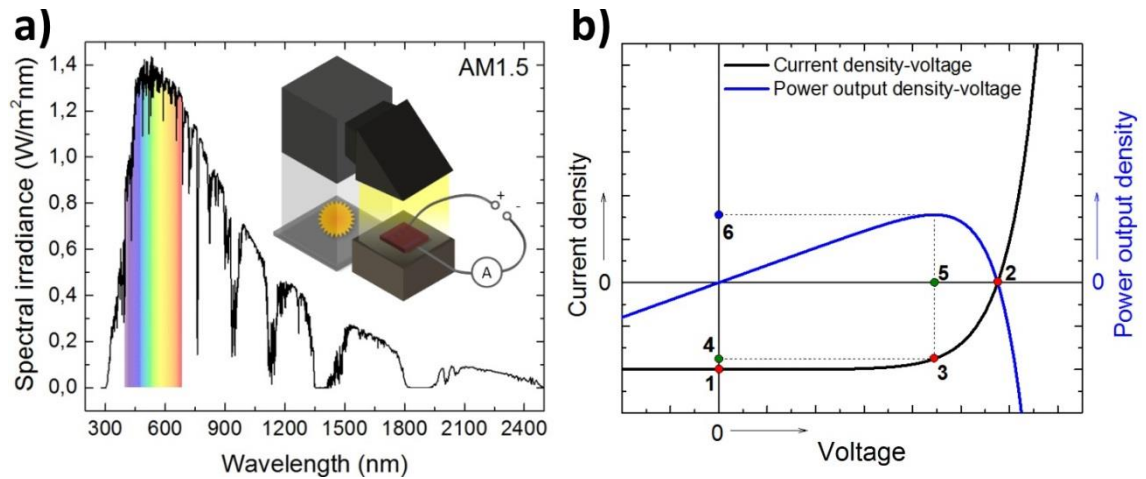


Figure 2.6: Characterization of solar cells. a) Spectral irradiance of the Sun with the intensity of 1000 W/m^2 corresponding to the AM1.5 standard. Inset: A simple schematic of a solar cell characterization setup, with a solar simulator employing a Xenon lamp as the light source, simulating the spectrum and intensity of the Sun. b) Typical current density-voltage (black) and power output density-voltage (blue) characteristic of a solar cell with enumerated characteristic points: 1-short-circuit current density (J_{SC}), 2-open

circuit voltage (V_{OC}), 3-maximum power point (MPP), which also marks the fill factor point, 4-current density at the maximum power point (J_{MPP}), 5-voltage at the maximum power point (V_{MPP}) and 6-maximum power output density (P_{MPP}).

Solar cells are characterized by applying a slowly varying bias over the electrodes, measuring the current through the circuit, obtaining current-voltage characteristic ($I - V$), or more representative current density-voltage characteristic ($J - V$), which already takes into account the size of the illuminated area. Solar cell electrical characterization curves exhibit a few important points, as enumerated in the representative $J - V$ and $P - V$ curves in Figure 2.6. The short circuit current density (J_{SC}) is the current density obtained when there is no bias across the electrodes and the electrodes are short-circuited. In these conditions charges exposed to a built-in electric field drift towards the respective charge selective layers and electrodes, running around the circuit. When the voltage potential of the cathode is increased, the current density decreases and is nulled at the forward bias called open circuit voltage (V_{OC}). At this point the voltage potential applied across the electrodes equalizes with the built-in field, forming a flat band structure, where the charge generation equals the recombination rate and thus no net current flows through the circuit. Increasing the voltage beyond this point promotes the photocurrent to run in the other direction where the power is drawn from the outer source. The power conversion efficiency (PCE) of the solar cell is calculated as:

$$PCE = \frac{P_{MPP}}{P_0} = \frac{V_{MPP} \times J_{MPP}}{P_0} = \frac{V_{OC} \times J_{SC} \times FF}{P_0}, \quad (2.2)$$

where P_{MPP} and P_0 denote the maximum power output density (i.e. power output per unit of surface) of the cell and the surface illumination power density (100 mWcm⁻² for AM1.5 standard) respectively. V_{MPP} and J_{MPP} denote the voltage and current density at the maximum power point respectively, while the fill factor (FF) is the ratio between the measured power output and the measured product of open circuit voltage and short-circuit current density:

$$FF = \frac{V_{MPP} \times J_{MPP}}{V_{OC} \times J_{SC}}. \quad (2.3)$$

The final performance of the solar cell depends on the parameters J_{SC} , V_{OC} and FF . How much of the photocurrent a solar harvesting layer can provide under the illumination depends primarily on the bandgap of the photoactive layer. Assuming that each photon with an energy larger than the bandgap photoexcites only one electron, then the maximum theoretically achievable J_{SC} is:

$$J_{SC} = q \int_{Eg}^{\infty} \Phi_{AM1.5}(E) dE, \quad (2.4)$$

where $\Phi_{AM1.5}(\lambda)$ denotes the spectral irradiance and q the elementary charge. In a real solar cell photon to electron conversion is not unity, thus the J_{SC} is:

$$J_{SC} = q \int_{Eg}^{\infty} EQE(E) \Phi_{AM1.5}(E) dE, \quad (2.5)$$

where $EQE(E)$ denotes the external quantum efficiency (i.e. incident photon to electron conversion efficiency). To maximize $EQE(E)$ the solar absorbing layer thickness needs to be optimized in order to absorb as many photons as possible while still allowing efficient transport of photoexcited carriers to the respective charge extracting layers and further to the electrodes.

V_{OC} , besides being dependent on the properties not directly connected to the electronic properties of the absorber material, for example on the solar cell structure and accompanied charge extraction layers, thickness of the absorber film and the nature of the bandgap (direct or indirect), shows a strong connection with the purity of the material (amorphous, polycrystalline or monocrystalline structure). More specifically it is highly dependent on the atomic structure and the disorder that the material exhibits. The origin and limitations of the open circuit voltage (V_{OC}) can be explained theoretically and experimentally. First, theoretically the V_{OC} is limited by the potential energy of the photoexcited electrons within the absorber:

$$V_{OC_tmax} = \frac{E_g}{q}, \quad (2.6)$$

where V_{OC_tmax} denotes the maximum theoretical V_{OC} , E_g is the absorber bandgap and q is the elementary charge. Furthermore, the V_{OC} in a real device is upward limited by the work function difference between the electron (ϕ_n) and hole (ϕ_p) extraction layers adjacent to the absorber, since this defines the charge potential difference of already extracted charges:

$$V_{OC_dmax} = \frac{E_g - (\phi_p - \phi_n)}{q}. \quad (2.7)$$

In addition, V_{OC} depends on the nature of the semiconductor bandgap (direct or indirect) as well, but most importantly, what ultimately defines the V_{OC} achieved in a device is the atomic structure and the disorder that the absorber exhibits. De Wolf *et al.* carried out the absorption measurements of MAPbI₃ thin film by a Fourier-transform photocurrent spectroscopy (FTPS), which allows very sensitive absorption measurement within a 6 orders of magnitude range and can probe the edge states and deep gap states [37]. The results showed very sharp absorption onset with practically no presence of deep states (Figure 2.7a) and a very low Urbach energy of 15 meV. The extent of the Urbach energy typically points to the structural disorder which leads to the energetical disorder close to the band edge, i.e. the larger the Urbach energy, the more disordered the structure [91], [92]. Deviation of the highest V_{OC} 's from the maximum theoretically achievable V_{OC_tmax} realized by various photovoltaic technologies depending on the measured Urbach energy is presented in Figure 2.7b [37].

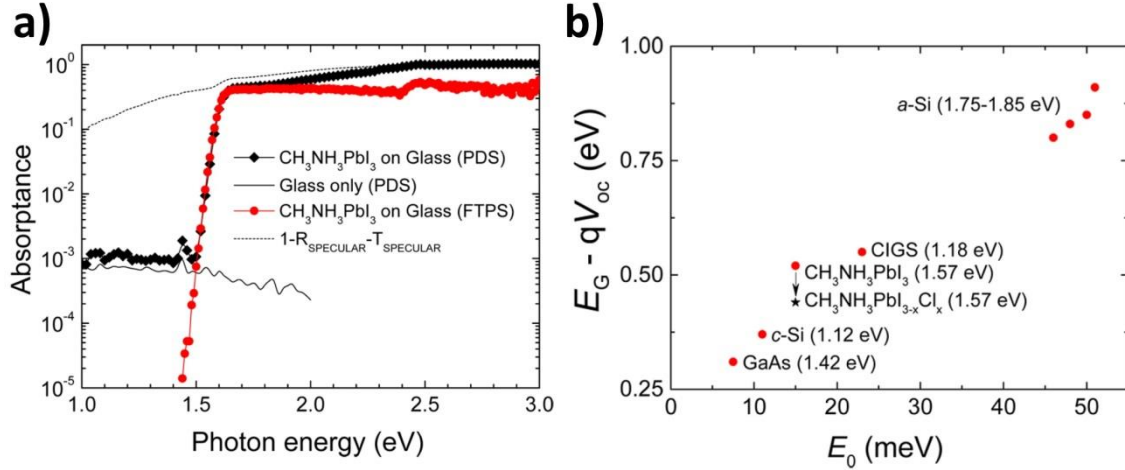


Figure 2.7: High sensitivity optical absorption of OMHPs. a) Absorption spectra of MAPbI_3 thin film deposited on glass substrates obtained by the sensitive absorption techniques PDS (black symbols) and FTPS (red symbols), probing edge and deep states. Source: Reproduced from [37]. b) Dependence of the difference of the best V_{oc} reached in a device from the maximum theoretically achievable V_{oc_tmax} on the measured Urbach energy V_0 for several photovoltaic technologies. Source: Reproduced from [37]. PDS-Photothermal deflection spectroscopy; FTPS-Fourier-transform photocurrent spectroscopy.

Yang *et al.* provided a macroscopic device model simulation to replicate $J - V$ curves of a functioning planar perovskite solar cell and tested which factors influence the V_{oc} [93]. Authors demonstrated that the exciton dissociation rate and deep states within the practical density only marginally contribute to the lowering of the V_{oc} . On the contrary, by varying the bimolecular recombination rate in their model they demonstrated that it possesses the strongest influence on the V_{oc} of the device. Apart from focusing on the V_{oc} alone, the simulations also revealed that J_{sc} and FF are significantly affected by the exciton dissociation rate and to some extent by the radiative and non-radiative charge recombination rates. These effects on solar cell parameters are considered only when the prerequisite conditions for high performance solar cells are met. For example, planar solar cells are sensitive to any significant deviation from planarity. Each layer needs to have a well-defined, uniform thickness to prevent interconnects between layers which are not adjacent to each other. For example the appearance of pinholes in the light harvesting layer typically causes a direct contact between the charge selective layers or even electrodes, opening a shunting current pathway, reducing the solar cells parameters and consequently screening the real properties of the light absorbing layer and its potential as an energy converter.

2.4.3 Hysteretic response in J-V characteristics and ion motion

The evolution of perovskite solar cell research and solar cell electronic characterization was marked by the appearance of an artifact of $J - V$ characterization, the hysteretic response during their dynamic testing [94]. Typically the characterization of solar cells is carried out by sweeping the bias across the electrodes in a backward and forward bias at specific voltage sweep speed. The measurement history – for example prebiasing and light soaking before the measurement, voltage sweep speed – affects the measured $J - V$ curve, as presented in Figure 2.8. This can reflect in substantial differences between the

backward and the forward scan which raises the question which is the real or more objective measure of the performance and more importantly, what causes this effect.

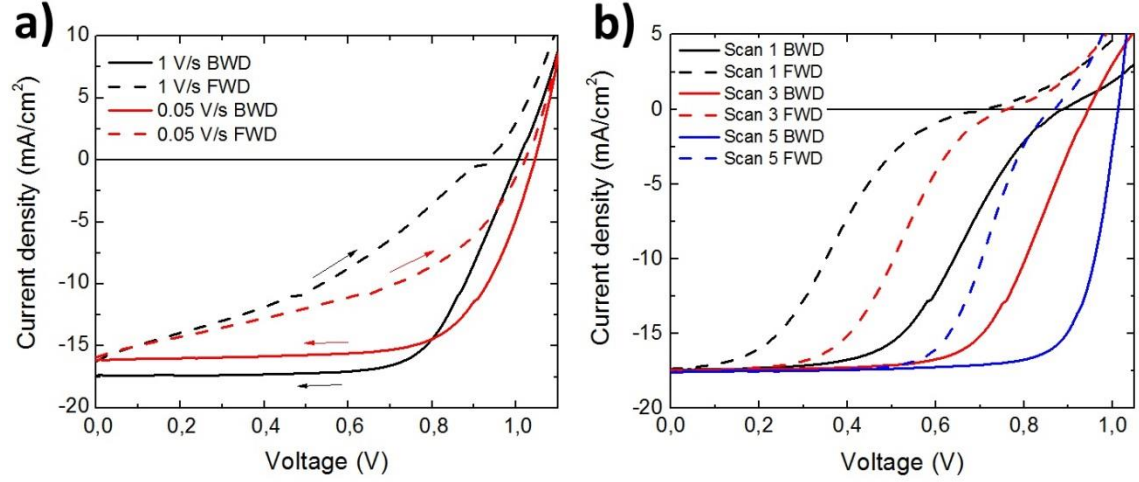


Figure 2.8: Hysteretic response in perovskite solar cells. a) $J-V$ characteristic of a perovskite solar cell showing scan speed dependence and hysteretic behavior seen as the difference between backward (1.2-0 V; solid line) and forward scan (0-1.2 V; dashed line). b) $J-V$ characteristic of a perovskite solar cell showing hysteretic behavior and its dependence on the number of consecutive measurements. Each measurement is done by first applying a 5 s prebias at 1.2 V, followed by a voltage scan in backward (solid line) and forward (dashed line) scan direction with a scan speed of 1 V/s . BWD-backward scan; FWD-forward scan.

Initially researchers proposed a few mechanisms happening in the bulk or at the interface of the light harvesting layer that could be responsible for the observed hysteresis, particularly ferroelectric effect [95], charge trapping states [96], [97] and ion migration. The first possible cause, the ferroelectricity, was eventually overthrown, since the hysteresis appears at a time scale of seconds up to tens of seconds, which is significantly slower than the occurrence of the ferroelectric effects in the perovskite layer. The major contributor out of those turned out to be the ion migration within the perovskite layer, however it is not exclusive [98].

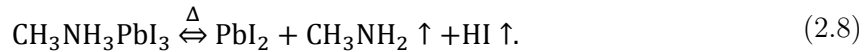
The OMHP crystalline structure is held together by predominantly ionic bonds. If the material is exposed to an electric field through the applied bias, ionic conduction through defect species is observed. There are three possible ions that can migrate, halide (I^- , Cl^- , Br^-), organic (MA^+) and the metal ion (Pb^{2+}). The general conclusion from the literature, obtained by calculating the activation energy (E_A) for all the possible migrating ions, is that Pb^{2+} , with its high activation energy is much less likely to migrate than more mobile MA^+ or even I^- for which the calculations showed the lowest activation energy [99]-[101]. Experimentally it's been proven that both MA^+ and I^- move under different external conditions, as an example in applied electric field [102], [103] and under light soaking which induces self-poling effect within the perovskite layer [104]. The expected channels for ion motion are through Schottky defects (ionic vacancies) and surface and grain boundaries. The appearance of point defects in perovskite polycrystalline films can be caused by the quick formation of the crystalline perovskite during processing, non-stoichiometric outcome of the crystal lattice [105] and intrinsic weak bonding in the crystal lattice which leads to low formation energy of vacancy related defects [106].

Within the solar cell under testing conditions migrating ions build up at the perovskite-charge extracting layer interface influencing the build-up of elementary charge compensating the opposite ionic charge. This can either have a beneficial [104], [107] or detrimental [108] effect on the device performance, depending on the device structure and perovskite composition. Whatever the final effect is, the electrical characterization needs to be adapted in order to test the »true« performance of the solar cells. If the device exhibits $J - V$ hysteresis, the guidelines for accurate performance determination include various voltage sweep speeds (fast and slow) as well as a steady state performance measurement. In the steady state measurement, the solar cell is first characterized by various voltage sweep speeds followed by a determination of the voltage at the maximum power point for both scan directions. The photocurrent through the solar cell is subsequently measured at fixed applied voltage in the vicinity of the maximum power point and tracked over time. Either a dynamically programmed voltage adjustment script is used to slightly change the applied bias around the maximum power point, or a few chosen biases are used in separate measurements of the steady state performance. If the photocurrent is stable over time, the calculated power conversion efficiency is taken as a reliable value.

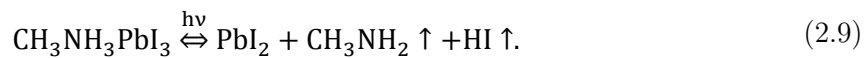
2.4.4 Stability of perovskite solar cells

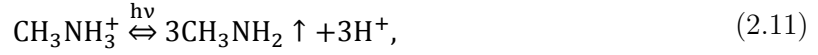
One of the important prerequisites for a novel photovoltaic technology to become suitable for large-scale manufacture and commercialization is to withstand standardized endurance tests, showing high resistance over thermal cycling and retaining undisturbed high performance over continuous light soaking at elevated temperatures and increased humidity. Since the beginning of the organometal halide perovskite era, however, solar cells with the perovskite as the light harvester exhibited pronounced problems with the stability, yet with the wider in-depth knowledge about the material, optimized processing and novel compound mixtures the stability improved significantly. In the following paragraphs I will briefly discuss the past and ongoing problems concerning the stability of the complete device incorporating organolead halide perovskites.

The source of stability issues can originate either from the perovskite layer or from other functional layers in a device. Perovskite layers incorporating organic cations are known to be especially susceptible to degradation mechanisms triggered by an increased temperature, intense illumination, presence of humidity and oxygen. Due to the very weak ionic interactions together with the »soft« perovskite structure prone to local changes, increased temperatures (85°C and above) and/or prolonged annealing times can induce a perovskite decomposition [109]-[111] which leads to the release of gaseous methylamine and hydrogen iodide following an endothermic reaction:



Analogous to the heat also light-induced degradation is promoted, specifically in the presence of TiO_2 acting as an oxidizer of I^- at the perovskite- TiO_2 interface described by the following reactions:





Here, the light-induced oxidation and reduction of iodine and methylamine respectively promote the release of hydrogen iodide. Without going into much detail, even a very small amount of water can trigger pathways towards degradation on the account of perovskite coordinating with water molecules through the methylammonium ion [112]. Beyond a certain point of exposure to humidity irreversible degradation proceeds with dissolution of methylammonium iodide followed by a phase segregation of PbI_2 and MAI [113]. In the recent 2 years, the stability of the perovskite layer was markedly increased by using a more rigid perovskite structure, incorporating less hygroscopic and mobile cations with increased decomposition temperature, for example Cs^+ and FA^+ [35], [114], as well as a mixture of halide anions for structural stabilization [115], [116].

Apart from the degradation of the perovskite layer under specific conditions and without encapsulation, other conventionally used layers structuring a perovskite solar cell suffer from over-time performance loss. The best performing hole transport layer Spiro, requires a Li-based dopant Li-TFSI (Bis(trifluoromethane)sulfonimide) and tBP (4-tert-Butylpyridine) as additives in order to increase its hole conducting properties [117]. Connected to these additives, Spiro exhibits a thermally-driven release of tBP at elevated temperatures (above 85°C) [118] and in addition slowly reacts with the perovskite layer through the interaction with iodine ion [119]. Furthermore, the typically used TiO_2 as an electron transport layer shows susceptibility to UV light-induced degradation additionally contributing to the number of stability issues of perovskite solar cells [120]. Last but not least, certain low-price metal electrodes can corrosively react with perovskite forming metal halides [121] or lose their ability of efficient charge conduction at the interface with a charge extracting layer due to metal oxidation (Ca and Al).

Chapter 3

Layered Materials – Transition Metal Dichalcogenides

Transition metal dichalcogenides are a family of diverse compound solids represented by a general chemical formula MX_2 , where M denotes a transition metal and X chalcogen atom. They belong to a larger group of 2D layered materials, for which specific growth is observed, i.e. individual structural units-monolayers, are stacked on top of each other forming a large bulk crystal with characteristic strong intra- (predominantly covalent) and weak interlayer (mostly of Van der Waals type) interactions. This characteristic growth allows one to isolate thinner fractions of the parent crystal, obtaining delaminated sheets with distinct mechanical, optical and electronic properties in relation to their bulk counterpart. TMDs gained significant scientific attention after the first isolation of a graphite monolayer-graphene [122], due to the versatility of chemical compositions and a variation of properties as a result of the chemical flexibility [123].

3.1 Crystal Structure of TMDs

A TMD monolayer consists of three close-packed atomic planes, two of chalcogen atoms surrounding the central transition metal plane (M-X-M). They appear in various distinct polytypes which describe first the relative position of adjacent atomic planes to each other and the stacking sequence of layers forming the complete crystal, named 1T, 2H and 3R. The number in the notation defines the number of layers appearing in the repeating structural unit of a bulk crystal, while the letter denotes the overall symmetry of the stacked layers, i.e. tetragonal (T), hexagonal (H) and rhombohedral (R). Molybdenum disulfide (MoS_2) and tungsten disulfide (WS_2), the main subjects of the studies presented in this thesis, naturally appear in the 2H polytype while the 1T polytype appears after their intercalation with monatomic metal ions and is known to be metastable. Side and top views of both polytype monolayers are presented in Figure 3.1. In the 2H polytype (or 1H for an isolated monolayer) sulfur atoms on each side of the transition metal plane are laterally aligned directly above each other while in the 1T one of the sulfur planes is shifted in relation to the other one. Monolayers of MoS_2 and WS_2 are about 6.5 Å thick and are highly flexible, withstanding high effective strains (25%) before they break [124].

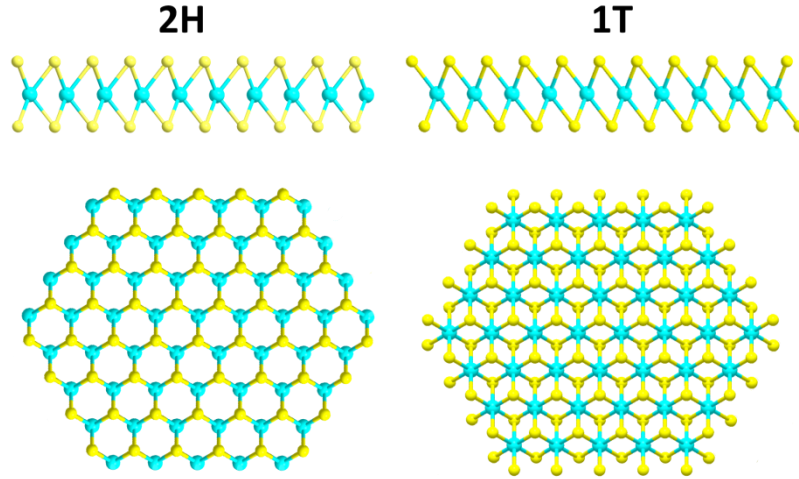


Figure 3.1: Atomic arrangement in 2H and 1T polytype. One of the side views and a top view of atomic arrangement in MoS_2 (or WS_2) monolayer in a 2H and 1T polytype. Cyan and yellow spheres represent transition metal (Mo or W) and sulfur atoms respectively.

3.2 Electronic and Optical Properties

Due to the abundance of elemental combinations TMDs express a wide variety of electronic properties, from semiconducting, semi-metallic to metallic with an appearance of specific phenomena like superconductivity and charge density wave in some of them [123]. Molybdenum- and tungsten-based TMDs show semiconducting nature with a typical indirect-to-direct band gap cross-over with transition from the bilayer to the monolayer form [125]-[127]. Together with the energy gap nature, the extent of the energy gap also depends on the thickness of the layer. When the thickness of the sample drops below 2 nm, which corresponds to a thickness of three MoS_2 (or WS_2) monolayers, this dependence starts to become more pronounced. While thinning down a few-layer sample the energy difference between the Γ and K point in the valence band (which present the coexisting indirect and direct gap respectively) of the Brillouin zone starts to decrease and reaches its minimum in a monolayer form, increasing the energy gap between the valence band maximum (VBM) and the conduction band minimum (CBM), as depicted in Figure 3.2a [125], [127]. These changes reflect in an observable increase of the energy gap of MoS_2 (WS_2) from the bulk value of 1.2 eV (1.3 eV) to the monolayer value of 1.9 eV (2.1 eV), accompanied by the blue shift of the lowest energy photoluminescence (PL) peak, (Figure 3.2b). Additionally, as a result of the indirect-to-direct band gap transition, the PL quantum yield is increased by several orders of magnitude from the bulk to a monolayer regime [125].

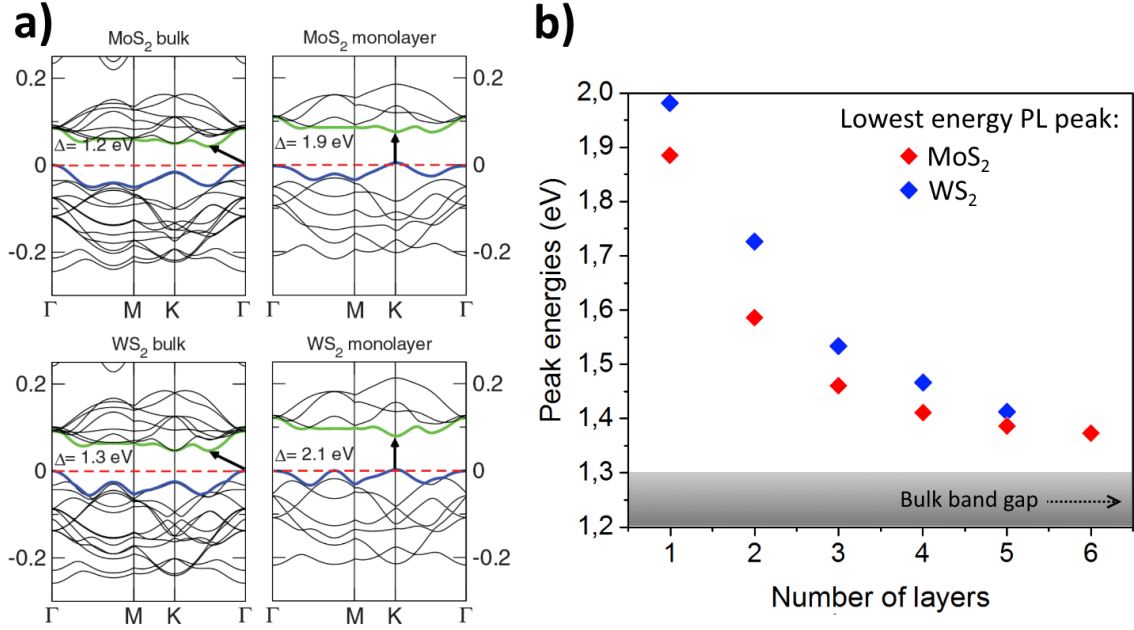


Figure 3.2: Electronic and optical properties of a bulk and monolayer MoS₂ and WS₂. a) Calculated band structure of MoS₂ and WS₂ monolayers and their bulk counterparts. Blue and green lines represent the valence band maximum (VBM) and the conduction band minimum (CBM) respectively. The arrows denote indirect or direct band gap for the bulk and monolayer respectively, while the dashed red line denotes the Fermi level. Adapted from [128]. b) Experimental data of the lowest energy photoluminescence peak dependence on the number of layers in MoS₂ and WS₂. Except from a monolayer all other PL peaks originate from an indirect bandgap transition. Data retrieved from [125] and [129].

When MoS₂/WS₂ layers are photoexcited they primarily form tightly bound excitons and other higher-order excitonic quasi-particles, for example trions (bound states of 2 electrons and 1 hole or 2 holes and 1 electron) and bi-excitons (bound states of two excitons) [130]-[132]. The binding energy of excitons depends on the number of layers, increasing with the reducing thickness reaching several hundreds of meV in a monolayer form [133], [134].

3.3 Synthesis

There are two complementary routes to obtain quasi-2D sheets of TMDs, either from a naturally or synthetically grown single crystal (top-down approach) or a direct growth from a combination of solid and gaseous precursors (bottom-up approach). The following subsections briefly describe the main techniques to obtain single or a few-layered sheets of TMDs, focusing mostly on MoS₂ and WS₂.

3.3.1 Exfoliation

Exfoliation, i.e. the act of separating thinner sheets from a larger piece of a crystal, became an important laboratory technique after the first isolation of graphene. It was carried out by a Scotch tape approach where thinner layers were delaminated from the parent crystal by pressing on and retracting off a piece of a sticky tape from the graphite

crystal and subsequently transferred to the substrate [135]. Similarly most of the pioneering works investigating various compounds with 2D structure used this technique to obtain single layers. This approach is suitable for the basic characterization of obtained nano-thin sheets, however, low yield and poor control over the thickness of the layers attached to the substrate limits its use in real, potentially large-scale applications. Thus other techniques were developed or adopted from the past research to increase the yield of exfoliation, such as mechanically induced exfoliation in liquids and chemical exfoliation based on the intercalation of guest species into the host material.

Layered inorganic materials have been exfoliated in liquids by an intense mechanical agitation either by a prolonged ultrasonication or high shear mixing of powders in appropriate solvents. With methods involving mechanical agitation strong local forces as a consequence of cavitation implosion produced by ultrasound traveling through the liquid medium or the turbulent flow of high-shear mixing promote delamination of particles into thinner sheets yielding stable colloidal suspensions readily produced in large quantities [136]. The stability of colloidal suspensions is provided by the incorporation of surfactant molecules into the suspension or by matching the solvent and material surface energy [137], [138]. These methods, however, tend to reduce the aspect ratio of the final nanosheets by the pronounced scission effect appearing during the processing and the thickness distribution of nanosheets can be relatively broad. In addition, intense agitation can lead to irreversible structural defects which can, together with the presence of surfactant molecules, significantly alter the electronic properties of the produced material. While the issues of the broad distribution of thickness to lateral size ratio and the presence of surfactants can be solved by specific nanosheet selective methods [139] and additional material cleaning measures [140] structural defect formation by intensive processing cannot be avoided.

3.3.2 Intercalation of TMDs

Intercalation chemistry deals with insertion of guest species, such as atoms, molecules and ions into the host material, driven either by diffusion or initiated by the application of an electric field (e.g. in electrochemical setup). By intercalation of guest species, the host material generally retains its core structure making this process reversible under specific conditions, however, there is often a charge transfer or complexation between the guest and the host involved upon intercalation and this can lead to structural changes. It has been known for several decades [141] that particularly in TMDs the intercalation proceeds into the van der Waals gap amid adjacent layers, increasing the interlayer spacing which is observed as a swelling of the crystal in a direction perpendicular to the layers. Intercalated species fill the structure up to the stoichiometric ratio in relation to the original host material, denoted with a chemical formula A_yMX_2 , where y designates the number of intercalants per one unit cell of the host ($y \leq 1$). MoS_2 , WS_2 and other TMDs have been intercalated with monatomic (Li^+ , K^+ , Na^+ , Cu^+ etc.) and molecular ions (e.g. tetralkylammonium ions), small molecules (e.g. hydrazine- N_2H_4 , ammonia- NH_3 , pyridine- C_5H_5N) and polymers (poly(ethylene oxide)-PEO, polyaniline-PANI, etc.). As a direct consequence of decoupling of the layers and the occurring charge transfer upon intercalation (electron donation from the guest to the host), electronic and optical properties of the composite can be significantly altered in comparison to the intrinsic bulk crystal. Thus intercalation can be used as a way to modify the basic properties of the host material.

Intercalation can also be used to assist with the exfoliation. Together with a decoupling of the layers, i.e. decrease of the interaction between the adjacent layers, the

reactivity of specific intercalants can be exploited for efficient exfoliation of crystals with a characteristic thickness of several micrometers into nano-thin sheets.

3.3.2.1 Chemical exfoliation of TMDs

A prime example of the MoS₂ chemical exfoliation is the intercalation of lithium into the interlayer space of MoS₂ powder or a bulk single crystal with a subsequent exothermic reaction that promotes delamination. The complete procedure is sketched in Figure 3.3. First the MoS₂ in 2H polytype is put inside an organolithium solution for several hours (e.g. *n*-Butyllithium). Lithium atoms are small enough to diffuse into the interlayer spacing of MoS₂, expanding the crystal while inducing partial phase transformation from a semiconducting 2H to a metastable metallic 1T phase by donating an electron to the MoS₂ lattice. The interlayer distance upon intercalation increases for around 50% from the initial 6.5 Å [142].

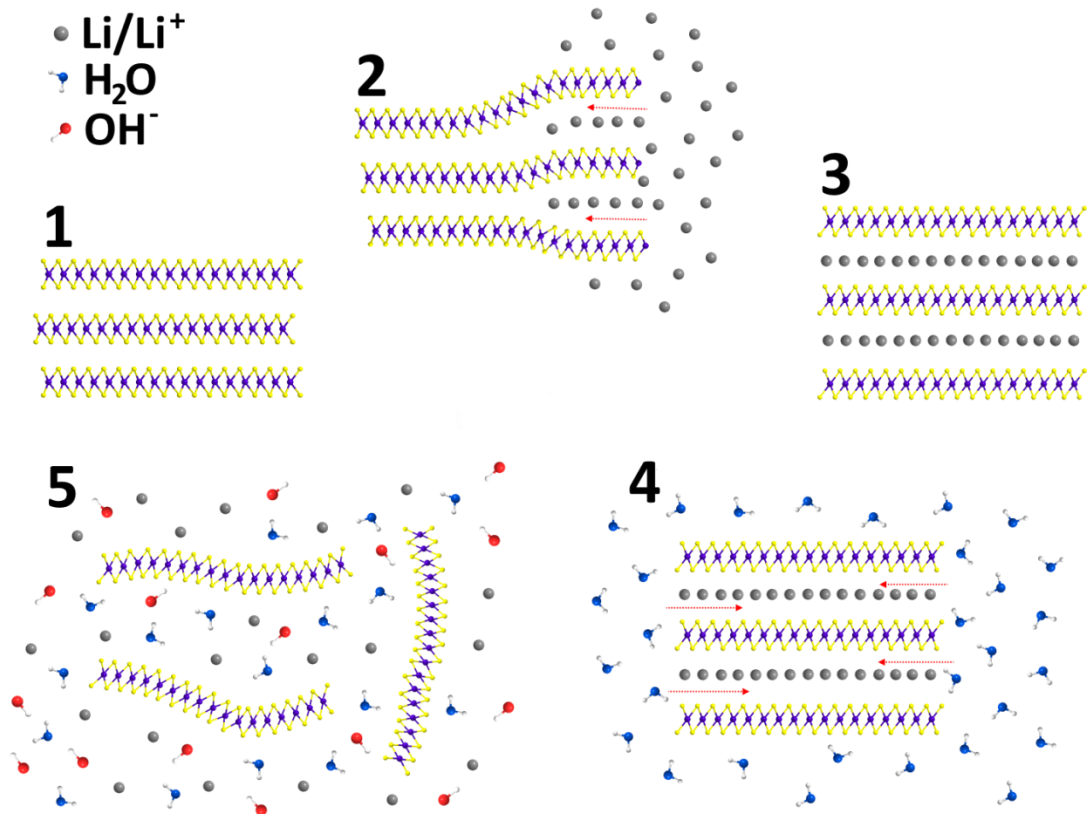


Figure 3.3: Step-wise sketch of the MoS₂ chemical exfoliation. 2H polytype MoS₂ (1) is intercalated with lithium by a diffusion driven process into the interlayer MoS₂ spacing (2). The intercalation results in increased interlayer spacing together with induced partial transition from the 2H to the metastable 1T polytype (3). After the complete intercalation water is added to exothermically react with lithium along which H₂ gas is released (4). Rapid evolution of H₂ gas helps with the separation of layers in aqueous suspension (5), while the suspension stability is provided by the repelling, negatively charged, exfoliated sheets of MoS₂. The side products of the lithium reaction with water are Li⁺ and OH⁻ ions in aqueous solution.

After the complete intercalation (i.e. when the ratio Li/MoS_2 reaches unity) the intercalated composite is exposed to water where an exothermic chemical reaction occurs accompanied by the evolution of hydrogen gas. Rapid formation of H_2 within the interlayer spacing induces forces perpendicular to the layers separating them apart. Charge transfer from the lithium to the MoS_2 during the intercalation causes the MoS_2 to become negatively charged, which prevents the subsequent restacking of the layers when suspended in water or other suitable solvent. Advantages of chemical exfoliation are an unmatched yield of monolayers and bilayers with increased lateral size in comparison to mechanical exfoliation in liquids and its scalability. The main drawback of this approach is poor control over the degree and homogeneity of the transformation from the 2H to the 1T phase. High resolution scanning transmission electron microscope (STEM) analysis showed co-existence of semiconducting and metallic phase with nano-sized domains, with specifically the latter one being a distorted one, which was observed as clusterization of metal atoms in the metallic phase [143]. Although this transition is reversible by aging or promoted by heating, even after the intense treatment there are still remains of the bi-phase nature.

3.3.3 Growth of TMDs

Alongside the various exfoliation methods growth techniques are gaining in importance among the researchers working with 2D materials since they can provide continuous, large area film growth with controlled thickness and crystallinity of the layers. Thus TMDs have been grown by chemical vapor deposition (CVD) [144], [145] atomic layer deposition (ALD) [146], molecular beam epitaxy (MBE) [147] and pulsed laser deposition (PLD) [148]. Large area growth of ultrathin inorganic layers is typically carried out on atomically flat substrates such as silicon oxide wafers or sapphire substrates, where the substrate lattice (unit cell) closely matches the one of the growth material. The transfer of continuous films from the growth substrate onto an arbitrary substrate on which a particular device will be built can be carried out by a polymer-assisted transfer without losing the intrinsic properties of the film [149], [150]. In this way the thickness and the controlled growth is applied separately and only later the films are transferred to the substrate of choice for a particular application. The possibility of a subsequent transfer opened a pathway for the assembly of Van der Waals heterostructures, where distinct atomically thin layers are stacked on top of each other to form ultrathin opto-electronic devices, like solar cells.

Chapter 4

Experimental Methods

4.1 Solar Cell Preparation and Characterization

4.1.1 Etching and cleaning of transparent electrodes

Solar cell preparation starts by patterning glass substrates containing a fluorine-doped tin oxide as a conductive transparent electrode. Areas of FTO we want to keep unetched are covered with a Scotch tape. Zinc powder is sprinkled over the uncovered areas and 2M HCl is added drop-wise over the zinc containing area where a reaction between the HCl and zinc powder produces hydrogen gas (observed as bubbling) which subsequently reduces the metal oxide. Within minutes the FTO is etched away, the remaining solution is then wiped off the substrate and the Scotch tape is removed. Etched substrates are afterwards successively cleaned in 1 vol.% Hellmanex solution in deionized water, clean deionized water, acetone and 2-Propanol by placing them in an ultrasonic bath for 10 min at the temperature of 55°C for each of the cleaning steps. Finally the substrates are dried with a stream of N₂ gas. Before further processing the substrates are exposed to O₂ plasma for 10 min in order to remove the remaining carbon-based contaminants.

4.1.2 Electron transporting layer

Electron transporting layers used in this thesis are titanium dioxide (TiO₂) in the form of anatase phase nanoparticle compact film, PC₆₁BM (Phenyl-C61-butyric acid methyl ester), pristine C₆₀ fullerene and siloxane functionalized C₆₀ fullerene (Sil-C60).

TiO₂ layers were formed by spin coating of a precursor on freshly cleaned FTO substrates at 2000 rpm for 30 s. After the spin coating the substrates were immediately put on a hot plate at 150°C. TiO₂ sintering was performed by a 30 min ramp to the final temperature of 500°C, at which the substrates were left for 45 min. After the end of the sintering cycle at the temperature of 500°C the substrates were left to cool down to the temperature of 100°C and were, still hot, transferred inside the glove box. TiO₂ precursor was prepared by thoroughly mixing Titanium(IV) isopropoxide with anhydrous 2-Propanol in a 1:8 volume ratio, adding 4.5 ul of 2 M HCl per 1 ml of precursor mixture. TiO₂ layer was used in combination with the PC₆₁BM as a combined electron transporting layer. PC₆₁BM was dissolved in anhydrous toluene at the concentration of 10 mg/ml inside the glove box and left stirring for 1 h. Afterwards the solution was spin coated on top of TiO₂ containing substrates at 4000 rpm for 30 s. Immediately afterwards the substrates were put on a hot plate at the temperature of 105°C and were left to anneal for 15 min.

Devices containing pristine C₆₀ film as an electron transporting layer were prepared inside the glove box by spin coating C₆₀ solution at 4000 rpm for 30 s. Afterward the

substrates were put on a hotplate at the temperature of 105°C for 15 min. C₆₀ solution was prepared with the concentration of 10 mg/ml in 1,2-Dichlorobenzene. Before spin coating the C₆₀ solution was stirred for at least 1 h to assure there is no undissolved material left.

4.1.3 Light harvesting layer – organolead halide perovskite

Light harvesting layers based on organometal halide perovskites were processed inside the nitrogen filled glove box with an active nitrogen flushing. Before the final solar cell preparation of each experimental set presented in the following solar cell related chapters a complete device optimization was carried out, focusing predominantly on the most suitable perovskite composition structured for a specific need.

All of the presented solar cells in this thesis employed a mixed cation (cesium, formamidinium and methylammonium) and anion (bromine and iodine) perovskite. Perovskite precursor solutions were produced by separately preparing stock solutions of cesium lead iodide (CsPbI₃), formamidinium lead iodide (FAPbI₃), methylammonium lead iodide (MAPbI₃) and formamidinium lead bromide (FAPbBr₃) and mixing them in the desired ratio. Each of the constituents of the precursor solution was prepared by dissolving an organic (methylammonium iodide, MAI; formamidinium iodide, FAI; formamidinium bromide, FABr) or inorganic (cesium iodide) salt together with a lead containing salt (lead iodide, PbI₂; lead bromide PbBr₂) in a solvent mixture of DMSO and DMF in a 3:7 volumetric ratio. According to the project, the perovskite composition was varied from the triple cation, where cesium-, formamidinium- and methylammonium-based precursors were used, or the double cation where only cesium and formamidinium were used. The latter composition, albeit being slightly less efficient in devices, was applied when improved environmental stability was needed due to specific subsequent processing of the solar cells (e.g. spray coating deposition in a normal atmosphere).

Perovskite layers were spin coated on predeposited ETLs by a solvent quenching technique, by first dropping 50 µl of perovskite precursor solution on the ETL-covered FTO substrate and rotating it at 2000 rpm for 10 s and at 5000 rpm for 30 s immediately after. After 5 s of the second spinning step (at 5000 rpm) 300 µl of anhydrous toluene was dripped over the still rotating substrate inducing immediate precipitation of the solid perovskite. After the end of the spin coating protocol the devices were thermally annealed.

Temperature and time of thermal annealing depended on the perovskite composition used. When a double cation recipe was used for the perovskite layer, the substrates were thermally annealed at the temperature of 170°C for 10 min. The higher temperature stability of double cation perovskite is due to the higher melting and evaporating point of cesium- and formamidinium-based salts. In contrast, when a triple cation perovskite was used containing methylammonium-based salts which have a lower melting point, the annealing procedure was set to 100°C for 1 h. After thermal annealing the substrates were left to cool down.

4.1.4 Hole transporting layer

Spiro as a hole transporting layer was prepared by dissolving 73 mg of Spiro in 1 ml of anhydrous chlorobenzene, adding 28.8 µl of tBP (4-tert-Butylpyridine) and 17.5 µl of 520 mg/ml Li-TFSI (Bis(trifluoromethane)sulfonamide lithium salt) solution in anhydrous acetonitrile. Thus prepared solution was spin coated on top of a perovskite film at 4000 rpm for 30 s. Before the deposition of the top metal electrode, devices

employing Spiro were left stored in a desiccator for 12 h in order to induce oxidation of the layer.

Colloidal WS_2 suspended in 2-Propanol was deposited by spray coating on top of the perovskite film using an air brush. The whole deposition procedure was carried out in a fume hood in normal atmosphere at 40% relative humidity. Depending on the desired thickness of the WS_2 layer, a specific volume of colloidal suspension was sprayed over the substrate heated on the hot plate at the temperature of 135°C . Nitrogen at the pressure of 0.2 bar was used as a carrier gas. The distance between the air brush nozzle and the substrate was approximately 25 cm.

4.1.5 Metal cathode

Before the top cathode evaporation one part of the perovskite layer was scratched off in order to allow direct contact of the metal electrode with the underlying ETL-anode junction. A 50 nm thin gold layer was deposited by a thermal evaporator through a shadowmask at the pressure of 10^{-6} mbar. A tantalum metal boat was used as a thermal source for evaporation. The thickness and deposition rate were monitored by a quartz crystal. The deposition rate was set to be $0.1 \text{ \AA/s}$ for the first 10 nm in order to achieve more homogeneous and compact growth and was later raised to $1 \text{ \AA/s}$ until 50 nm thickness was reached.

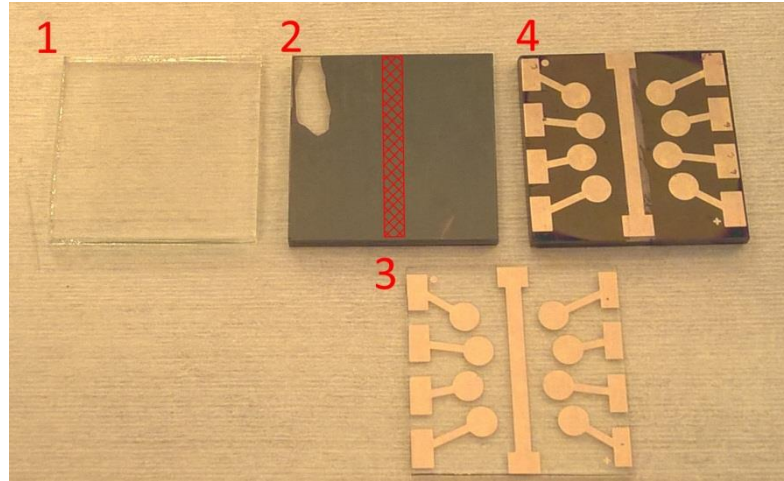


Figure 4.1: Deposition of layers on FTO. FTO glass substrate covered with TiO_2 layer (1) and with perovskite layer on top (2). Pattern of the gold electrode thermally evaporated on a bare glass (3) and completed solar cell with gold electrode (4). In order to contact the bottom electrode the central part of the perovskite is scratched off right before the deposition, marked with a red mesh in (2). In this way the central metal stripe is used as a contact to the anode. Cross and dot symbols appearing in the evaporated electrode pattern are used for the correct alignment with the evaporation and measurement shadow mask and for enumerating electrodes on each substrate.

4.1.6 Solar simulator setup

Solar cells were measured on a solar simulator setup consisting of a solar simulator Newport Oriol Sol3ATM with an AM1.5 output light source, Newmark Systems, Inc. (ET-150-21) software controlled X-Y stage with 16 slot holder and a Keithley 2440 voltage/current source/measure unit as presented in Figure 4.2. All substrates were masked in a way that only the circular area of the electrode was illuminated. Before the

start of each set of measurements the solar simulator lamp was first left to stabilize and the light intensity coming from the source was afterwards analyzed by a silicon photodiode, at the position at which all the substrates were subsequently measured.

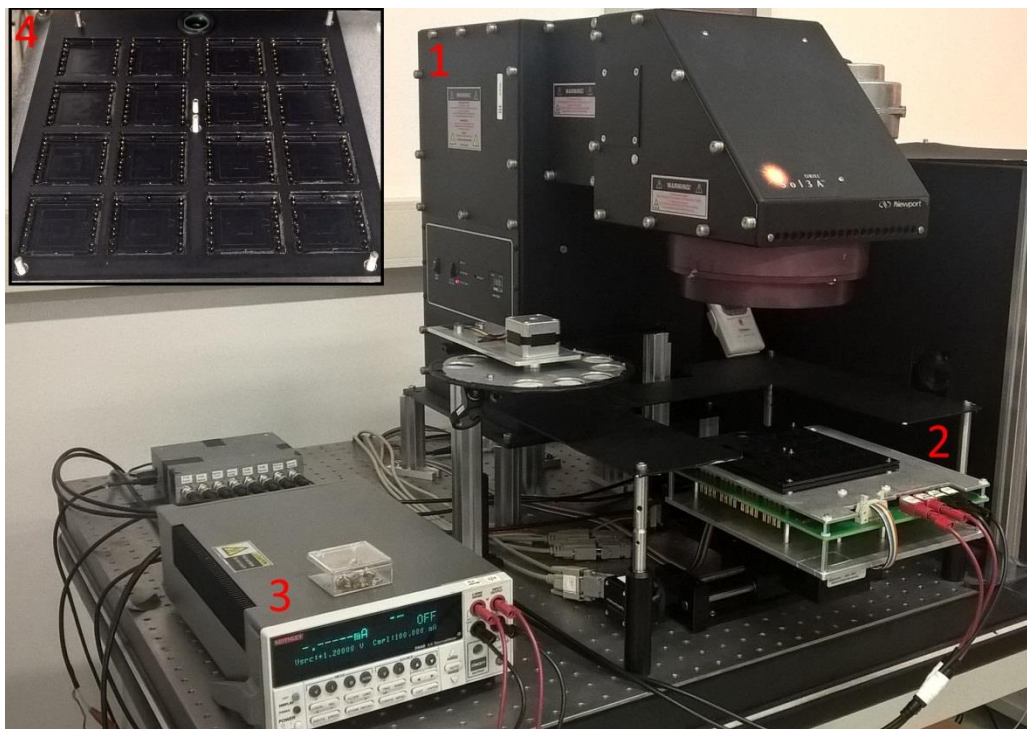


Figure 4.2: Solar simulator measurement setup. Solar simulator with an AM1.5 light output (1), X-Y stage with 16 substrate slot holder (2) and a Keithley 2440 as a voltage and current source/meter (3). Solar cells placed in the substrate holder are contacted with pogo pins (4).

4.2 Exfoliation of MoS₂ and WS₂

4.2.1 MoS₂ chemical exfoliation

Chemical exfoliation of MoS₂ was carried out in an argon filled glove box with an oxygen level below 1 ppm. 100 mg of MoS₂ was first placed in an elongated vial. 1 ml of 1.6 M *N*-Butyllithium (*n*-BuLi) was injected into the vial using a glass syringe. Approximately 1 ml of anhydrous hexane was added to the mixture to reduce the concentration of *n*-BuLi. The vial was left undisturbed for 48 h to fully intercalate lithium containing complexes into the MoS₂ interlayer spacing. After that time the solution was carefully decanted and the intercalated MoS₂ powder was washed for two times by adding 2 ml of anhydrous hexane, gently shaking the mixture and removing the hexane after the sedimentation of the powder. When most of the hexane was removed the vial was closed by a rubber cap, which allows puncturing by metal needle connected to the syringe. The vial was transferred out of the glove box and placed inside the sonication bath. Just before the injection of Milli-Q water inside the vial another needle was placed into the rubber cap to allow release of hydrogen gas evolved during the reaction between the lithium and water. 10 ml of water was slowly injected into the vial during sonication. When the evolution of hydrogen was significantly reduced the mixture was transferred

into a 100 ml bottle with Milli-Q water and was kept sonicating for 1 h. The suspension of chemically exfoliated MoS₂ was afterwards centrifuged at 1000 rpm to sediment out the unexfoliated material, followed by a 3 times successive centrifugation at 8000 rpm in order to remove lithium ions formed as a reaction product between the lithium and water. The washing step was carried out by removing the supernatant, adding fresh Milli-Q water to the sediment in each washing step. After the washing, the powder was again redispersed in absolute ethanol using sonication bath obtaining a stable colloidal suspension.

4.2.2 WS₂ exfoliation

WS₂ powder was exfoliated in sodium cholate solution in ethanol:water mixture ratio of 0.35:0.65. Typically 10 mg/ml of WS₂ and 3.5 mg/ml of sodium cholate hydrate was placed in a 250 ml bottle adding a mixture of ethanol and water. The bottle was placed inside the sonication bath and sonicated for a cumulative time of 100 h. Afterwards, the bottle was left undisturbed for 48 h in order to sediment out the unexfoliated material. The remaining dispersion was then centrifuged at 10000 rpm and successively washed with ethanol:water mixture, following the washing protocol used in chemically exfoliated MoS₂. Lastly, two additional centrifugation steps were used for a solvent exchange, ultimately ending with a suspension in 2-Propanol.

4.3 Absorption and Photoluminescence Spectroscopy

Absorbance was approximately determined by measuring the transmittance without taking into account the sample's reflectivity. Measurements were performed on a PerkinElmer Lambda 1050 UV/Vis/NIR Spectrometer equipped with a 150 mm integrating sphere employing an InGaAs detector.

Photoluminescence spectra were acquired on a Horiba Jobin Yvon iHR320 Spectrometer with a Symphony II CCD Detector using a Xenon 450W source (FL-1039).

4.4 Electron Microscopy

Electron microscopy was used to characterize materials and devices. A scanning electron microscope (SEM) Jeol JSM-6010LV was used to characterize materials with typical dimensions in the range of μm and of devices, particularly surface morphology of deposited layers and analysis of film uniformity in the cross-section view.

Transmission electron microscope Jeol JEM-2100 was used to characterize the size and the shape of TMD nanosheets and their atomic structure. The energy of the incident electrons was set to 200 keV.

4.5 Ultraviolet and X-Ray Photoelectron Spectroscopy

Photoelectron spectroscopy (PS) is a general term describing various spectroscopy techniques which analyze the emission of electrons from the specimen when it is exposed to high energy photons. Briefly described here are the X-ray (XPS) and ultraviolet (UPS) photoelectron spectroscopy.

UPS is used to photoexcite electrons residing in the valence band with photons coming from a gas discharge lamp with energies of several to several tens of electronvolts (e.g. 21.22 eV for the 1 α He emission line), corresponding to the ultraviolet spectral region. Depending on the position within the valence band photoexcited electrons can be

emitted from the surface of the specimen which are further collected and discriminated by their kinetic energy within the electron energy analyzer. The information depth, i.e. the depth out of which electrons receiving the kinetic energy of photons can reach the surface of the specimen, is only about 2-3 nm, rendering this technique very surface sensitive. An example of UPS spectrum is presented in Figure 4.3. The valence band maximum position with respect to the Fermi level is determined by linearly interpolating the low binding energy onset towards the zero intensity base line. The Fermi level is determined by measuring the UPS spectrum of a reference metal electrode. High binding energy (or low kinetic energy) onset features the signal from secondary electrons. The ionization potential of the sample (i.e. position of the VBM with respect to the vacuum level) is determined by subtracting the width of the photoelectron spectrum (Δ) from the incident photon energy.

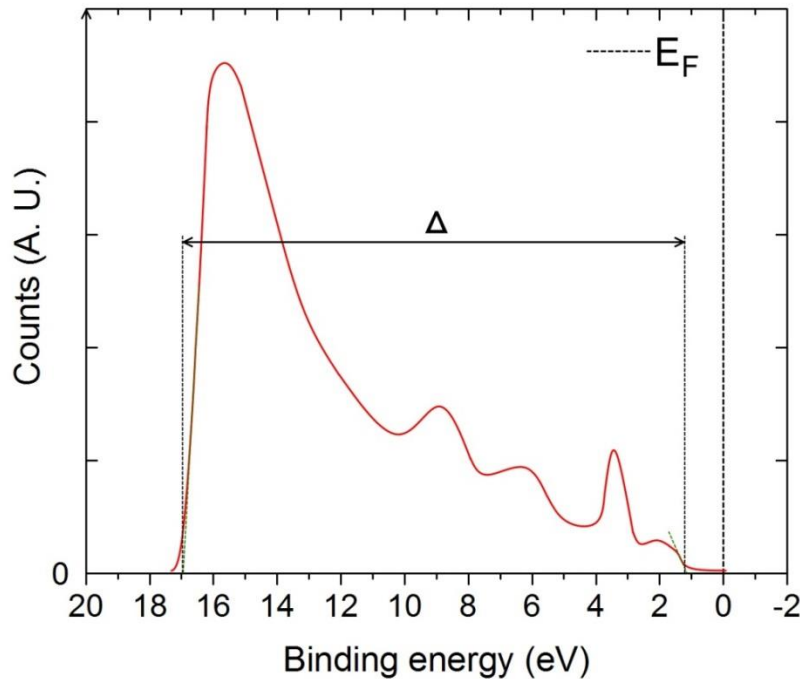


Figure 4.3: Example of a UPS spectrum. Typical UPS spectrum with an X-axis presenting the binding energy of the electrons photoemitted from the specimen into a detector. Fermi level position is determined by measuring the reference spectrum of a metal electrode with a known work function. The energy width of the spectrum (Δ), determined by the energy difference between the low kinetic energy secondary electron onset and the low binding energy onset, is used to determine the ionization potential of the specimen.

XPS uses X-rays as a photoexcitation source for the core electrons of atoms residing at or within a few nm below the surface of the specimen. By measuring the kinetic energy of the photoemitted electrons XPS provides information about the present elements and their chemical state. An example of an XPS spectrum of MoS₂ is presented in Figure 4.4. In an overview spectrum of a wide range of electron binding energies we can extract the information about the atoms constituting the sample, while detailed determination of electron energies gives information about the chemical bonding and oxidation states of atoms.

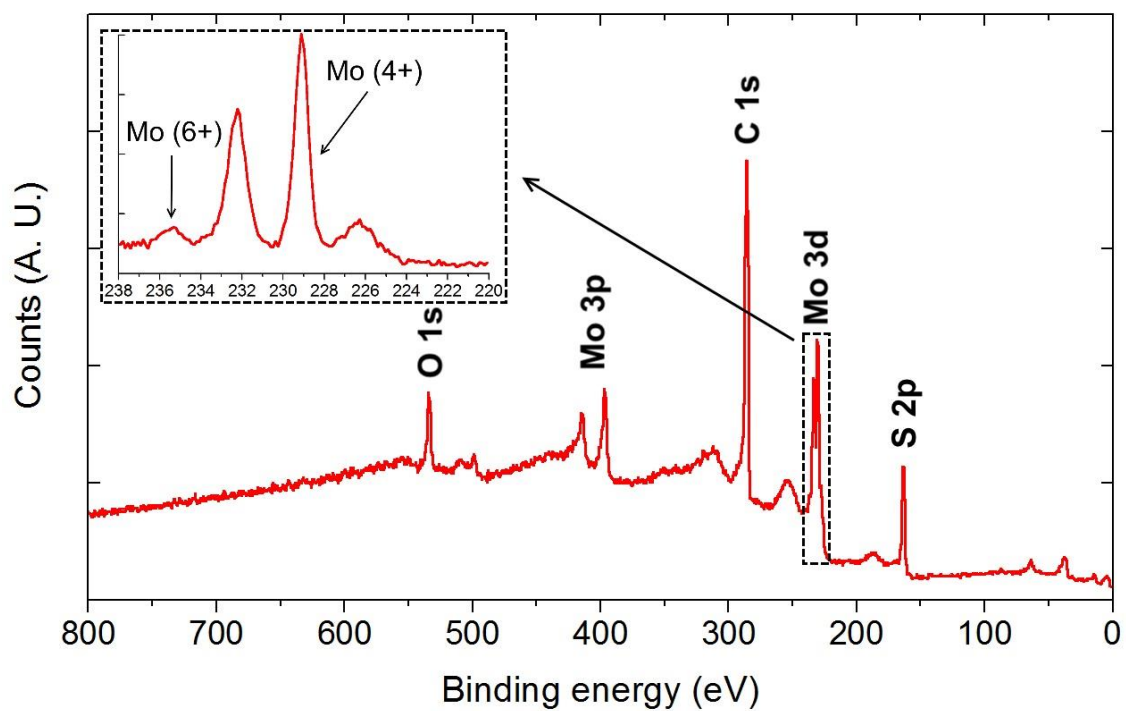


Figure 4.4: Example of an XPS spectrum. XPS overview spectrum of MoS₂ with characteristic signal for electrons coming from atomic orbitals of molybdenum, sulfur, carbon and oxygen. Inset: Magnified part of the spectrum characteristic for molybdenum 3d orbitals showing molybdenum in mixed chemical states (6+ and 4+).

Chapter 5

Synthesis of MAPbI₃ Sub-Micrometer Particles

This chapter presents a novel synthesis of sub-micron-sized MAPbI₃ perovskite particles based on the use of solely non-hazardous solvents water and 2-Propanol. Through the step-wise synthesis the size of formed perovskite particles can be controllably reduced by increasing the number of successive PbI₂ recrystallization and MAPbI₃ formation steps. Thus synthesized perovskite particles were applied and tested in a simple photoconductor prepared by the bar-coating deposition technique. Finally, solvent annealing treatment is demonstrated on the preformed particle films inducing growth of quasi single crystals on flat substrates.

The presented synthesis is a part of a broader project involving printable perovskite particles with various compositions used in photodetectors with tunable response. The manuscript presenting results of the project was in the state of preparation at the time of the dissertation finalization.

5.1 Introduction

Preparation of organolead halide perovskites bases on solution processing of perovskite precursor typically deposited by a spin coating technique. As a deposition technique, spin coating is a useful approach for the deposition on substrates of characteristic size up to few centimeters, however, for larger substrates it becomes less applicable due to the problems of retaining thickness homogeneity throughout the substrate. In addition, the process of spin coating produces a lot of waste liquid during the substrate rotation. Considering that the perovskite precursor solutions are made in polar aprotic solvents, for example DMF, DMSO and NMP, which are toxic and harmful [151]-[154], the process is by far not health and environment friendly. Furthermore, the quality of the perovskite film and the final performance of the device employing it depends profoundly on other conditions during deposition and thermal annealing step, for example the atmosphere (saturation with solvent vapors), temperature, spin coating parameters, etc. These parameters make the deposition rather complex, requiring detailed control for reproducible results.

For an industrial scale deposition all of the aforementioned parameters influence the final product, quality, reproducibility and the price of fabrication which determines the economic viability of mass manufacture. Until now most of the published examples on large area perovskite deposition involved the use of perovskite precursor solution in high boiling point polar solvents. By using large area deposition techniques, as an example inkjet or screen printing [155] and blade [156], spray [157] or slot-die coating or a simple

drop casting [158]-[160], significant increase in the production throughput has been reached in addition to the reduction of waste solution amount in comparison to spin coating, which is more common at the lab scale.

To overcome the problems of perovskite film formation during the deposition and the solvents toxicity, research has diversified into production of nanoparticles suspended in less polar solvents, where the perovskite crystal structure remains stable. This resulted in a number of publications describing the synthesis of colloidal perovskite particles with a 3D [87], [161]-[164] or 2D [165] structure. Colloidal suspensions and dispersions were produced with additional capping ligands which prevent particle aggregation suspended in nonpolar solvents toluene, hexane or similar. The final concentration of particles in dispersion is typically low (order of mg/ml or less), limiting their practical use in printing of solar cells or other opto-electronic devices where films several hundreds of nanometers thick are required to fully absorb the incident light.

In this chapter I present a straightforward synthesis procedure for MAPbI₃ cuboidal perovskite particles where the size of the particles is reduced by the number of successive PbI₂-MAPbI₃ reversible transformation steps down to an average sub-micron size. In contrast to other published synthetic procedures our synthesis method is based solely on the use of water and alcohol, with recyclable side products. Furthermore, we demonstrate a simple application – a photoconductor incorporating synthesized MAPbI₃ perovskite particles, where the device is prepared by a large-scale bar-coating deposition method. As a proof of concept, we present a possible experimental pathway toward the improvement of perovskite crystallinity for obtaining high quality polycrystalline and quasi single crystal films.

5.2 Experimental Methods

5.2.1 Synthesis

Synthesis of submicron MAPbI₃ perovskite particles was performed in several steps. 200 mg of lead iodide powder (PbI₂ anhydrous – Sigma Aldrich) was thoroughly ground in a ceramic mortar for 10 minutes inside the nitrogen filled glove box. 1 g of MAI was dissolved in 10 ml of anhydrous 2-Propanol at the temperature of 80°C. During vigorous stirring 200 mg of ground PbI₂ was slowly added to the MAI solution inducing rapid transformation into MAPbI₃ perovskite. Formed MAPbI₃ particles of typical dimensions of several micrometers were left to sediment and the remaining MAI solution was decanted. Sedimented perovskite particles were taken outside of the glove box and transformed back to PbI₂ by repeatedly washing them with deionized water and with 2-Propanol to remove any residual MAI. Washed PbI₂ was dried on a petri dish heated on a hot plate at the temperature of 80°C and collected afterwards. The procedure of MAPbI₃ formation and subsequent recrystallization back to PbI₂ was performed for additional 2 cycles to reduce the size of synthesized particles. At the last MAPbI₃ formation step, the particles were washed with anhydrous 2-Propanol to remove any unreacted MAI. Most of the solvent was removed to obtain highly concentrated particles in the form of a paste.

5.2.2 Deposition of perovskite particles

Films of MAPbI₃ particles were prepared by bar-coating of the dense black paste on top of the substrate, creating films with a thickness of about 20 μm .

5.2.3 X-ray diffraction

X-ray diffraction pattern was acquired on Bruker D8 advanced diffractometer with Bragg-Brentano geometry, a Cu-based X-ray source ($K\alpha_1; \lambda=1.544060 \text{ \AA}$) operating at 40 kV and 40 mA, with a 0.02° (1 s) step.

5.2.4 Solvent annealing of perovskite particles

Solvent annealing of perovskite films was carried out by placing a perovskite film on a hotplate at the temperature of 120°C . A smaller glass slide was placed next to the perovskite film onto which $20 \mu\text{l}$ of DMF was added when the substrate was already at its final temperature. Both substrates were covered by a low profile Petri dish, slightly lifted on one side to provide the flow of DMF out of the cover. The whole annealing procedure lasted only 1 min.

5.3 Results

The step-wise synthesis of MAPbI_3 is followed by an SEM, as presented in Figure 5.1. The MAPbI_3 synthesis starts from a solid PbI_2 powder (Figure 5.1a) which was initially ground in a ceramic mortar to decrease the size of the particles and to increase the surface to volume ratio of the precursor material (Figure 5.1b). The step of grinding improves the efficiency of intercalation of MA^+ and I^- ions inside the PbI_2 lattice. Afterwards, the ground powder was slowly added to a stirring, highly concentrated MAI solution at increased temperature of 80°C . As soon as the PbI_2 is exposed to the MAI solution a rapid intercalation of MA^+ and I^- ions into the PbI_2 van der Waals gap occurs, followed by an instant redistribution of ions into a cubic perovskite structure. MAPbI_3 particles of a few micrometers in size are formed (Figure 5.1c). In order to obtain size-reduced PbI_2 , the MAPbI_3 particles were washed with deionized water, extracting the MAI out of the structure and leaving platelike hexagonal PbI_2 particles undissolved (Figure 5.1d). Repeating the MAPbI_3 particle synthesis procedure starting from now size-reduced PbI_2 particles further decreases the size of the synthesized perovskite particles (Figure 5.1e and Figure 5.1f).

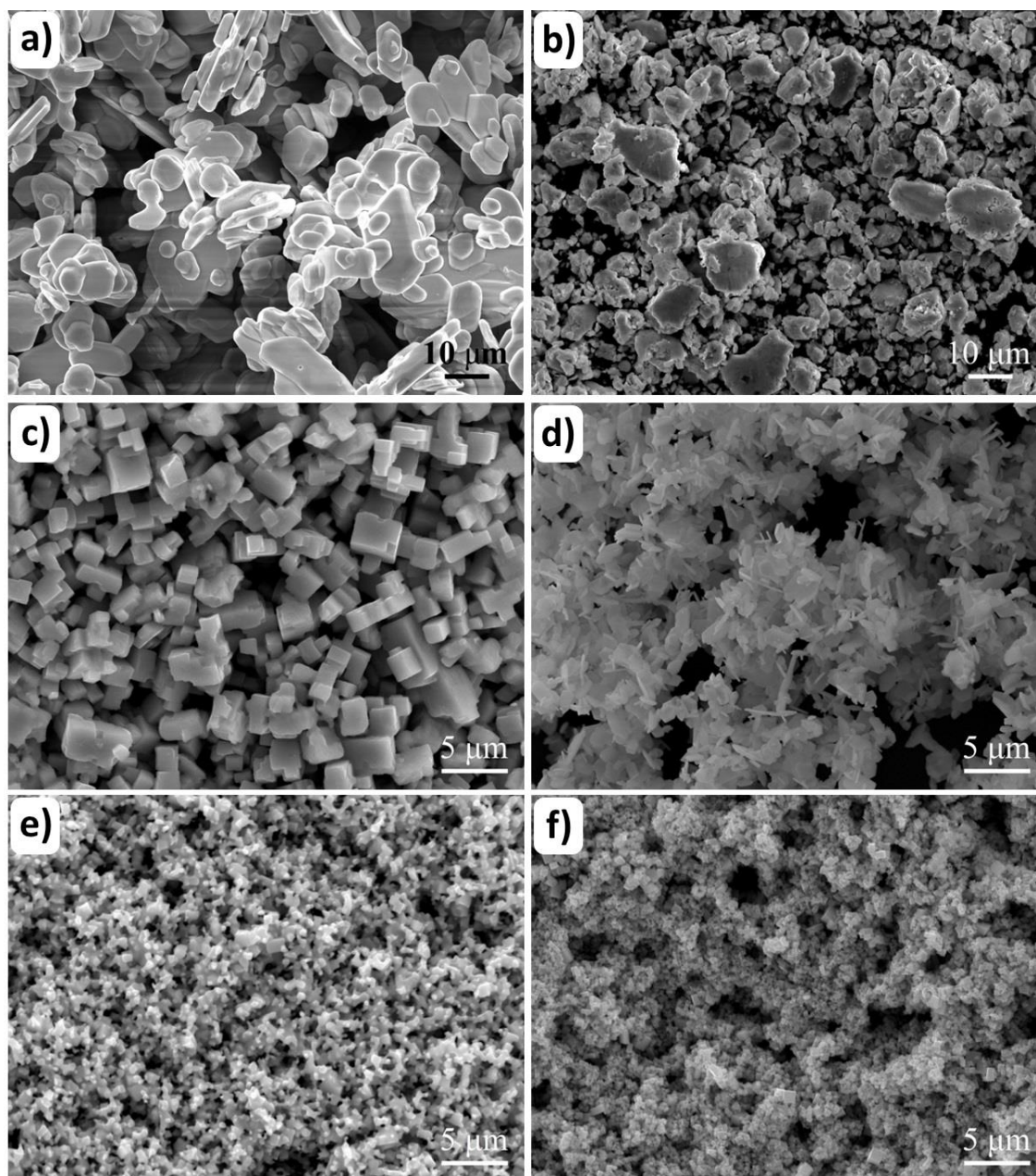


Figure 5.1: SEM representation of the MAPbI₃ synthesis steps. a) Starting PbI₂ powder. b) PbI₂ ground in a ceramic mortar. c) First cycle of perovskite particle synthesis. d) PbI₂ recrystallization from perovskite particles. e) and f) a second and a third cycle of perovskite particle synthesis, respectively.

Synthesized perovskite particles with typical sizes below 1 μm were deposited onto glass substrates by a large-scale deposition method, specifically by a bar-coating procedure. With this method, the substrate is fixed on a flat surface while a metal bar is rolled over the substrate at a micro-adjusted height above the substrate's surface in order to uniformly redistribute the material which is in the form of an ink, solution or dispersion. Highly concentrated perovskite particles in a small amount of solvent, used as a cohesive medium rather than dispersing solvent, were put at the edge of the substrate and distributed throughout the substrate by the overrunning metal bar. With a few optimization steps we were able to deposit a 20 μm thick perovskite film uniformly

covering substrates as large as 25 cm² (Figure 5.2a). Films produced in this way showed rather rough surface with randomly oriented particles which scattered light isotropically, seen as an opaque black color. Reducing the film thickness well below 10 μm showed noticeable nonuniformities in the form of uncovered areas and scratches produced by rare larger particles dragged by the bar over the substrate. Thinner inhomogeneous or uniform thicker films inhibited their accurate characterization by optical absorption, since either the incomplete coverage of a much thinner layer would produce artifacts in the optical absorption spectrum, or on the other side, thicker films absorb practically all the light incident on to the surface. Thus bar-coated MAPbI₃ films were characterized by a steady state diffuse reflectance and photoluminescence spectroscopy.

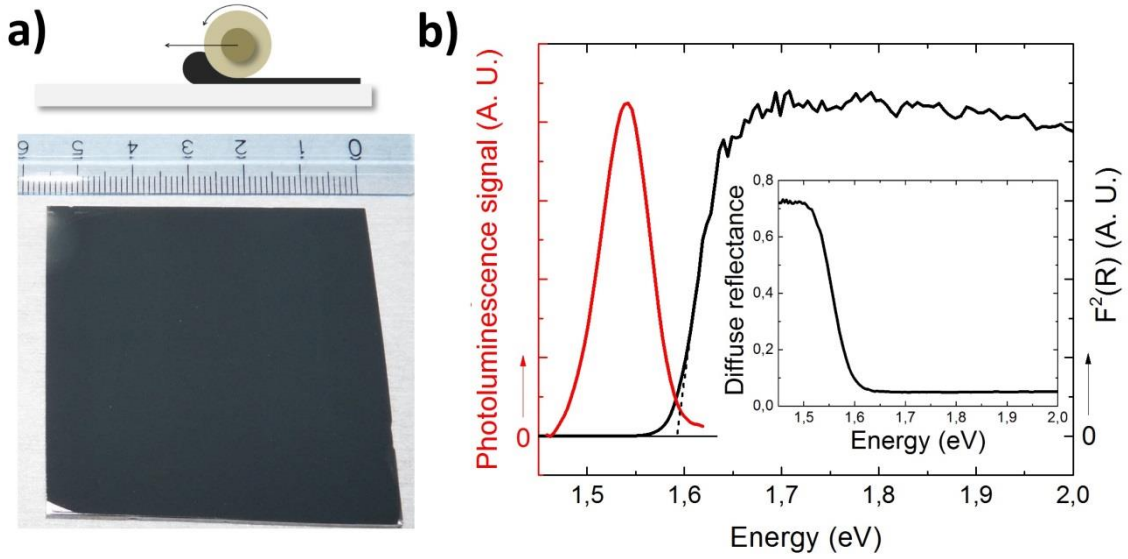


Figure 5.2: Deposition on large-scale substrates and MAPbI₃ film characterization. a) Submicron-sized MAPbI₃ particles bar coated on top of a large area (>25 cm²) glass substrate with a film thickness of 20 μm . b) Tauc plot (black curve) of an absorption spectrum obtained by applying the Kubelka-Munk transform on a diffuse reflectance spectrum (inset graph) and a steady state photoluminescence spectrum of a MAPbI₃ particle film (red curve).

Diffuse reflectance spectrum was obtained by a spectrometer with an integrating sphere and transformed by following the Kubelka-Munk relation:

$$F(R) = \frac{K}{S} = \frac{(1 - R)^2}{2R}, \quad (5.1)$$

where $F(R)$ denotes Kubelka-Munk transform of the reflectance spectrum, and K and S are the absorption and scattering coefficients, respectively. According to the Kubelka-Munk theory, $F(R)$ is proportional to the absorption coefficient. Figure 5.2b presents a Tauc plot derived from the Kubelka-Munk transform of the diffuse reflectance spectrum (inset of Figure 5.2b). In the Tauc plot we took into account the quadratic dependence of the absorption coefficient on the photon energy of the direct bandgap semiconductors [166]. The absorption onset was extrapolated with a linear function, extracting the bandgap value of around 1.59 eV, in accordance to various literature values [37], [167], [168]. We can clearly distinguish the perovskite onset in the reflectance spectrum, which is in accordance with a highly absorbing, black color of the particles. Additionally we

measured the steady state PL spectrum of the prepared films. The photoluminescence signal reached the peak at the energy of around 1.54 eV, slightly red shifted from the absorption onset and in correspondence with the literature values of a typical MAPbI₃ PL signal [84], [169].

In order to evaluate the crystallinity and the phase composition of the particles we performed X-ray diffraction on deposited films. As the characteristic size of particles constituting the film is below 1 μm , X-rays coming from the source with an energy of around 8 keV have a penetration depth much longer than the characteristic size and would thus probe the entire volume of the particles. X-ray diffraction pattern of the synthesized perovskite particles and a simulated diffractogram for MAPbI₃ compound are plotted in Figure 5.3.

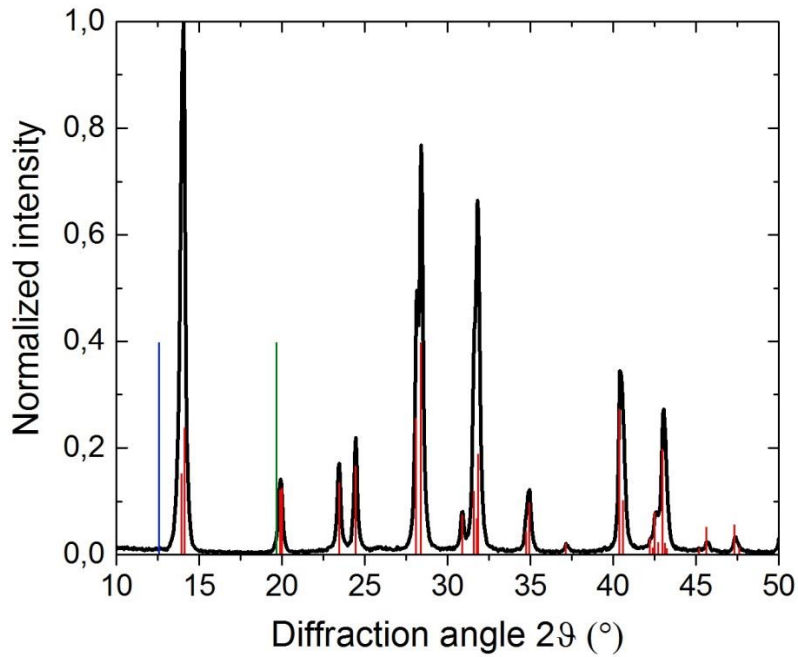


Figure 5.3: X-ray diffraction (XRD) characterization of the synthesized MAPbI₃ particles. Normalized X-ray diffraction pattern of synthesized perovskite particles (black curve) together with the red lines denoting the simulated XRD pattern taken from the work of Zhu *et al.*, the blue and green line marking a typical reflection of a possible PbI₂ and MAI impurity phase respectively [14], [68], [170].

The diffraction pattern of synthesized perovskite particles completely matches the simulated diffractogram of MAPbI₃. In addition, there are no detected phase impurities in the form of unintercalated PbI₂ (blue line) or an excess of MAI, proving that the formation of MAPbI₃ from PbI₂ was complete.

To prove the applicability of the synthesized particles we developed a simple photoconductor, consisted of interdigitated gold electrode formed on a glass substrate which was covered by synthesized MAPbI₃ particles (Figure 5.4a). The current-voltage response of the device was measured in the dark and under AM1.5 illumination coming from below the substrate, as presented in Figure 5.4b.

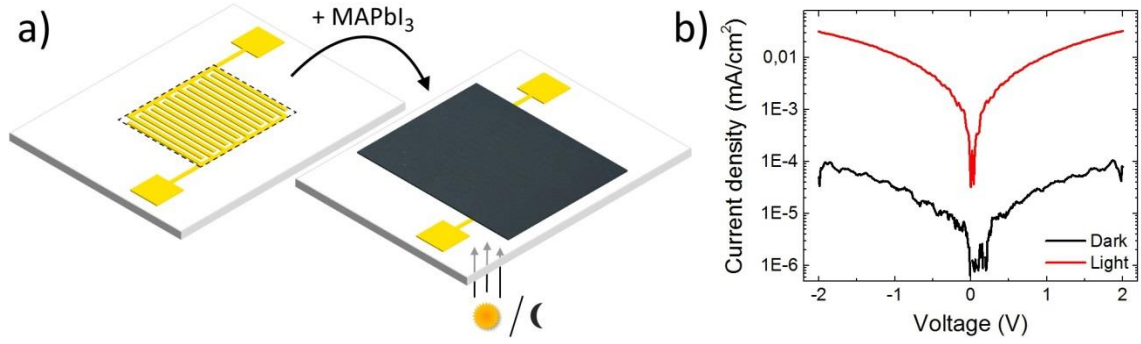


Figure 5.4: Characterization of MAPbI₃ photoconductor. a) A scheme of the interdigitated electrode together with a film of MAPbI₃ particles deposited by a bar-coater, forming a base of a simple photoconductor circuit. The dashed line marks the surface of the interdigitated electrode, which was 1 cm². The width of the gap and single electrode line was in both cases 5 μm, thus the effective area of the device was 0.5 cm². b) Current-voltage plot of the photoconductor in the dark and under AM1.5 illumination with the intensity of 100 mWcm⁻².

The black curve in Figure 5.4b is the current-voltage response of the photoconductor in the dark condition, where the device was insulated from environmental light. Dark current at the maximum applied bias (± 2 V) was about 80 nA. The noise present in the curve comes from the system and the measurement unit after FFT filtering applied to the original curve. The dips of the current at the borders of the voltage range are the result of the filtering. During the illumination the current (red curve) was markedly amplified, reaching around 25 μA, which presents an amplification ratio of approximately 300. The photoresponsivity of the photoconductor, defined as:

$$R = \frac{I_{Light} - I_{Dark}}{P_{Light}}, \quad (5.2)$$

where I_{Light} and I_{Dark} denote the current in light and dark conditions respectively at the maximum operating voltage applied and P_{Light} denotes the incident light power illuminating the device, was calculated to be around 0.25 mA W⁻¹. Both $I - V$ curves, in dark and light conditions showed nonlinear behavior (Figure A.1 in Appendix A), which suggests that there is a Schottky barrier between the perovskite film and the gold electrodes.

When the perovskite particles are exposed to photons with an energy greater than the semiconductor energy gap mostly free charges are generated in the perovskite particle. In order to evaluate the contribution of both charge types to the photoconductivity of the film we separately deposited a layer of a typical electron (PCBM) and hole (Spiro) extracting layer on top of the perovskite film and measured changes in the photoconductivity. The $I - V$ curves were now measured in the dark and light conditions (10mW, 525 nm laser light) with a peak bias value of 5 V as presented in Figure 5.5a.

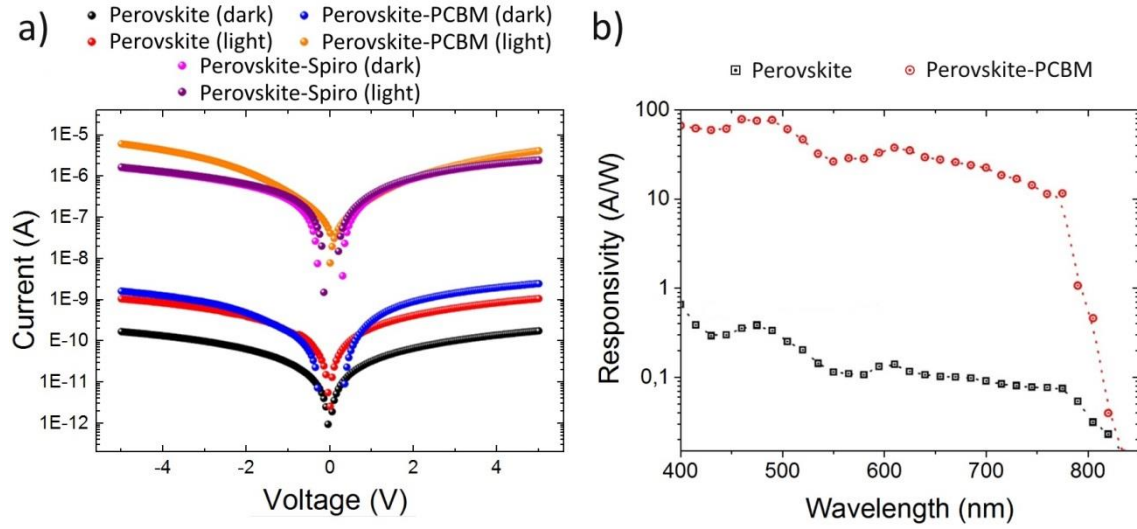


Figure 5.5: Charge extracting layers in a photoconductor. a) Current-voltage plot for MAPbI₃ particle films in dark and light conditions with or without an electron (PCBM) or hole (Spiro) extracting layers. 10 mW 525 nm laser light source was used for light conditions. The laser spot size was in the range of 2 mm² and was smaller than the size of the circuit. b) Dependence of the responsivity on the wavelength of the incident light for the samples with and without the electron extracting layer.

Deposition of an electron extracting layer on the perovskite film had a substantial impact on the photocurrent, while in the case of the hole transporting layer both dark and photocurrent increased but were very similar in values. For the perovskite film without any additional layer the amplification of the current under the illumination was around 10-fold. Devices with pristine perovskite film and the one with an additional electron extracting layer (PCBM) were measured in a setup with a monochromator, tracking the photocurrent dependence on the light wavelength. The responsivity of both devices in terms of the incident light wavelength is presented in Figure 5.5b. The power of the incident light was 0.1-1 μ W, and devices were measured at a bias of 5 V. After coating the perovskite film with PCBM the photoconductor responsivity increased by two orders of magnitude over the whole operating spectrum.

Lastly, the transient photocurrent response at switching from light to dark conditions was measured in both films as presented in Figure 5.6. A much faster response time is observed for the samples covered with PCBM in comparison to the intrinsic film without any additional layers.

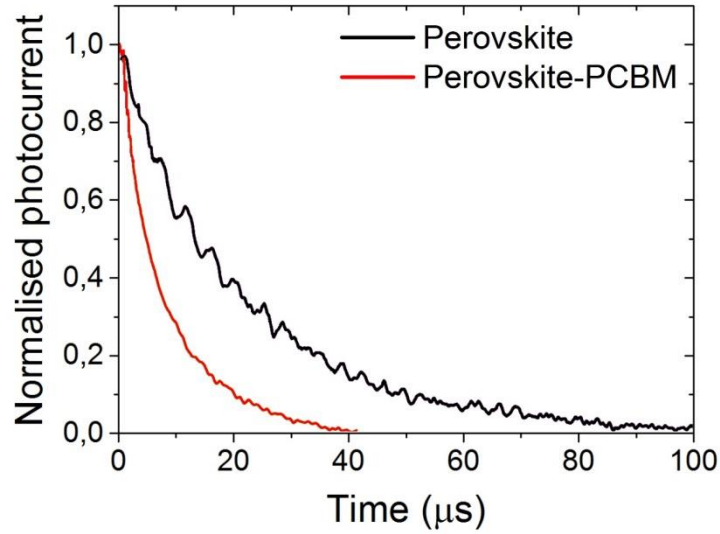


Figure 5.6: Normalized transient photocurrent response of the photoconductor. The response was measured after the switching from light to dark conditions for intrinsic perovskite films and the one covered with PCBM.

Since the gap ($5\ \mu\text{m}$) between the interdigitated electrodes in the application presented is considerably longer than the characteristic size of the particles, we can predict that the particle to particle interface will be notably reduced due to the shape of the particles and thus the conduction of charge carriers will be affected. In addition, the films deposited by bar coating show high porosity, which in combination with humidity exposure in a normal atmosphere can lead to significantly faster degradation imposed by the water vapor. As a proof of concept and as a basis for the future experiments we tested a solvent annealing method for a rapid recrystallization of perovskite crystals into larger ones on already deposited films. Bar-coated films were exposed to DMF vapor at high temperatures (120°C) for a short time and later characterized by an SEM, as presented in Figure 5.7.

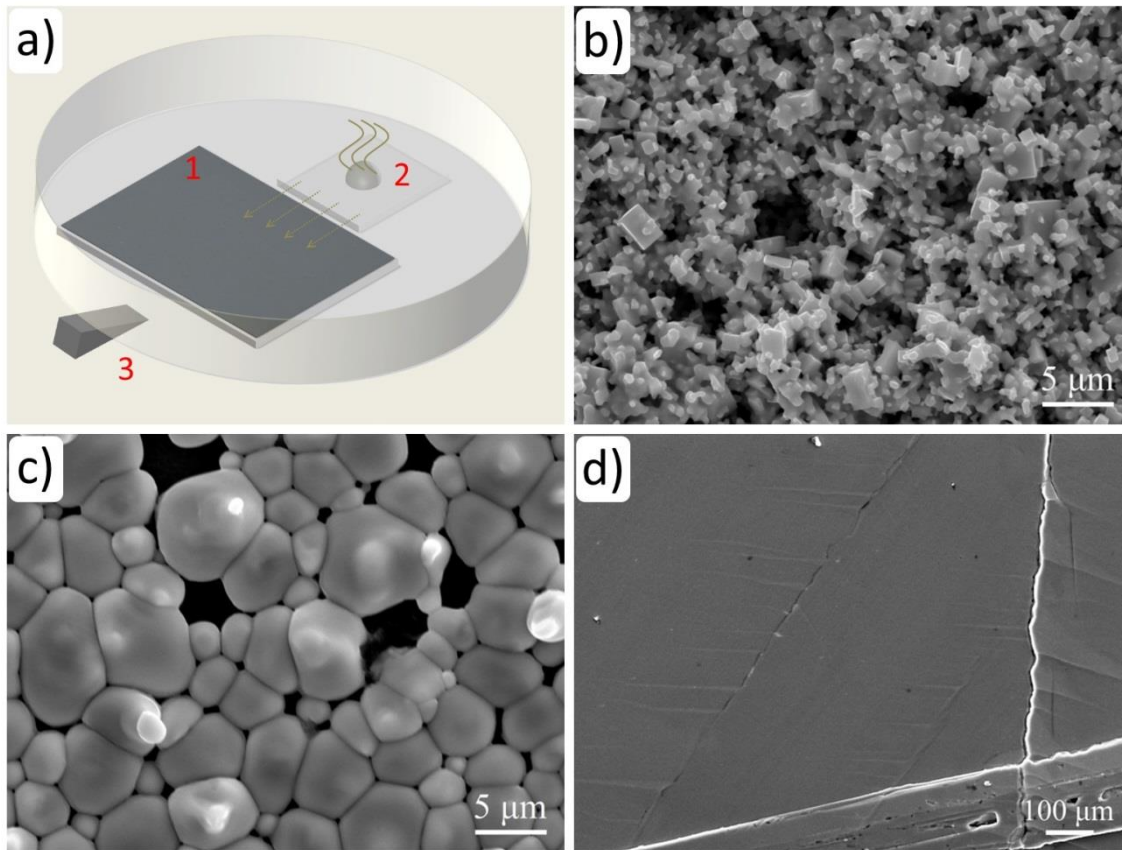


Figure 5.7: Solvent annealing effect on the perovskite particle film. a) A scheme of the solvent annealing procedure with the perovskite film (1), source of the DMF vapor (2) and a low profile cover slightly lifted on one side (3). All of the elements are kept on a hotplate at the temperature of 120°C. Arrows denote the directional flow of the DMF vapor. b) Starting perovskite particle film, approximately 20 μm thick. c) A part of the solvent-annealed film displaying large grains with characteristic size of up to several micrometers, created by the fusion of smaller particles. d) A part of the solvent-annealed film with a single crystal structure of up to a millimeter lateral size.

Solvent-annealed films show a complete change in the morphology with a general observation of the fusion of smaller particles into larger ones. There were two distinct regions found on the solvent-annealed film, one with the interconnected grains of a few μm in size, with small voids in-between (Figure 5.7c) and a region with an almost mm sized single crystals (Figure 5.7d). Higher magnification SEM images are provided in Appendix A where a smooth surface of the recrystallized perovskite layer is observed on a sub-micron scale. The main reason for the large discrepancy between the two regions lies in the poor control over the evaporation and flow of the DMF vapors over the substrate. When the perovskite film is exposed to vapors, DMF molecules start to saturate the crystal structure which is reflected in the melting. If the saturation with the vapor persists for a longer time, the phase separation starts to occur, inducing irreversible changes during recrystallization. If the temperature is set high enough that the dynamics of saturation and evaporation favors the latter process, then the recrystallization can occur without the loss of phase homogeneity. Various rates of evaporation, directional flow of the vapors and the speed of crystallization process of the perovskite melt can lead to different morphologies obtained after the drying. In order to have a better control over

the morphology of solvent-annealed films, an advanced experimental setup is needed, however at this point the experiment proves the possibility of the effective film recrystallization, significantly increasing the perovskite grain size.

5.4 Discussion

MAPbI₃ crystal formation upon exposure of PbI₂ to MAI in solution takes place by two consecutive steps. First the solid lead iodide, being a host material, is intercalated by organic salt dissolved in anhydrous 2-Propanol. In the second step the ions are rearranged to form the perovskite structure. The speed of the intercalation and the subsequent rearrangement are, besides concentration, size of the intercalants and the solvent used, governed by the temperature of the solution in which the transformation takes place. At the chosen temperature of 80°C and a high MAI concentration the transformation to MAPbI₃ is practically instantaneous (1-5 s [163]). Since MAPbI₃ is slightly soluble in pure anhydrous 2-Propanol (actually only MAI is soluble in 2-Propanol, while PbI₂ is practically insoluble), thus if one leaves particles in a very low concentrated MAI solution or in pure 2-Propanol this would lead to a slow dissolution of MAI and formation of PbI₂ phase. In our case however, high MAI concentration ensures that between the dissolution and the crystal growth of MAPbI₃ the latter prevails. An important feature of the growth properties in MAI rich gaseous or liquid environment is that the characteristic size of obtained MAPbI₃ is controlled by the low-dimensionality of PbI₂, more specifically the thickness of the host PbI₂. It is well known that upon the formation of MAPbI₃ the increased characteristic thickness of the perovskite crystal is proportional to the starting thickness of the host PbI₂, with the proportionality factor of around 1.8 [62], [171]. It is also interesting to note that in our case the perovskite particles were of cubic-like shape, with sizes defined by the thickness of the PbI₂ platelets, while in the case of gaseous MAI driven transformation into the perovskite, the lateral shape of the 2D PbI₂ is preserved and only the thickness of the crystal increases [171]. We speculate that the speed of the MAPbI₃ formation affects the morphology and the shape of the final product, since the gas-assisted transformation usually takes place at a much slower rate of intercalation and recrystallization to perovskite crystal structure than a transformation in solution.

The synthesis method described here exploits the multistep-induced PbI₂ size reduction realized by the recrystallization in water, which turned out to be an important step towards perovskite size reduction. From the perspective of using diversely sized and shaped PbI₂ as a host material for a subsequent perovskite particle formation there are a few possible approaches. PbI₂ can be grown for example by CVD [171], [172], from a solution forming either macroscopic single crystals with a large aspect ratio [173], microscopic platelets [174] or colloidal particles [175], [176] grown from the melt [177], [178] or produced by other, more sophisticated techniques such as pulsed laser ablation [162], [179]. However, these methods either lack the size control or the quantity of the produced material is rather low and they are consequently less applicable to a large-scale production and deposition. In our case both the size control and a large production are combined with a process of successive perovskite formation steps and its subsequent dissolution, leaving only PbI₂ reduced in size. In contrast to the majority of reported perovskite syntheses where toxic and health hazardous solvents are used, the advantage of our synthesis method is that it employs only water and 2-Propanol and all of the dissolved components obtained by washing and recrystallization can be recycled by a rotary evaporator. Thus, there is practically zero waste and the amount of the produced material is only limited by the amount of the starting precursor.

Being characterized as pure perovskite MAPbI₃ phase, the particles were deposited on a glass substrate and on interdigitated gold electrodes and used as a simple photoconductor. Amplification of the current in light conditions with respect to dark depends on a few parameters found in our system. First we have to take into account the relatively large spacing between the electrodes and the connection between individual particles. Large spacing, significantly longer than a typical charge diffusion length would mean a higher number of recombined photoexcited charges before they reach the electrode. Interconnection between particles with reduced interface area will additionally hamper the conductivity of both types of charges. Next parameter which has an influence on the responsivity, as it is evident from different measurements, is the intensity of the illumination. The higher the intensity of the incident light, the higher the photoexcitation rate and the density of photoexcited charges. This increases the charge scattering and the chance of a meeting of the opposite type charges, which is reflected in an increased recombination and consequently in lower responsivities.

As presented in Figure 5.5a we measured the electric current through the intrinsic film and films with deposited electron (PCBM) and hole (Spiro) transport layer that are typically used in perovskite solar cells. With these additional layers we selected the charge type which will prevail in the film through an effective charge transfer from perovskite to either PCBM (electrons) or Spiro (holes). Measurements revealed that when Spiro is deposited on the film, there is practically no distinction between the electric currents through a device in dark and light conditions. We can see a significant rise of the current offset (both in dark and light conditions the current is much higher than in an intrinsic film) which can be ascribed to the porosity of the films, which leads to a Spiro film formed at the bottom amid the perovskite particles. The hole conductivity of the Spiro film is much higher than the combined electron and hole conductivity of the intrinsic perovskite film, thus prevailing in the measured (photo)current. On the contrary, when PCBM is deposited on the perovskite film, the current gain in light conditions is much more prominent. The result of this measurement suggests that when PCBM is deposited on the film, photoexcited electrons are efficiently transferred from the perovskite to the PCBM, leaving holes as the main charge contributor to the photocurrent. In addition, PCBM was already found to passivate surface traps, which also adds up to the diminution of charge recombination [96], [180]. If there is any film of PCBM formed at the bottom of the substrate, it should not add up significantly to the photoconductivity as this would be observed in the responsivity-wavelength dependence which would have to roughly follow the optical absorption of PCBM. In our case the responsivity-wavelength dependence follows the absorption spectrum of perovskite, starting at the absorption onset at around 810 nm (Figure 5.5b). The transient current response when the device is brought from light into dark conditions as shown in Figure 5.6 confirms that the charge extraction is much more efficient when PCBM is deposited on top of the perovskite film. Without the PCBM less photogenerated charges are extracted and they reside in the perovskite crystal structure for longer a period of time before they are extracted, contributing to the slowly retreating current.

Solvent annealing turned out to be a rapid method for recrystallization of thicker films created from the starting sub-micrometer perovskite particles. Rapid melting of perovskite particles and subsequent release of solvent vapor leads to various morphologies driven by the parameters used in annealing (e.g. temperature, amount of solvent, directional flow of the vapors, etc.). If the control over the final morphology is achieved in the future experiments, both of the presented morphologies can be used in various applications. Few micrometer-sized fused grains (presented in Figure 5.7c) could be used for lateral devices, for example in basic photodetectors (X-ray or visible) where the electrodes are beneath the particles and pinholes would not have a direct effect on the

performance. For large single crystals the application could be extended to vertical devices as well (solar cells) if the number of pinholes are minimized and the junctions between the crystals are not exposing the electrode beneath. In the case where electrodes would be put on top in the form of flexible layers (e.g. carbon cloth electrodes [181]) pinholes with characteristic lateral size smaller than the thickness of the perovskite film would not have any detrimental effect on the performance of a device, since there is no deposition involved which could cause shunting paths between electrodes.

5.5 Conclusions

We demonstrated a simple, yet effective and environmentally friendly MAPbI_3 particle synthesis, with high yields and a good control over the particle size by the number of steps carried out in the synthetic procedure. Obtained particles were deposited on large substrates with a bar-coating technique, creating thick films which were used in a simple opto-electronic device. Finally we demonstrated a possible route towards large single crystals of perovskites directly on flat substrates, created by a rapid solvent annealing technique. The work presents a few novel steps of synthesis, deposition and monocrystalline perovskite formation that could mark the future use of organolead halide perovskites for large-scale production in various opto-electronic devices.

Chapter 6

Self-Assembled Siloxane Functionalized Fullerene Layers in Perovskite Solar Cells

This chapter presents the work on functionalization of transparent conductive oxide (TCO) electrode by self-assembled fullerene derivative used as an electron transporting layer in perovskite solar cells. The work addresses a few of the issues connected to the electrical instability of conventionally structured perovskite solar cells as well as to a complex, high-temperature preparation of typically used metal oxides as an electron transporting layer. The work presented is based on the synthesis of siloxane functionalized fullerene derivative which can self-assemble on top of a clean transparent conductive oxide electrode. A monolayer of these molecules turned out to be sufficient to act as an electron transporting layer in perovskite solar cells, greatly diminishing the effect of hysteresis, a source of electrical instability. Performance of solar cells employing self-assembled monolayer of siloxane functionalized fullerenes showed no degradation upon irradiation with ultraviolet light in contrast to conventionally used TiO_2 . Furthermore, the work presents a step forward in simplification and scalability of the deposition of electron transporting layers by using a low-temperature dip coating technique suitable for large-scale industrial manufacture.

At the time of the completion of the doctoral dissertation, results presented here were included in the paper accepted in the *Journal of Materials Chemistry A*, 2017, DOI: 10.1039/C7TA02405C.

6.1 Introduction

Perovskite solar cells made by using low-cost fabrication techniques have already exceeded the threshold of 20% stabilized efficiency [7], [114], [182], [183]. Thus, they have the potential to enable a reduction in the cost of generating electricity from sunlight in comparison to conventional material systems. However, significant effort is still required in the development of device architectures that can guarantee reliable and cost effective solar cells in order to move these promising lab-scale results towards quick industrial scale-up.

Anatase titanium dioxide, processed as a compact (cTiO_2) and/or mesoporous layer, is a wide band-gap semiconductor often used as the electron transporting layer in standard structured PSCs because its electronic structure supports efficient collection of photoexcited electrons from the perovskite conduction band, whilst the large valence

band offset blocks holes effectively [7], [184]. However, it usually requires high-temperature sintering (at least 450°C) [59], induces electrical instabilities reflecting in the current-voltage hysteresis [94], [185], [186] and causes degradation of solar cell's power output under the illumination of the UV solar spectrum region [120], [187]. The limitations of TiO₂-based ETLs can be partly avoided by additional interfacial thin films of fullerenes [188], their derivatives [56], [189]-[195] or other organic layers [196]. Another approach is to completely replace the metal oxide ETLs with fullerene-based organic layers either as a standalone [197]-[203], multilayered films [204]-[206] or in the form of a bulk heterojunction with the light harvesting layer [97], [207]-[209]. From the point of view of the deposition method, organic layers are mostly spin-coated, however, thermal deposition in vacuum [56], [197], [198], [202], [206] and dip coating with self-assembly were also demonstrated as promising alternatives [75], [160], [196], [210].

Apart from the incorporation in a standard device structure, Phenyl-C61-butyric acid methyl ester (PC₆₁BM) and other fullerene-based molecules found their use in highly efficient inverted perovskite solar cells [50], [105], [211]-[221]. The main reasons behind the use of fullerene-based molecules are their good electron transporting properties in conjunction with the ability of interface trap states passivation, improving the charge extraction and consequently reducing electrical instabilities in the form of J-V hysteresis [96], [97], [180], [207].

One of the key challenges for the fully solution-based preparation of solar cells employing organic layers, such as fullerenes, is ensuring that the subsequent processing steps do not damage layers processed earlier in the fabrication procedure. Since in the standard n-i-p architecture the perovskite is most commonly solution-processed on top of the ETL, the layer incorporating fullerenes needs to be indestructible during further processing with polar aprotic solvents, e.g. DMF, DMSO, γ -Butyrolactone (GBL) or similar, and insensitive to moderate thermal annealing. If this criterion is not met, the quality and reproducibility of the final device may be greatly reduced due to the dissolution of the fullerene film [199]. Last but not least, solution deposition methods for C60 and its derivatives must minimize the consumption of expensive materials by using low-waste deposition methods and applying ultrathin layer thicknesses, making dip coating, supported by the self-assembly of organic layers on top of the substrate, the most suitable deposition technique. Control of the material consumption and the film thickness is of paramount importance for the reduction of parasitic absorption within a device and the overall costs of the large-scale device manufacturing.

The aforementioned processing challenges have so far been approached by covalent binding of fullerene derivatives or other molecules to the TiO₂ [196], [210] or SnO₂ surface [222]. Another possible solution would be a direct functionalization of the underlying transparent electrode. One of the most used methodologies for the covalent modification of conductive ceramics such as tin-doped indium oxide (ITO) and fluorine-doped tin oxide is the silanization technique. Silane molecules are generally cheap, easy to handle, and can be quickly bound to oxygen containing substrate surfaces using standardized recipes either via dip coating, spray coating or CVD, which makes the silanization approach a well-recognized technology in industrial coating applications [223]. The silanized layers show long-term stability to moisture, UV, heat and solvent resistance once cured, together with a good adhesion to many different substrates [224], [225]. By controlling the humidity conditions during the process, it is possible to tune the thickness of the functional layer, from a monolayer (dry conditions) to a thick cross-linked multilayer (humid conditions) [226]. Of course, this can alter the chemical and electronic properties of the modified substrate as well as the processability and quality of the coating.

The possibility of decorating C60 with alkyl siloxane moieties by employing azomethine ylides cycloaddition reactions and subsequently of covalently modifying silica nanoparticles and films with good yields has already been demonstrated [225], [227]. Recently, Wojchietowski and co-workers presented the use of a crosslinked silanized fullerene molecule, creating a thick (10 nm) fullerene layer as an ETL for PSCs [228]. The crosslinking of the spin-coated silanized fullerene layer was in their case initiated by exposing the layer to vapors of trifluoroacetic acid.

Here we show, for the first time, the possibility of a direct functionalization of the semitransparent electrode by the formation of an electron transporting layer through a silanization-promoted self-assembled monolayer of functionalized fullerene molecules, overcoming the use of thick charge selective layers provided by other deposition techniques. By using a scalable dip coating technique, we demonstrate the fabrication of a conformal, chemically robust layer resulting in efficient and stable solar cells with reproducibility comparable to analogously prepared cells based on a spin-coated C60 layer, without the use of TiO₂ or any other additional material as ETL.

6.2 Experimental Methods

6.2.1 Device fabrication

Glass substrates coated with fluorine-doped tin oxide (FTO, 10 Ohm/sq) were successively cleaned in a Hellmanex solution (1 vol.% in de-ionized water), de-ionised water, acetone and 2-propanol by ultrasonic agitation. Afterwards they were treated with O₂ plasma for 10 min. Sil-C60 SAM treatment: Silanization of the substrates was carried out in a dry box at a relative humidity below 10%. Clean substrates were dipped inside a 0.1 mgml⁻¹ Sil-C60 solution in anhydrous toluene (Sigma-Aldrich-244511) for 45 min at 50°C. Later the substrates were rinsed with anhydrous toluene twice and dried on the hotplate at 110°C for 20 min. For comparison, Sil-C60 SAM samples in humid air under the fume hood were prepared following the same procedure just described. The relative humidity inside the fume hood during the FTO modification was above 60%.

Thin films of pristine C60 were prepared by spin coating 10 mgml⁻¹ C60 (Solenne 99.5%) solution in 1,2-Dichlorobenzene (Sigma-Aldrich-240664) at 4000 rpm for 30 s on clean FTO substrates immediately after the 10 min O₂ plasma treatment. The substrates were subsequently annealed at 110°C for 20 min. These steps were performed in a nitrogen-filled glove box.

The compact TiO₂ layer was prepared by spin coating compact TiO₂ precursor on top of a clean and O₂ plasma treated FTO at 2.000 rpm, subsequently sintered on a hotplate at the temperature of 500°C for 45 min. The precursor was prepared by mixing Titanium(IV) isopropoxide (Sigma-Aldrich 377996) with anhydrous 2-Propanol (Sigma-Aldrich 278475) in a 1:8 volume ratio, adding 4.5 µl of 2 M HCl per 1 ml of precursor mixture.

The perovskite precursor solution for the SEM morphological study was prepared by mixing 1 M solutions of cesium lead triiodide (CsPbI₃) and formamidinium lead triiodide (FAPbI₃) in a 0.175:0.825 volume ratio. CsPbI₃ and FAPbI₃ were prepared by mixing equimolar amounts of CsI (Sigma-Aldrich 203033) and PbI₂ (Alfa Aesar 12724) and FAI (DYESOL 879643-71-7) and PbI₂ respectively. Both precursor solutions were prepared in a solvent mixture of anhydrous Dimethyl sulfoxide (Sigma-Aldrich 276855) and *N,N*-Dimethylformamide (Sigma-Aldrich 227056) in a 3:7 volume ratio. Spin coating of the perovskite layers was done with a solvent quenching technique [68], [70] in a 2-step manner, first 2000 rpm (2000 rpms⁻¹ ramp) for 10 s followed by a 5000 rpm (5000 rpms⁻¹

ramp) for 30 s. 300 μl of toluene was dripped onto the substrate after 10 s of the second step. Substrates were immediately put on a hotplate at 170°C for 10 min.

Perovskite precursor solution for solar cells was prepared by mixing 1 M formamidinium lead bromide (FAPbBr_3), formamidinium lead iodide (FAPbI_3), cesium lead iodide (CsPbI_3), and methylammonium lead iodide (MAPbI_3) in a 0.1:0.65:0.05:0.2 volume ratio. FAPbBr_3 and MAPbI_3 were prepared by mixing equimolar amounts of formamidinium bromide (DYESOL 146958-06-7) and lead bromide (Alfa Aesar 10720) and methylammonium iodide (DYESOL 14965-49-2) and lead iodide, respectively. All precursor parts were prepared in a solvent mixture of DMSO and DMF in a 3:7 volume ratio, except the CsPbI_3 , which was prepared in 3:2 DMSO:DMF volume ratio. Spin coating of perovskite layers for solar cells was done with a solvent quenching technique in a 2-step manner, first 2000 rpm (2000 rpm s^{-1} ramp) for 10 s followed by 5000 rpm (5000 rpm s^{-1} ramp) for 50 s. 300 μl of toluene was dripped onto the substrate after 30 s of the second step. Perovskite films were annealed at the temperature of 110°C for 1 h. After the annealing, the substrates were left to cool down. Afterwards 2,2',7,7'-Tetrakis[*N,N*-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene (Spiro) was spin coated at 4000 rpm (4000 rpm s^{-1} ramp) for 30 s. The solution was prepared by adding 73 mg of Spiro into 1 ml of chlorobenzene (Sigma-Aldrich-284513), then adding 28.8 μl of 4-tert-Butylpyridine (Sigma-Aldrich-142379) and 17.5 μl of 520 mg/ml Bis(trifluoromethane)sulfonamide lithium salt (Sigma-Aldrich-544094) solution in anhydrous acetonitrile (Sigma-Aldrich-271004). After the Spiro deposition the samples were removed from the glovebox and left in a desiccator for 12 h to complete the Spiro doping. Devices were completed with a 50 nm Au top contact, thermally evaporated at a pressure of 1×10^{-6} mbar.

6.2.2 Device Characterization

All devices were measured under AM1.5 simulated solar illumination (Oriel Sol3A, Newport) calibrated using a certified Si reference diode at an intensity of 100 mW cm^{-2} , except for devices used for treatment comparison in humid and dry environment, which were measured at an intensity of 88 mW cm^{-2} . The current density-voltage (J-V) characteristics and the stability of the current/power output with time were recorded with a Keithley 2400. No light soaking or prebiasing was applied before the J-V measurements. The calculated power conversion efficiency curves were, only in this case, normalized to 1 sun intensity. The illuminated electrode area, defined with a black anodized aluminium mask, was 9.38 mm^2 .

The stability of the solar cells to UV light exposure was tested by storing the devices in a nitrogen filled glovebox (equivalent to a perfect encapsulation against oxygen and water). Devices were exposed to a 36 W UV lamp (spectral irradiance presented in Figure B.8), or kept in the dark as a control. To measure their performance, the devices were periodically removed from the glovebox temporarily for measurements using the aforementioned solar simulator, and then immediately returned.

6.2.3 Electrochemical characterization

Cyclic Voltammetry (CV) was performed using a potentiostat/galvanostat PGSTAT302N (Ecochemie, MetroOhm) in acetonitrile (ACN) solutions with 5 mM ferrocene as redox probe and 0.1 M tetrabutylammonium tetrafluoroborate (TBATFB) as electrolyte. A platinum counter electrode (Amel) and a Ag/AgCl (KCl sat) reference electrode (Mettler Toledo) were used. The working electrode was a bare FTO or a Sil-C60 SAM sample masked with a kapton tape shaping 0.025 cm^2 active area.

Measurements were performed at room temperature in standard conditions. The scan rate was 0.025 Vs^{-1} . At least three CV scans were collected and the last one is shown in the manuscript. Electrochemical impedance spectroscopy (EIS) measurements were performed using the Frequency Response Analyzer (FRA) module of the potentiostat, biasing samples at 0.46 V (versus Ag/AgCl) with 5 mM ferrocene in ACN, using a perturbation signal of 10 mV scanning frequencies from 1 Mhz to 0.1 Hz. NOVA 1.11 software was used for fitting FRA experimental data and analyzing CVs.

6.2.4 Computational details

Density functional theory (DFT) calculations were carried out using the Gaussian 09 program (revision B.01) [229]. The hybrid B3LYP functional and the 6-311G(d,p) basis set were employed.

6.2.5 Wettability measurements

An OCA 15 EC system was used for the study of the contact angle of water drops on different substrates. Measurements were carried out by the sessile drop method. The volume of the water droplet used for determination of contact angles was $1 \mu\text{l}$. Digital images were captured with a CCD-camera with a resolution of 752×582 pixels. The image is elaborated by the software SCA-20, in order to define the exact value of the contact angle.

6.2.6 SEM image grain size analysis

Grain size analysis was performed using Gwyddion 2.40 software, using watershed grain analysis and related statistical tools [230]. Error bars are given by averaging 4 different samples for each condition.

6.3 Results and Discussion

Figure 6.1 displays the anchoring mechanism of *N*-[3-(triethoxysilyl)propyl]-2-carbomethoxy-3,4-fulleropyrrolidine (Sil-C60) on bare fluorine doped tin oxide electrode. The synthesis of Sil-C60 has been carried out following a slightly modified previously reported procedure [198], which results in a higher yield of modification (experimental details in Appendix B) [225]. Self-assembly of Sil-C60 on the surface of an FTO electrode was carried out in a low humidity environment ($<10\%$ R.H.) inside a dry box by the immersion of the FTO substrates into a 0.1 mgml^{-1} Sil-C60 solution (see Experimental Methods). Thoroughly cleaned bare FTO surface was activated by oxygen plasma (O_2 plasma) in order to increase the amount of hydroxyl surface terminated groups, boosting the subsequent covalent attachment of Sil-C60. Dry conditions and quick reactions promote the self-assembly mechanism avoiding the development of thick cross-linked coatings. After a final curing step at a relatively low temperature (110°C), an FTO surface modified with a covalently anchored self-assembled monolayer of functionalized C60 molecules was obtained, defined from now on as Sil-C60 SAM.

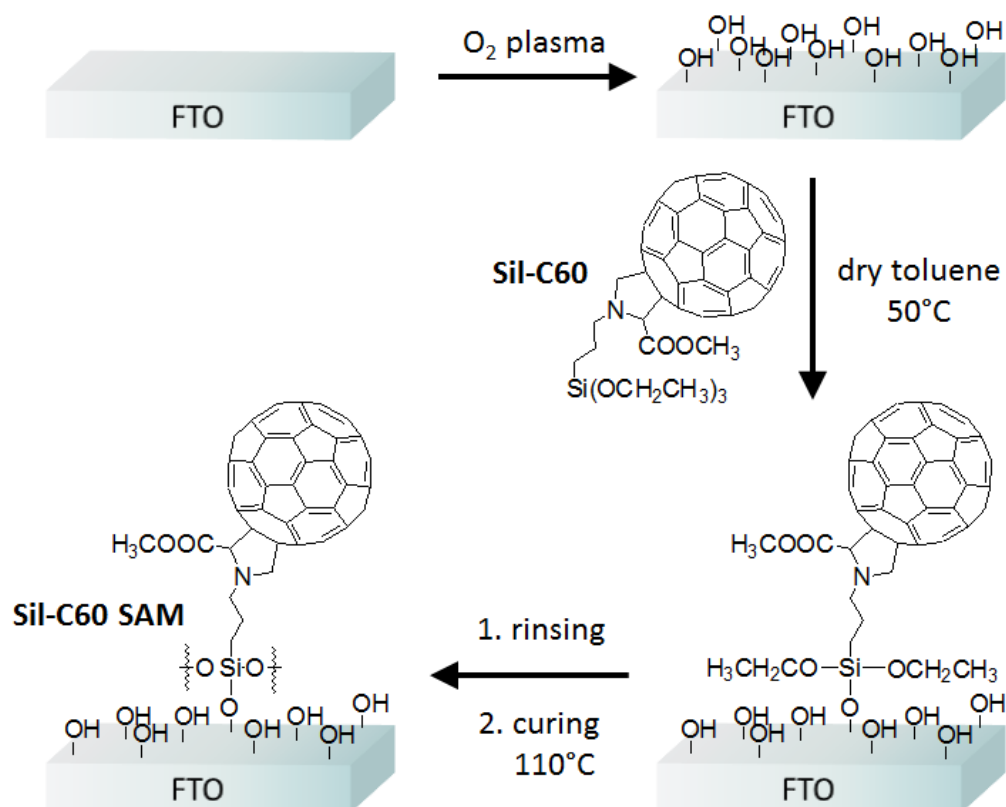


Figure 6.1: Schematic illustration of the Sil-C60 SAM deposition. Illustration of the fullerene self-assembled monolayer (Sil-C60 SAM) fabrication process, involving the covalent anchoring of Sil-C60 on an oxygen plasma-activated FTO substrate.

We assessed the chemical stability of the functionalization by comparing the FTO/Sil-C60 SAM substrate with a solution-processed C60 layer by measuring water contact angles of the modified substrates before and after the treatment of the samples in a hot (120°C) DMF bath. We thus simulated potentially damaging conditions for such an organic layer during the perovskite processing, which have been previously used, for example, in the hot casting technique [24], [66] or a 2-step perovskite deposition technique using precursor solutions at an elevated temperature [58]. The results of contact angle measurements are presented in Figure 6.2 and summarized in Table 6.1.

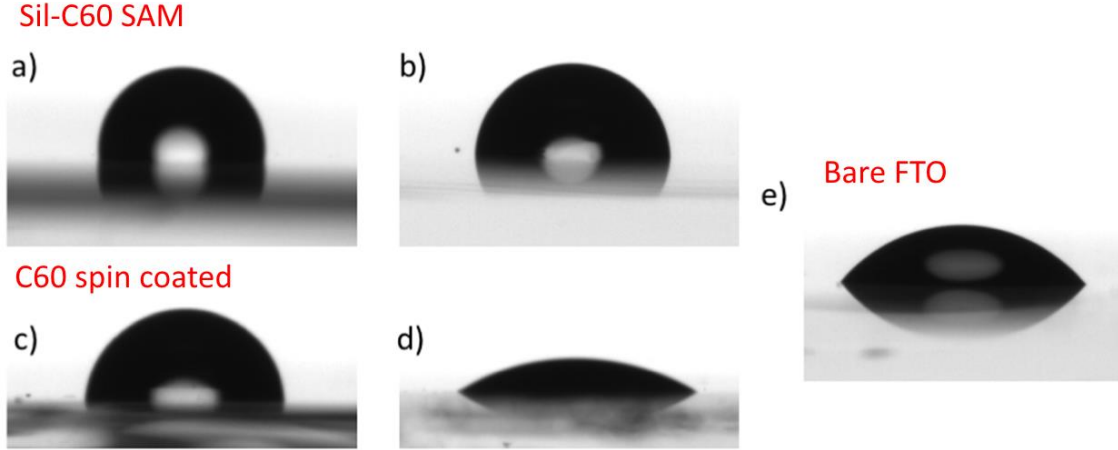


Figure 6.2: Wettability measurements on various ETLs. Wettability measurements on FTO-modified surfaces with Sil-C60 (Sil-C60 SAM) and solution-processed fullerene (C60 spin coated). a) and c) refer to as-deposited samples while b) and d) denote samples after 5 min immersion in a hot DMF bath; e) refers to a bare FTO used as a reference sample. The volume used to form water droplets was 1 μ l.

Measurements revealed high water contact angle on top of the Sil-C60 sample before and after the treatment in a hot DMF bath, while the spin-coated C60 fullerene sample shows a strongly reduced contact angle after the treatment, with a value which is smaller than that of a bare FTO. This is probably due to highly polar DMF molecules remaining chemisorbed on the surface, increasing the hydrophilicity of the substrate. These results confirm the robust covalent origin of the bond between Sil-C60 and FTO, whereas in the case of spin-coated C60 the layer is only weakly interacting with the surface, which results in its partial dissolution after hot DMF treatment. Moreover, the relatively high standard deviation of the contact angle value before DMF treatment for the C60 spin-coated sample reveals an intrinsic inhomogeneity of the surface coverage as a result of a combined effect of electrode surface roughness and spin coating dynamics which can ultimately affect the reproducibility of solar cells built structured on top.

Table 6.1: Water contact angles on various samples. Summary of wettability measurements on samples shown in Figure 6.2. Error bars refer to at least five repetitive measurements on the same sample in different areas and three different substrates per each type.

	Contact angle ($^{\circ}$)	
	As deposited	After DMF treatment
Bare FTO	53 ± 1	/
Sil-C60 SAM	98 ± 3	85 ± 0.5
Spin coated C60	76 ± 10	19.7 ± 0.5

Before proceeding in the PSCs development, and in order to gather information on the thickness and surface coverage of the FTO by the Sil-C60 SAM before and after the DMF treatment, we tested the functionalized substrate through cyclic voltammetry (CV)

and electrochemical impedance spectroscopy (EIS). Experimental details on electrochemical measurements are given in the Experimental Methods section. First, the barrier effect towards the diffusion of a charged redox probe in solution after electrode modification was studied by CV (Figure 6.3a) [231]. Here, the positively charged redox probe (ferrocene) is employed to assess the faradic response of a bare FTO electrode and of a functionalized one. The CV clearly shows a quasi-irreversible electrochemical process occurring at the bare FTO surface ($\Delta E = 0.24\text{V}$), whereas almost no faradic current is detected when performing CV on Sil-C60 SAM under the same conditions. These results suggest a complete modification of the FTO surface by the Sil-C60 molecules [205]. Stability tests, i.e. several CVs in ACN, confirm the chemical and electrical resistance of the modification (Figure B.4 in Appendix B).

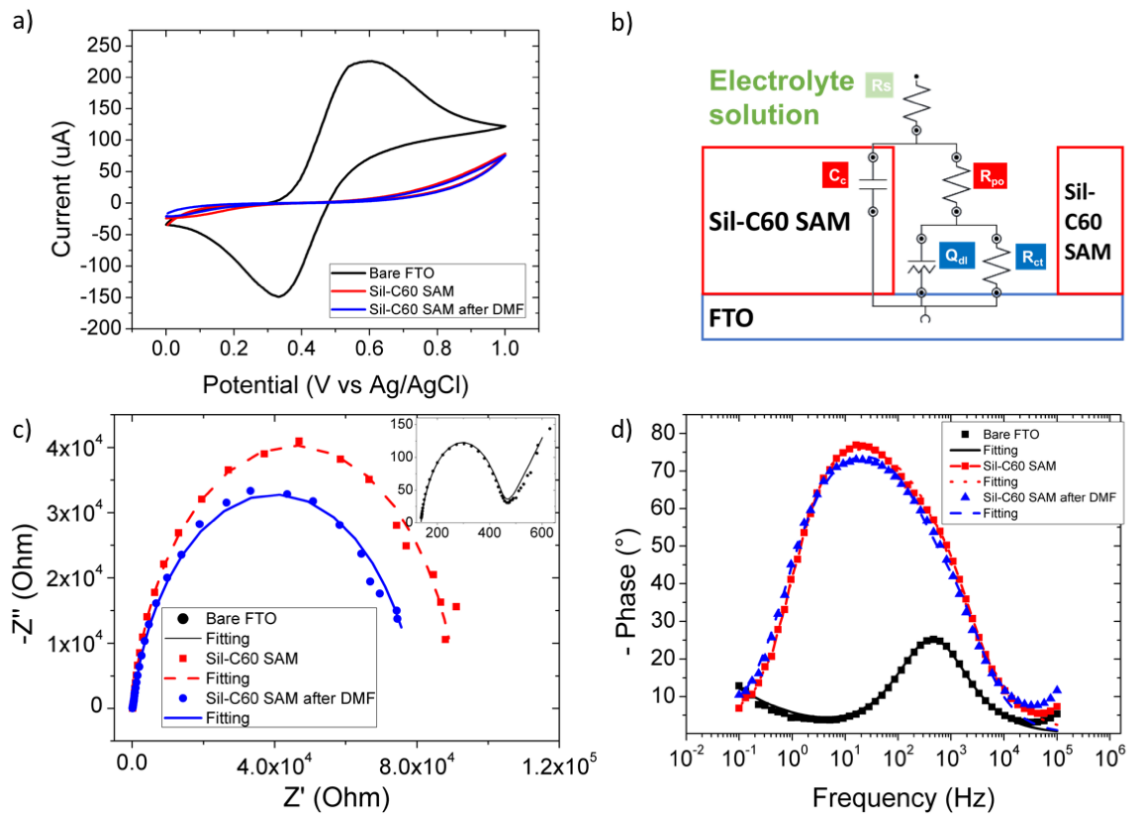


Figure 6.3: Electrochemical characterization of Sil-C60 SAM and FTO surface. Electrochemical characterization of Sil-C60 SAM before and after DMF treatment and bare FTO. a) Cyclic voltammetry (CV) with a ferrocene redox probe (5 mM in ACN solution); b) equivalent circuit for defective Sil-C60 SAM used for the fitting of experimental impedance data in panel c) and d); c) Nyquist plot and d) Bode phase plot of Sil-C60 SAM sample; the inset graph in c) shows Nyquist plot of the bare FTO sample. CVs were performed at 25 mVs^{-1} (reference electrode: Ag/AgCl; electrolyte: TBATFB 0.1 M in ACN; EIS performed at 0.46 V versus Ag/AgCl with 5 mM ferrocene). Fitted parameter values are shown in Table B.1 and Table B.2.

Electrochemical impedance spectroscopy (EIS) also allows characterization of the thickness of the fullerene layer. A simple equivalent circuit model is used for fitting the experimental data and is presented in Figure 6.3b. This circuit is often used for modeling damaged thin coatings in corrosion studies [232], [233] R_s represents the solution resistance, R_{po} is the ion resistance through the coating (pores or pinholes present within

the coating), C_c is the capacitance related to the ion accumulation at the surface of the intact coating, R_{ct} is the charge transfer resistance between the electrolyte and the FTO, and Q_{dl} is a constant phase element (CPE) related to the pseudo-double layer capacitance at the FTO surface [234]. Table B.1 and Table B.2 summarize all of the fitted values for the different samples. It is possible to determine the thickness of the coating starting from Q_{dl} and to estimate the surface coverage starting from R_{ct} [235]. Therefore, by fitting the experimental data in Figure 6.3c and Figure 6.3d, coating capacitance values of $C_c=649$ nF and 675 nF for the Sil-C60 SAM sample and Sil-C60 SAM sample treated with DMF respectively are obtained. Using Eq. B.1 it is possible to obtain information about the thickness of the coating, by knowing the dielectric constant of the coating. Assuming a value that should be similar to a bare fullerene and PCBM (3.9-4.5 [236]) we obtained a nominal thickness for the silane layers of approximately 1.4 ± 0.2 nm substantially unchanged before and after the DMF treatment. Moreover, the surface coverage calculated with Eq. B.2 is estimated to be 99.5%, a result in agreement with CV outcomes [234]. The Nyquist plot in Figure 6.3c and the Bode phase plot in Figure 6.3d offer a complete view of the mechanisms involved in the electrochemical reaction at the electrode interface. The bare FTO (black curve in the inset graph in Figure 6.3c) exhibits behavior consistent with a modified Randles cell: one semicircle at higher frequencies, i.e. a single time constant for the phenomenon; and a well-defined Warburg diffusion element in the circuit at low frequencies [237]. In contrast, the Sil-C60 SAM modified FTO samples show elliptical semi-circles with larger radii, i.e. we can assume the existence of two distinct time constants originating from different phenomena. Thus, in agreement with the time constants obtained by fitting the electrical circuit model in Figure 6.3b, two RC contributions are found (Figure 6.3d, blue curve): the main peak at lower frequencies (at about 10 Hz) is assigned to the charge transfer reaction at the interface between the solution and the coating (i.e. the actual electrochemical reaction taking place at the modified real interface), whereas the higher frequency peak (at about 1 kHz) is due to an electrochemical reaction taking place at the surface of the underlying FTO electrode, quite similar to the bare FTO resonance peak (black curve in Figure 6.3d). We can then conclude that the slower phenomena (i.e. the ones at lower frequencies) occurring at the modified interface are the limiting electrochemical reactions occurring at the modified electrode, thus explaining the lack of faradic current in CV in Figure 6.3a.

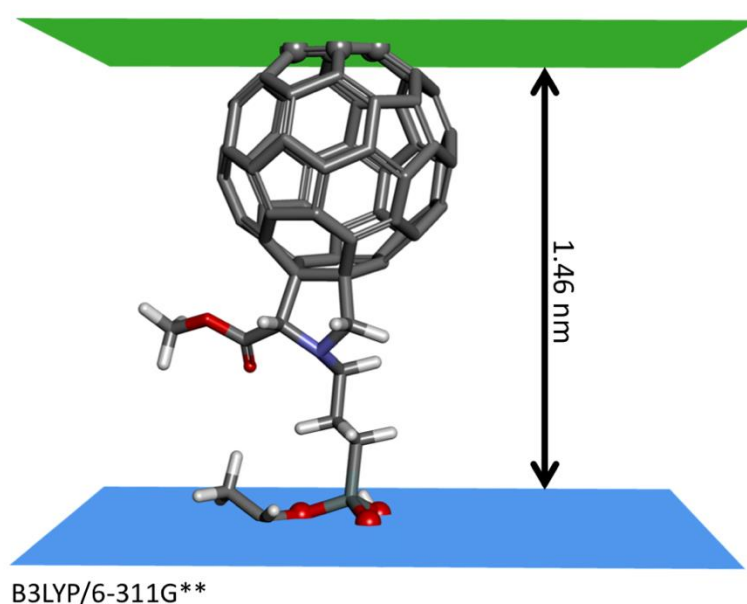


Figure 6.4: DTF calculated Sil-C60 minimized geometry. Minimized geometry of Sil-C60, as calculated through DFT, highlighting the distance between the siloxane oxygen atoms and the opposite edge of C60 (see text).

To develop a model for better description of the Sil-C60 SAM morphological properties we performed DFT calculations (B3LYP/6-311G**, see Experimental Methods for details) on isolated Sil-C60. The calculations revealed a distance of 1.46 nm between the plane containing the three oxygen atoms bound to Si and the furthest parallel plane containing C atoms on the C60 moiety (see Figure 6.4). Based on this estimation and on the outcome of our electrochemical study, which provided a value of 1.4 nm for the thickness of the fullerene-based layer on top of FTO, we can infer the presence of a Sil-C60 monolayer covering the FTO surface, that remains unchanged after the DMF treatment.

Together, EIS and wettability measurements performed on the Sil-C60 SAM sample (Table 6.1) suggest a high yield of modification throughout the FTO surface with Sil-C60 molecules with small contact angle deviations over the various spots examined, showing the formation of a conformal and strongly hydrophobic surface. The huge change in the wettability of the anode surface due to the presence of a homogeneously distributed fullerene layer is likely to considerably influence the process of perovskite growth during device realization.

In order to understand whether the altered surface properties of various substrates influence the perovskite growth mechanism, we deposited thin perovskite films by spin coating a mixed cation $\text{Cs}_{0.175}\text{FA}_{0.825}\text{PbI}_3$ precursor [35], using a solvent quenching technique (see Experimental Methods). We acquired both cross-section and surface morphology SEM images of perovskite films deposited on O_2 plasma treated bare FTO (Figure 6.5a and Figure 6.5d), FTO covered with compact TiO_2 (Figure 6.5b and Figure 6.5e) and FTO covered with Sil-C60 SAM (Figure 6.5c and Figure 6.5f). Cross-section images revealed smaller crystallites interconnected into a quasi-continuous film on the bare FTO and compact TiO_2 covered FTO. In the case of a perovskite layer formed on Sil-C60 SAM modified FTO, single perovskite grains proceed from the top to the bottom of the perovskite layer. This increase in the crystallinity may reduce the trap density of states and associated trap-assisted recombination [76], [238]. Software analysis of the surface morphology SEM images (Figure 6.6) shows a gradual increase of the average

grain size from bare FTO (250 nm), to FTO covered with compact TiO_2 (270 nm) and then to FTO modified by Sil-C60 SAM (300 nm).

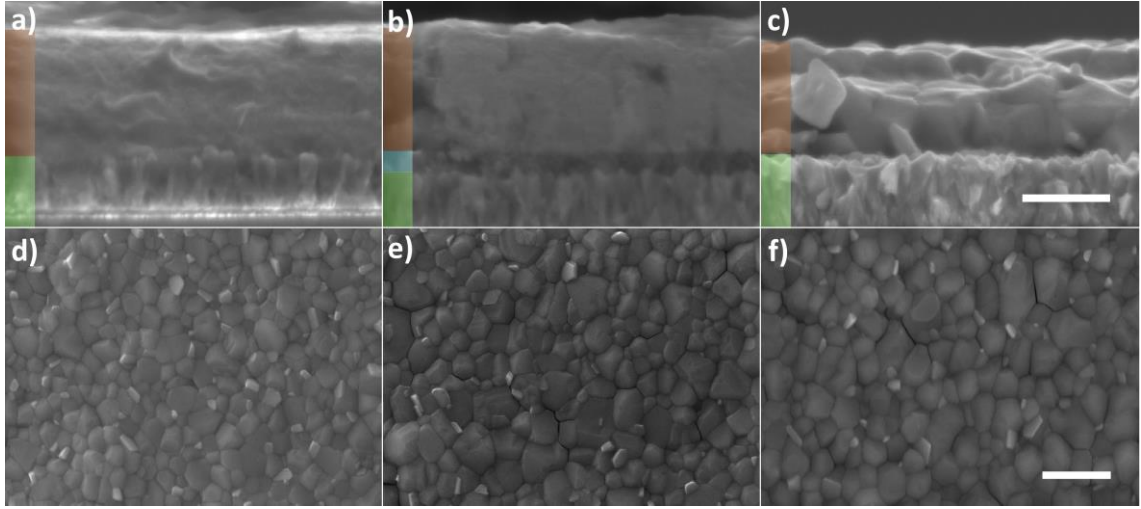


Figure 6.5: Morphological characterization of perovskite films on various substrates. Cross-section (a-c) and surface morphology (d-f) SEM images of perovskite films formed on a bare FTO (a and d), FTO covered with compact TiO_2 (b and e) and FTO modified by a Sil-C60 SAM (c and f). Shaded parts of cross-section images mark the FTO (green), compact TiO_2 (blue) and perovskite layer (brown). The length of a scale bar for cross-section images is 500 nm, for surface morphology images 1 μm .

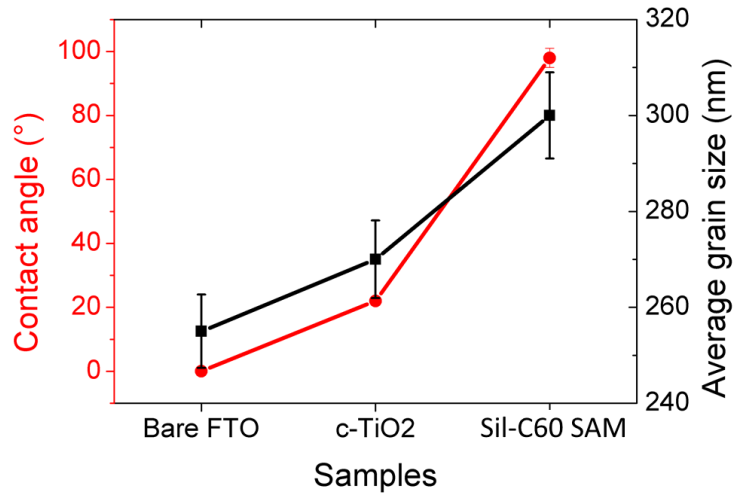


Figure 6.6: Contact angle and average grain size correlation. Correlation between the contact angle values and the average perovskite grain size obtained on various substrates.

Perovskite solar cells with Sil-C60 SAM, spin-coated C60, compact TiO_2 and bare FTO were fabricated in a n-i-p architecture (i.e. the ETL is deposited directly on the transparent electrode) and tested. The active layer was a mixed cation and anion $\text{CS}_{0.05}\text{FA}_{0.75}\text{MA}_{0.2}\text{PbBr}_{0.3}\text{I}_{2.7}$ perovskite, while Spiro was used as the hole transporting material. The device top contact was a gold cathode. The choice of using a triple cation perovskite over the conventional MAPbI_3 was based solely on the demonstrated increased environmental stability and stability under constant light illumination, providing equally high or even improved performance over MAPbI_3 [6], [114]. We carried out a coarse

optimization of a perovskite precursor solution, varying the halide (iodine to bromine) ratio to achieve near optimum performance of the solar cells. Figure 6.7a shows the current density-voltage (J-V) characteristics of the best devices.

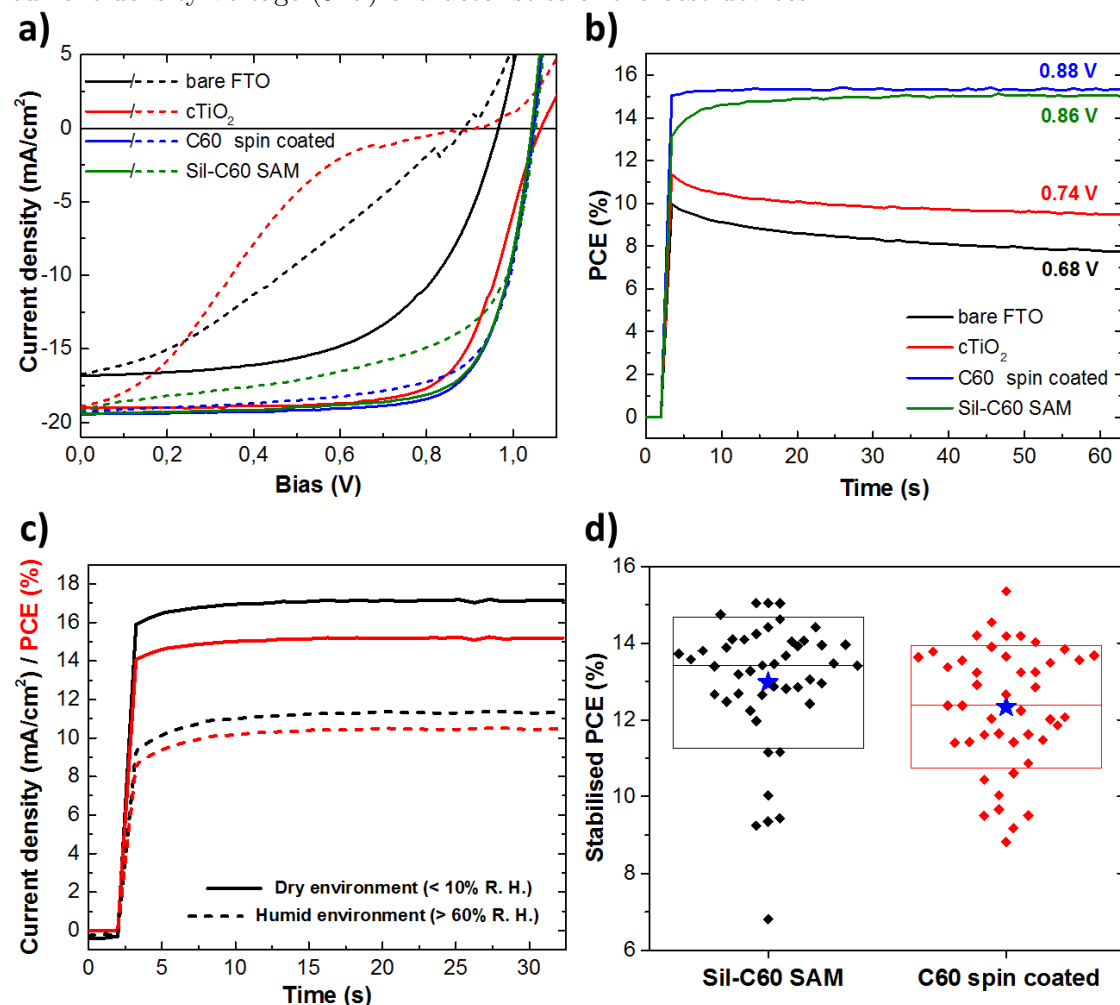


Figure 6.7: Perovskite solar cell characterization. a) J-V characteristics of devices prepared with no or with various ETLs (as indicated in the legend), presenting backward (solid line) and forward (dashed line) voltage scan direction, measured with a scan rate of 50 mVs^{-1} at the intensity of 1 sun. b) Stabilized power conversion efficiency of the best devices measured at the maximum power point. c) Stabilized photocurrents (black lines) and PCEs (red lines) of a typical Sil-C60 SAM-based device prepared in either dry (solid curves) or humid environment (dashed curves), measured at the maximum power point of 0.76 V and 0.8 V, respectively. d) Stabilized PCEs device statistics on Sil-C60 SAM and spin-coated C60 as ETLs obtained after 60 s of illumination near the maximum power point. A star symbol marks the average value and the box encloses measurements within the standard deviation. The horizontal line inside the box marks the median value. The size of the illuminated area of all devices was 9.38 mm^2 .

The figures of merit of the solar cells are presented in Table 6.2. The results reveal that devices based on FTO covered with spin-coated C60 or with Sil-C60 SAM show reduced hysteric behavior during the voltage sweep of 50 mVs^{-1} in comparison to a conventional compact TiO_2 -based device or a device without any ETL. It is well known that the interface between the bare compact TiO_2 and perovskite layers results in J-V

hysteresis [239], [240]. In order to determine the steady state performance of solar cells regardless of the voltage scan rate, we tracked the power conversion efficiency over time at a fixed applied voltage near the maximum power point (MPP) for each device, as shown in Figure 6.7b. C60 spin coated and Sil-C60 SAM show stable temporal photocurrents, reaching up to 15% PCE in both cases. The sample with FTO only and with the compact TiO_2 (cTiO_2) layer showed lower starting performances at the MPP and a reduction over time. Although we carried out a perovskite layer optimization, we believe that there is still room for improvement in solar cell performance of fullerene-based devices, especially in achieving higher photocurrents by fine-tuning perovskite layer thickness, chemical composition and the whole process of spin coating. Still, stabilized PCEs obtained with the Sil-C60 SAM employing solar cells demonstrate improved or comparable performance to other standard structured, fully solution-processed PSCs where organic-based ETLs are deposited by techniques with increased material consumption [199], [201], [209], [228]. We attribute high performance of Sil-C60 SAM to a combined effect of efficient electron extraction properties of fullerene-based molecules, beneficial influence on perovskite film formation and thickness dependent parameters, such as lower series resistance and parasitic absorption. The latter property marks Sil-C60 SAM as the most rational choice for tandem solar cells, where minimal parasitic absorption is sought for.

Table 6.2: Solar cell parameters from the best performing devices extracted from the J-V characteristics presented in Figure 6.7a. BWD and FWD denote backward and forward scan, respectively.

	Bare FTO		cTiO_2		C60 spin coated		Sil-C60 SAM	
	BWD	FWD	BWD	FWD	BWD	FWB	BWD	FWD
V_{oc} (V)	0.97	0.88	1.06	0.92	1.05	1.05	1.04	1.05
J_{sc} (mAcm^{-2})	16.8	16.7	19.0	18.9	19.5	19.4	19.4	19.2
FF	0.58	0.31	0.71	0.21	0.74	0.71	0.74	0.60
PCE (%)	10.3	5.1	14.5	3.7	15.4	14.6	15.2	12.4

How effective is the anchoring of the functionalized fullerene molecule depends on the substrate surface termination groups and the environment in which the self-assembly is carried out. To evaluate the preferred treatment conditions, we performed the Sil-C60 self-assembly onto FTO in a dry ($<10\%$ R. H.) or humid ($>60\%$ R.H.) environment. As presented in Figure 6.7c, devices produced in humid conditions showed decreased performance in terms of stabilized photocurrent and PCE at the maximum power point. We attribute this outcome to a poor bonding of Sil-C60 in the presence of water in the atmosphere in which the treatment is performed and in the Sil-C60 solution. A high concentration of water molecules in the chemical environment favors the cleavage of Si-O-Si bonds leading to the formation of patched areas of different thicknesses. Poor charge selectivity in uncovered areas contributes to a higher recombination rate of photogenerated charges nearby the electrode, effectively reducing the extracted photocurrent [241].

In order to evaluate the reproducibility of the solar cell fabrication, which depends mainly on the coverage of the perovskite layer and its underlying charge selective layer, we prepared and tested two large sets of devices employing Sil-C60 SAM and spin-coated C60 as ETL. Each device was measured by applying a bias at the MPP (priorly determined by the 50 mVs^{-1} scan measurement, using the backward scan as the reference), tracking the photocurrent and associated power conversion efficiency in time.

After 1 minute the device's PCE was taken as a stabilized value and used in the performance statistics presented in Figure 6.7d. Both sets show similar dispersion of results with average stabilized PCE values of 13.0% and 12.3% for the Sil-C60 SAM and spin-coated C60-based devices, respectively. These results confirm that although the thickness of the Sil-C60 SAM is considerably lower than the thickness of a spin-coated C60 (about 20 nm, measured by a profilometer, in agreement with the recent study [228]), it still acts as a stable electron extraction layer. This represents a significant advantage over the pristine fullerene ETL by virtue of increased chemical stability, and requiring less material using a scalable dip-coating technique. The performance statistics of compact TiO_2 -based devices was here omitted since they did not show stabilized PCEs (Figure B.7).

Finally, we have performed some preliminary experiments to evaluate the stability of each of the electron transport layers to ultraviolet light exposure under inert conditions. This experiment is important because the UV portion of sunlight commonly causes continuous cell degradation [242] in particular in devices employing TiO_2 , which has known issues involving the formation of deep lying surface defects [187], [243]. Devices were exposed to UV light continuously for 16 h in the glove box and subsequently measured under the solar simulator in normal atmosphere. The procedure was repeated for four consecutive days, with an exception of the increased illumination time on the last day (19 h), which amounted to total 67 h of UV light exposure. At that point significant differences in performance change appeared between the samples. The final results are summarized in Figure 6.8, where the average power conversion efficiency normalized to the initial values of 6-8 pixels is shown for the higher efficiency scan direction (the trends for all device parameters and opposite scan direction are given in Appendix B). We observe that the power conversion efficiency of all control samples (without the UV exposure) remains relatively constant over increased storage time. However, when devices with compact TiO_2 are exposed to UV, they exhibit continuous and rapid degradation, mainly due to a reduction in the fill factor of the backward scan direction (Figure B.5). In contrast to compact TiO_2 , devices employing C60 or Sil-C60 SAM show increased stability without any performance degradation after 67 h of UV exposure.

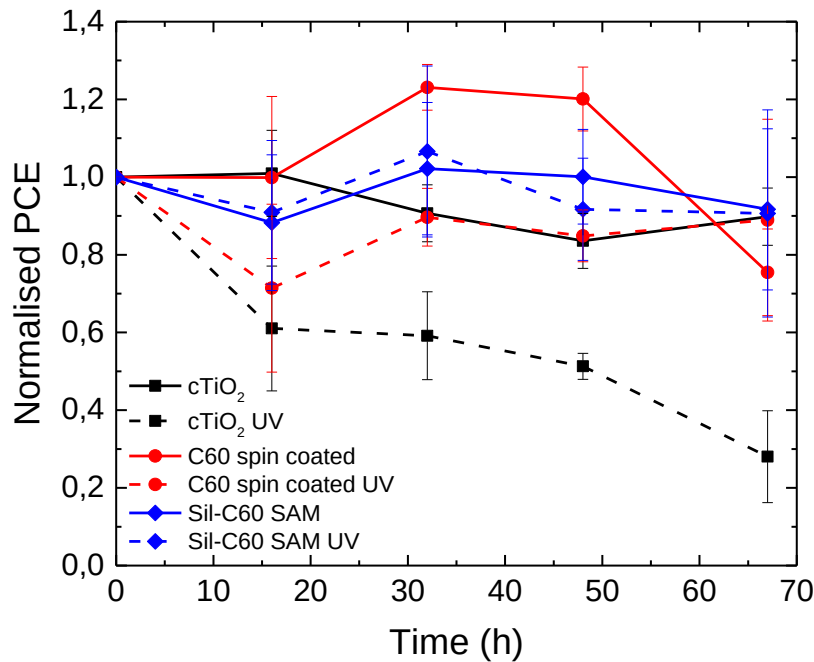


Figure 6.8: Normalized device performance upon UV exposure. Stability of the power conversion efficiency (higher efficiency scan direction, open-circuit to short-circuit) of devices fabricated with different electron transport layers over time, with or without continuous UV exposure with a 36W lamp, as indicated in the legend.

6.4 Conclusions

We show that functionalized fullerene molecules can covalently bind to a clean, oxygen terminated surface of an FTO electrode, forming a robust and conformal self-assembled monolayer. This is enough to act as an efficient and reliable electron extracting layer in perovskite solar cells, reducing the current-voltage hysteresis, without the use of any conventional ETLs. The application of strongly bound fullerene molecules as an interfacial layer not only eliminates the need of any high-temperature processing and increases the stability of the device to UV irradiation but also significantly simplifies large-scale deposition and reduces the material consumption through the mechanism of self-assembly, which makes this approach much more attractive for industrial scale production.

Chapter 7

Nano-Thin WS₂ Films as a Hole Transporting Layer in PSCs

This chapter presents the work on the application of exfoliated WS₂ as a hole transporting layer in perovskite solar cells. The work combines the main subjects of this thesis, organometal halide perovskites and layered materials in solar cells with stabilized power output of up to 6%. The main advantages of exfoliated WS₂ in perovskite solar cells in comparison to other typically used materials are its simple and low-cost synthesis and scalable deposition without affecting the composition of the perovskite film laying underneath. Deposition of WS₂ can be carried out in an uncontrolled atmosphere and does not need any additional treatment, e.g. doping, like in conventionally used organic hole transporting layers. At the time of the completion of the doctoral dissertation the manuscript was in preparation and further experiments were still ongoing to provide firm proofs of a hole-only transfer from the perovskite to WS₂.

7.1 Introduction

Perovskite solar cells are considered the fastest growing photovoltaic technology up to date due to the unmatched performance evolution in the recent years. Their performance rise can be ascribed to the solution of various problems, from stability improvement of the light harvesting layer by the use of organic and inorganic cations and halide anion mixtures [35], [114], [244], smart processing of the perovskite layer, development of the solar cell structures and the underlying layers. At this point of the research the temporal performance evolution of perovskite solar cells has converged to near its limit in a single junction configuration. Thus the research has diversified into improving long-term stability, designing new solar cell structures and furthermore simplifying production while reducing the manufacturing cost.

Despite the high initial performance of the optimized n-i-p (standard) perovskite solar cell structure, where the cell is illuminated from the side where electrons are extracted, the biggest concerns step out of the shade only during prolonged irradiation which reflects in a significant drop of solar cell's power output over time [245]. Although the reason for this performance drop is still not completely elucidated, it has been ascribed to various correlating factors. A few of these are a moisture ingress through the established organic hole transport layer towards the light harvesting layer and subsequent chemical reactions that cause irreversible degradation [113], and an oxygen-induced degradation [246]. The most detrimental is by far the moisture reaction with the perovskite layer. The contact and reaction between them is promoted by the poor film formation of spin-coated organic layers on top of the perovskite layer. One such organic layer conventionally used

as a hole transporting layer is Spiro (Spiro). It is a solution-processed organic molecule which requires external doping, first by introducing the additives Bis(trifluoromethane)sulfonamide lithium salt (Li-TFSI) and 4-tert-Butylpyridine (tBP) and later by exposure to an oxygen rich atmosphere to induce Spiro oxidation [247]. The oxidation reaction is poorly controlled due to its reversibility [117]. Furthermore, Spiro films show poor crystallinity with pinholes [248] protruding throughout the layer allowing moisture ingress as well as the diffusion of the metal cathode towards the perovskite layer which inevitably leads to a device malfunction [249]. Prolonged light soaking of the solar cell results in an increased device temperature which causes evaporation of tBP and degradation of the Spiro layer [118]. Last but not least, the majority of organic layers used in perovskite solar cells were recently determined as the most fragile layers with very low fracture resistance that often leads to cracking and delamination [250]. The origin of these detrimental effects probably resides in the deposition techniques (spin coating) as well as the amorphous nature of Spiro.

In order to overcome the aforementioned downsides of Spiro together with its large price tag we propose the use of inorganic exfoliated tungsten disulfide (WS₂) as a hole transporting layer in perovskite solar cells. WS₂ is a member of a large family of layered transition metal dichalcogenides. In its bulk form it exhibits an energy gap of about 1.3 eV, however, the energy gap can be tuned by lowering the thickness of individual nanosheets approaching the monolayer limit (2.0 eV). As a common and abundant material, together with its straightforward synthesis it is a viable option to replace organic layers in perovskite solar cells.

Here we demonstrate the use of exfoliated WS₂ as a hole transporting layer in a standard structured perovskite solar cells. The WS₂ layer is deposited by spray coating of its colloidal suspension in an uncontrolled atmosphere without affecting the underlaying perovskite film. The novel interfacial layer exhibited satisfactory charge selectivity which resulted in a stable solar cell power output.

7.2 Experimental Methods

7.2.1 WS₂ exfoliation

WS₂ powder (Sigma Aldrich) was added into a Sodium cholate (Sigma-Aldrich) solution (35 mgml⁻¹) in a mixture of ethanol and water (v:v 0.35:0.65) with a starting WS₂ concentration of 100 mgml⁻¹. The exfoliation was carried out by sonication in an ultrasonic bath for 80 h. Afterward a crude size selection was initiated by centrifuging at 2000 rpm for 10 min to remove any unexfoliated material followed by a 3-step successive high speed centrifugation at 10000 rpm for 1 h in order to remove the excess surfactant. After each centrifugation step the supernatant was decanted and a fresh starting ethanol and water mixture was added to the sediment with subsequent redispersion in the ultrasonic bath. 2 additional high speed centrifugation steps were used for solvent exchange with absolute 2-Propanol. Prior to the spray deposition the suspension was again thoroughly sonicated in a sonication bath for at least 30 min.

7.2.2 Solar cell preparation

Perovskite solar cells were prepared in a standard device configuration. First the FTO substrates were etched to form a desired electrode pattern by using Zn powder and 2 M HCl. Etched substrates were successively cleaned in 1 vol.% Hellmanex solution, de-ionized water, acetone and 2-Propanol in an ultrasonic bath heated at 55°C. Substrates

were then dried with a N_2 flow followed by a 10 min O_2 plasma treatment. The compact TiO_2 precursor was prepared by thoroughly mixing Titanium(IV) isopropoxide (Sigma-Aldrich 377996) with anhydrous 2-Propanol (Sigma-Aldrich 278475) in a 1:8 volume ratio, adding 4.5 μ l of 2 M HCl (Sigma-Aldrich 435570) per 1 ml of precursor mixture. Afterwards the precursor solution was spin coated on freshly O_2 plasma treated substrates at 2000 rpm for 30 s. Immediately afterwards, the substrates were put on a hotplate at the temperature of 150°C. Sintering of TiO_2 was initiated by a 30-min ramp to the final temperature of 500°C, at which the substrates were left for 45 min. After the end of the sintering cycle at 500°C the substrates were left to cool down to 100°C and were, still hot, transferred inside the glove box.

Prior to the perovskite layer deposition a 10 $mgml^{-1}$ [60]PCBM (Solenne BV) solution in anhydrous toluene (Sigma-Aldrich 244511) was spin coated on top of $cTiO_2$ at 2000 rpm for 60 s, dried at the temperature of 110°C for 15 min and cooled down to room temperature before further processing. 1 M perovskite precursor solution of $CS_{0.175}FA_{0.825}PbBr_{0.3}I_{2.7}$ was prepared by mixing 1 M $CsPbI_3$, $FAPbI_3$ and $FAPbBr_2I$ solutions in a 0.175:0.675:0.15 volume ratio. All basic precursor solutions were prepared in a 3:7 DMSO:DMF volume ratio. The final precursor solution was then spin coated onto the FTO/ $cTiO_2$ /[60]PCBM covered substrates with a 2-step spin coating procedure, first 10 s at 2000 rpm followed by a 5000 rpm for 30 s. After 10 s of the second step, 300 μ l of anhydrous toluene was dripped onto the spinning substrate. After the end of the second spin coating step, the substrates were put on a hotplate at 170°C for 10 min and then left to cool down. Spiro (2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene), a hole transport layer of the control solar cells, was spin coated onto the perovskite film at 4000 rpm for 30 s. The Spiro solution was prepared by adding 73 mg of Spiro into 1 ml of chlorobenzene (Sigma-Aldrich-284513), then adding 28.8 μ l of 4-tert-Butylpyridine (Sigma-Aldrich-142379) and 17.5 μ l of 520 $mgml^{-1}$ Bis(trifluoromethane)sulfonamide lithium salt (Sigma-Aldrich-544094) solution in anhydrous acetonitrile (Sigma-Aldrich-271004). Control devices employing Spiro were transferred out of the glove box into a desiccator to induce Spiro oxygen doping for 12 h. Perovskite-covered substrates prepared for WS_2 deposition were transferred out of the glove box and put on a hotplate at 130 C. WS_2 colloidal suspension in absolute 2-Propanol was spray coated over the substrates from a distance of approximately 15 cm using N_2 as a carrier gas at the pressure of 0.2 bar. Immediately afterwards the substrates were brought back to the glove box. Both sets of devices, the controls and those employing WS_2 as a hole transport layer were finished by a 50 nm of thermally evaporated gold (Au) at the pressure of 10^{-6} mbar.

7.2.3 X-ray diffraction

X-ray diffraction pattern was acquired on a Bruker D8 advanced diffractometer with Bragg-Brentano geometry, a Cu-based X-ray source ($K\alpha_1; \lambda=1.544060 \text{ \AA}$) operating at 40 kV and 40 mA, with a 0.02° (1 s) step.

7.2.4 UV-Vis spectroscopy

Absorption spectra were measured on a Perkin Elmer Lambda 1050 spectrometer.

7.2.5 Ultraviolet photoelectron spectroscopy

Photoemission spectra were acquired on Kratos Axis Ultra spectrometer using a He I (21.22 eV) discharge lamp as a photon source.

7.2.6 Electron microscopy analysis

High resolution transmission electron microscopy (HR-TEM) was performed on a Jeol JEM-2100 microscope. 10 μl of WS₂ colloidal suspension in water/ethanol mixture with the concentration of about 0.1 mgml⁻¹ was drop-casted onto a holey carbon copper grid (mesh 300) and dried.

Scanning electron microscope images were acquired with a Zeiss SUPRA40 Field Emission SEM.

7.2.7 Photoluminescence

The steady state photoluminescence signal was acquired on a Raman setup with a green laser (532 nm) as the excitation source. The light intensity of the laser was attenuated by a factor of 10⁻⁶ to avoid saturation of the signal on the detector and degradation of the perovskite layer. Average thickness of the WS₂ layer on top of the perovskite film was about 5-7 nm. The wavelength step for the PL detection was 0.05 nm with 0.1 s of acquisition time at each step.

7.3 Results and Discussion

The WS₂ colloidal suspension was prepared by intense sonication of WS₂ powder in a sodium cholate solution (details in Experimental Methods). The result of the exfoliation was determined by optical absorption spectroscopy and transmission electron microscopy (TEM). Absorption spectrum of the as-exfoliated WS₂ colloidal suspension, cleaned of excess surfactants, is presented in Figure 7.1a where a clear WS₂ excitonic feature centered around 627 nm (1.98 eV) is observed. According to the analysis reported in the literature the measured excitonic peak position indicates an average thickness of the nanosheet ensemble of about 5-8 monolayers with lateral sizes on the order of 100 nm [233]. The WS₂ colloid was additionally analyzed with a TEM to evaluate the morphological properties on nanometric scale, as presented in Figure 7.1b-d. The imaging revealed irregularly shaped interconnected nanosheets with lateral dimensions of 50 nm and above with varying thickness as seen in the contrast variation over the image. Unfortunately, drying of the colloid during the deposition on the amorphous carbon support could induce additional restacking, thus we cannot directly correlate the observed nanosheets to the presence as in suspended colloid. On very thin parts we can distinguish an atomic structure with a typical close-packing of the transition metal atoms (Figure 7.1d).

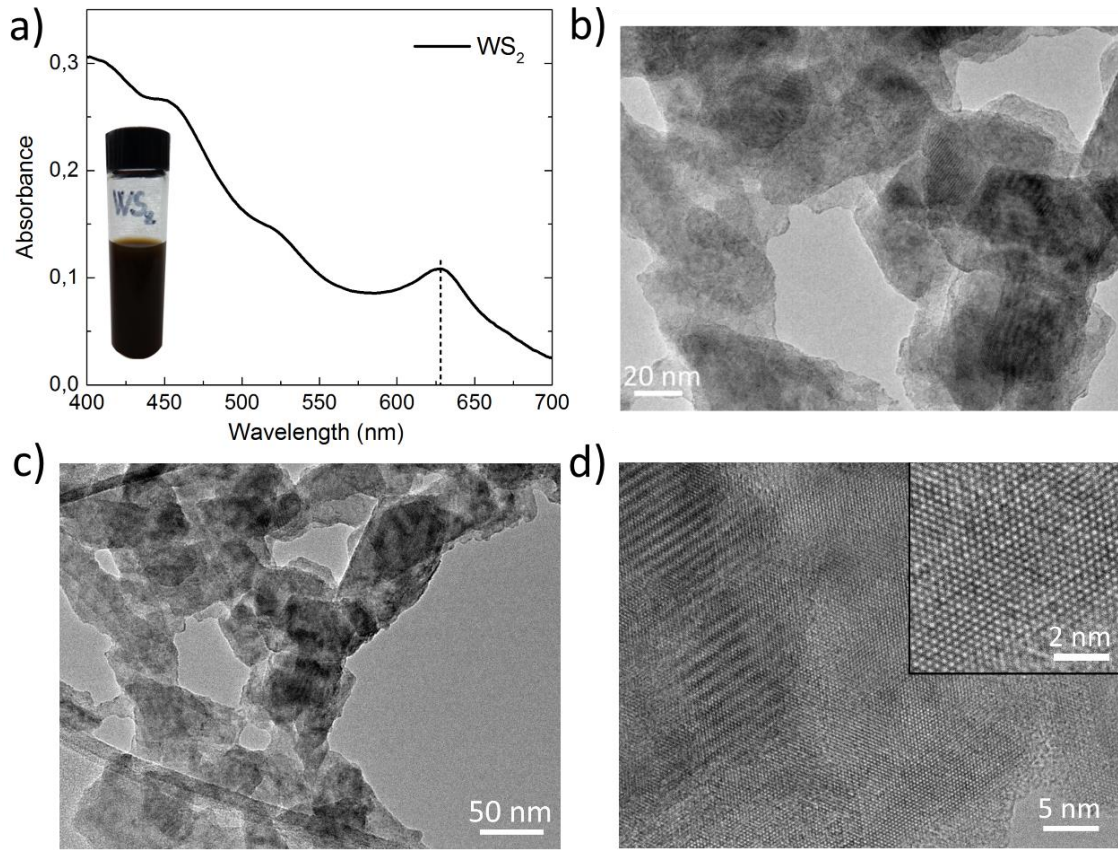


Figure 7.1: Characterization of exfoliated colloidal WS₂. a) Absorption spectrum of colloidal WS₂ in a solvent mixture of ethanol and water (0.35:0.65) displaying a characteristic excitonic feature centered around 627 nm. b) and c) TEM image of the respective colloid presenting interconnected nanosheets of WS₂ with lateral sizes of several tens of nanometers. d) High-resolution TEM image of thinner sheets where the atomic arrangement can be clearly seen.

Perovskite solar cells were prepared in a standard device configuration as thoroughly described in Experimental Methods. In summary, fluorine-doped tin oxide was etched and cleaned in an ultrasonic bath and O₂ plasma. TiO₂ precursor was spin coated on top and sintered at 500°C to form a thin and compact metal oxide base for the bilayer ETL structure. Still hot substrates (100°C) were transferred into the glove box where a thin layer of PC₆₁BM was deposited on top of the substrates as an interfacial layer improving the quality of the subsequent perovskite film. The perovskite layer was deposited by a two-step spin coating based on cesium and formamidinium mixed cation precursor since this composition exhibits improved stability over MAPbI₃ when exposed to the humidity [35]. We first analyzed the effect of the WS₂ deposition technique on the stability of the perovskite layer. Since in our case colloidal WS₂ in 2-Propanol is deposited by a spray coating technique, we replicated the effect of spray coating on the perovskite layer by spraying the neat perovskite layer using pure 2-Propanol without the WS₂. The deposition protocol used in this test was nearly identical to the one used for the final solar cells (temperature of the substrate and the spraying rate) except that we fixed the volume of the used solvent to 4 ml. We then compared the neat perovskite with the sprayed one using X-ray diffraction as depicted in Figure 7.2.

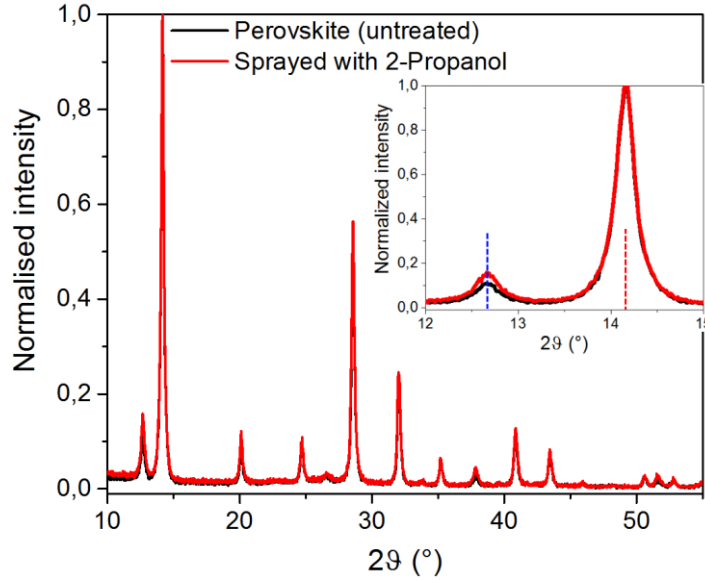


Figure 7.2: Normalized XRD pattern of the untreated and sprayed perovskite film. For the sprayed perovskite film the same protocol was used as in the deposition of colloidal WS₂ applied in a device. Blue and red dashed lines denote the most prominent diffraction peaks of PbI₂ and the perovskite, respectively.

X-ray diffraction patterns of the neat and sprayed perovskite film are practically indistinguishable, with only a minor difference in the relative intensity of the PbI₂ and the perovskite's most prominent diffraction planes (blue and red dashed lines of the inset magnified pattern). This result implies that the spray coating procedure under normal atmosphere does not significantly affect the quality of the perovskite layer. The results of this measurement can be ascribed to the less hygroscopic nature of cesium- and formamidinium-based salts in comparison to the conventionally used methylammonium-based ones. Thus the spray coating with 2-Propanol as the suspension medium was chosen for the WS₂ deposition in solar cells.

Hole transporting layers were then deposited on top of a freshly formed perovskite film by spin coating Spiro as a reference HTL or by spray coating the colloidal suspension of WS₂ in 2-Propanol. For the WS₂ employing solar cells we varied the amount of the colloidal suspension deposited on top of the perovskite layer in order to track the performance dependence on the WS₂ film thickness. All devices were finished by a thermal evaporation of 50 nm of gold (cathode). Figure 7.3 displays the results of the solar cell characterization employing various amounts of colloidal WS₂ or conventional Spiro as a hole transport layer. The backward and forward scan J-V curves of the best performing electrode for each configuration are plotted and the extracted solar cell parameters are collected in Table 7.1. From the results we can deduce that 2 ml of WS₂ colloidal dispersion, resulting in an average film thickness of 5-7 nm, returns the highest performing device, apart from the control solar cell.

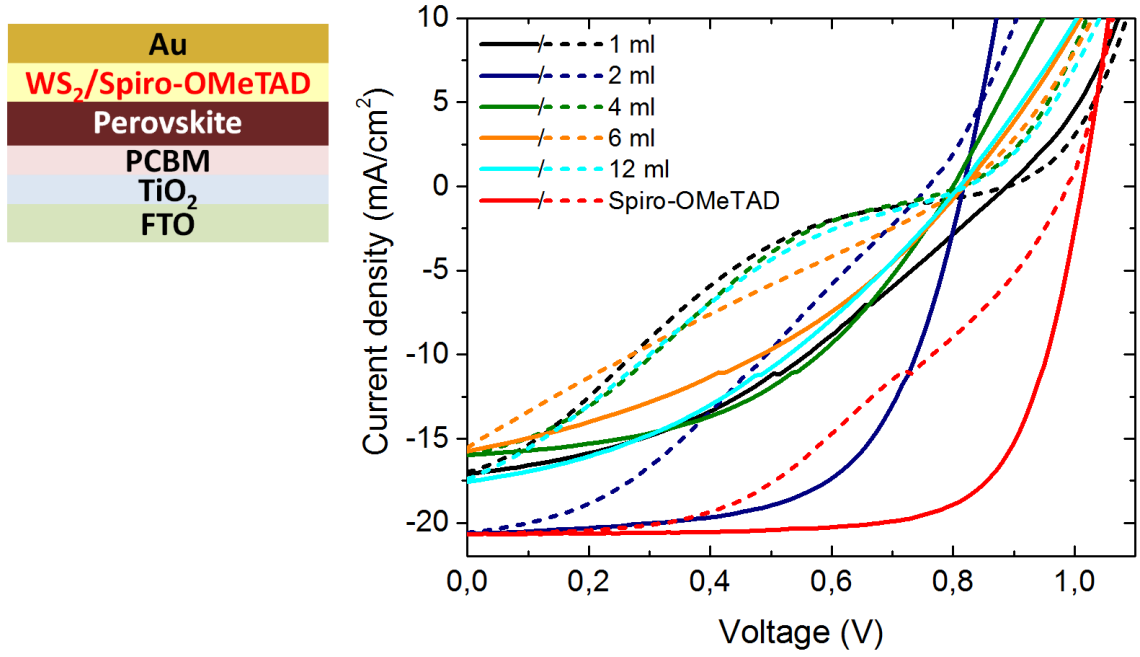


Figure 7.3: Characterization of WS_2 containing perovskite solar cells. Current density-voltage characteristic of solar cells employing various amounts (volume) of colloidal WS_2 deposited as a hole transport layer compared to the reference solar cell employing Spiro. Solid and dashed lines denote the backward (1.2 V $\rightarrow$ 0 V) and forward (0 V $\rightarrow$ 1.2 V) scan, respectively. Measurements were done at the illumination intensity of 1 sun (AM1.5) without any prebiasing or other preconditioning (e.g. light soaking). Voltage scan speed was set to 20 mVs^{-1} .

Table 7.1: Solar cell parameters extracted from the J-V curves presented in Figure 7.3 for the backward (BWD) and forward (FWD) scan direction.

	1 ml (WS_2)		2 ml		4 ml		12 ml		Spiro	
	BWD	FWD	BWD	FWD	BWD	FWD	BWD	FWD	BWD	FWD
J_{SC}	17.0	17.1	20.6	20.6	15.9	16.0	17.4	17.6	20.7	20.7
V_{OC}	0.89	0.89	0.76	0.82	0.81	0.80	0.82	0.81	0.98	1.01
PCE	2.8	5.8	5.4	10.5	3.1	6.1	3.0	5.5	9.0	15.3
FF	0.18	0.38	0.34	0.62	0.24	0.47	0.21	0.38	0.44	0.73

In comparison to the control, solar cells employing WS_2 show reduced open-circuit voltage by around 0.2 V, relatively independent of the WS_2 thickness above the optimal produced with 2 ml of colloidal suspension. Since the lowering of the V_{OC} does not depend on the thickness of the WS_2 layer, we can deduce that the lowering is directly connected to the perovskite- WS_2 interface and the electronic properties of the WS_2 . The fill factor and the short-circuit current density, however, reduce with increased WS_2 thickness, which can be ascribed to the increased series resistance of the WS_2 layer. Along the reduction in the fill factor the hysteretic behavior is reduced as well. Due to a severe hysteresis of the solar cell employing optimum WS_2 thickness (2 ml), we tested the device under constant applied bias near the maximum power point (0.57 V for the respective sample) and tracked the photocurrent through the solar cell over time. The results of the measurement are presented in Figure 7.4.

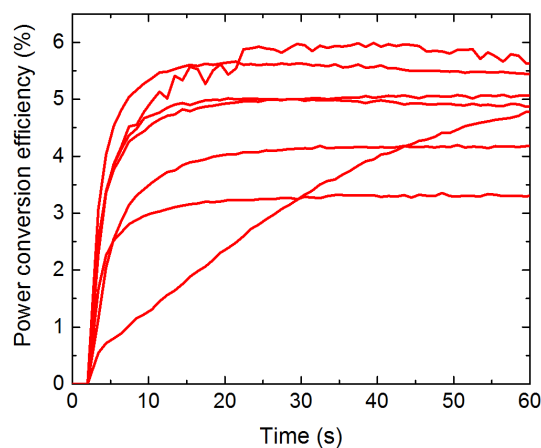


Figure 7.4: Stabilization curves for optimal WS₂ employing solar cell. An optimal solar cell employing WS₂ (2 ml of colloidal suspension) tested under constant applied bias of 0.57 V tracking the photocurrent in time.

Tracking the photocurrent under the constant applied bias revealed relatively quick temporal photocurrent response after the start of the illumination (3 s) stabilizing at the calculated power conversion efficiencies from 3 to 6%. The slower response of one of the curves corresponds to the first measured electrode of the substrate. As the measuring setup cannot isolate individual electrodes from the light source when one of the electrodes is being measured, the other electrodes are exposed to light before the actual measurement. Only the first electrode does not receive any light soaking thus the low transient response.

To assess the morphological properties of the device and particularly the inorganic hole transport layer we acquired a cross-section and surface SEM image of a semi-complete device covered by 6 ml of WS₂ devoid of the gold cathode, as seen in Figure 7.5. Functional layers structuring the solar cell are marked in the cross-section image. WS₂ on the perovskite layer appears to uniformly cover the surface, however, the film is rough due to the wide distribution of WS₂ plate thicknesses.

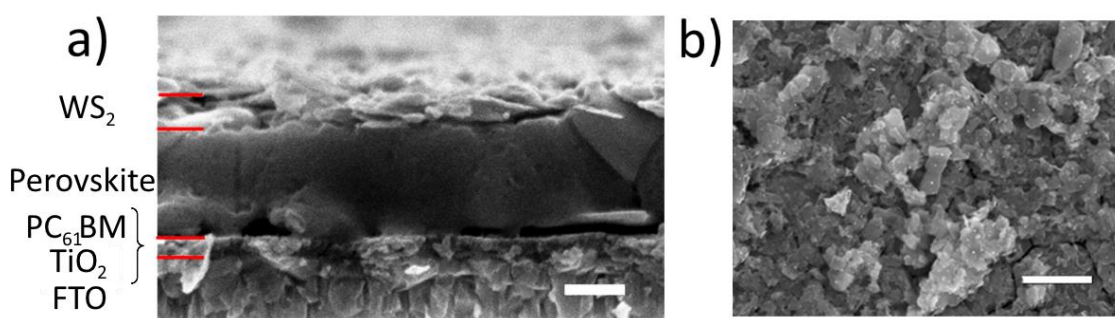


Figure 7.5: Device cross-section and a surface morphology image acquired by an SEM. a) Cross-section image with marked layers. Scale bar: 500 nm. b) Surface morphology image of the WS₂ layer deposited directly on the perovskite layer. Scale bar: 200 nm.

As can be seen from the surface morphology image (Figure 7.5b) WS₂ flakes are larger in lateral size in comparison to the neat colloidal dispersion characterized by the TEM. The effect of increased flake size can be ascribed to additional restacking in 2-Propanol, which is not the best dispersive solvent for WS₂. In addition, the process of spray coating

can induce nanosheet restacking during the evaporation of the solvent incident onto the substrate.

Furthermore, we performed steady state photoluminescence spectroscopy of a standalone perovskite layer and a bilayer perovskite-WS₂ in order to acquire better insights on the electronic processes at the perovskite-WS₂ interface. The source for the photoexcitation was a 532 nm green laser, whose light intensity was decreased by 6 orders of magnitude to avoid signal saturation and at the same time perovskite degradation. Both samples were prepared on a single substrate by spray coating one half of the perovskite film with WS₂ colloidal suspension in 2-Propanol using the same deposition procedure as in the solar cell preparation protocol. The average thickness of the WS₂ film was around 5 nm, meaning that about 45% of the incident photons reached the perovskite film below the WS₂ by taking into account the measured absorption of the WS₂ monolayer at the 532 nm wavelength [251]. Furthermore, we treated one part of the substrate encompassing both the standalone perovskite as well as the perovskite-WS₂ bilayer with an O₂ plasma and measured the PL response of all the samples upon photoexcitation. Preparing all of the samples on a single substrate eliminated the possibility of the sample-to-sample variation of the perovskite film impacting the results of our analysis.

Normalized photoluminescence signals of all distinct regions of the sample are presented in Figure 7.6 together with the sketch of the sample structure. Photoexcitation of charges in the perovskite film led to a strong PL signal centered around 766 nm (1.62 eV) as a result of an efficient radiative recombination of the photoexcited free charges in the absence of charge extracting layers. On the perovskite-WS₂ bilayer without the plasma treatment the PL signal was reduced by more than 300 times compared to the perovskite alone, while in the case of the O₂ plasma-treated bilayer there was no PL signal detected. These results confirm that there is an efficient transfer of photoexcited charges from the perovskite to the neat or oxygen plasma treated WS₂ layer. Oxygen plasma treatment was used to simulate otherwise unlikely oxidation during the spray coating and thermal treatment and how this would affect the charge transfer mechanism between the oxidized WS₂ and the perovskite.

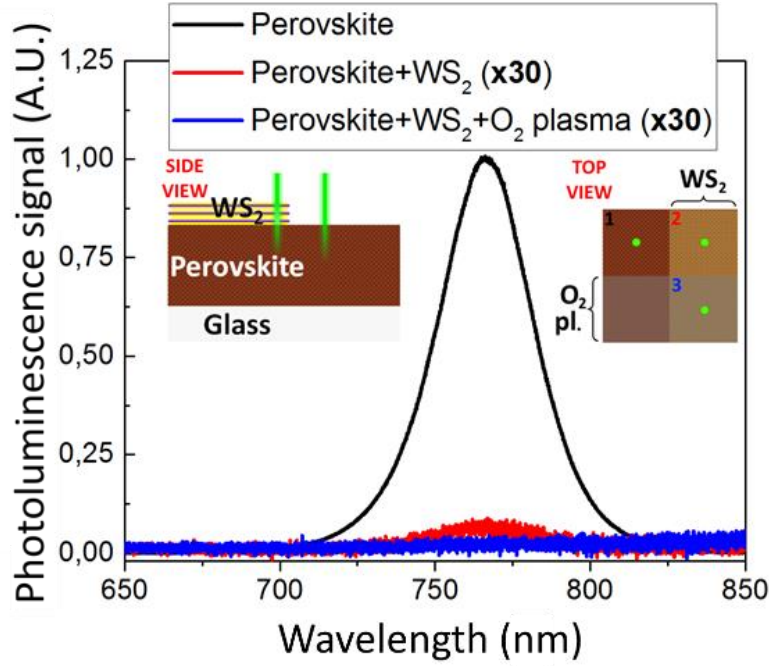


Figure 7.6: Photoluminescence of perovskite-WS₂ bilayer. Comparison of photoluminescence signals of the perovskite film and the perovskite-WS₂ bilayer with and without the O₂ plasma treatment (note the amplification of the bilayer PL signal by a factor of 30). All samples were prepared on one substrate by covering only half of the perovskite film with WS₂ and exposing one part of the substrate containing both the bilayer and the standalone perovskite film to O₂ plasma as sketched in the inset of the graph. With this we avoided possible sample to sample variation in perovskite quality due to the complex processing. To emphasize the degree of quenching, the photoluminescence signal from the bilayer was amplified by a factor of 30.

Whether the transfer of photoexcited charges from the perovskite to the WS₂ layer involves either electrons, holes or both charges (energy transfer) depends on the band alignment between the two semiconductors. In order to reconstruct the perovskite-WS₂ band alignment we determined the Fermi level and the position of the valence band maximum of both semiconductors with UPS. The results of the Fermi level and valence band maximum of the neat WS₂ and the perovskite layer are presented in Table 7.2. Raw data from the measurements are presented in Figure D.1 in Appendix D. According to the values obtained from the measurement, a prediction of the possible band alignment between the neat WS₂ and the perovskite is sketched in Figure 7.7.

Table 7.2: The Fermi level (W_F) and the valence band maximum (VBM) positions of the neat WS₂ and the perovskite with respect to the vacuum level as measured by UPS. Except for the WS_{2-x}O_x the conduction band minimum (*CBM) was calculated by taking into account the energy band gap of the respective semiconductors.

	W_F (eV)	VBM (eV)	*CBM (eV)
WS ₂	4.18	-5.13	-3.83
Perovskite	4.36	-5.86	-4.22

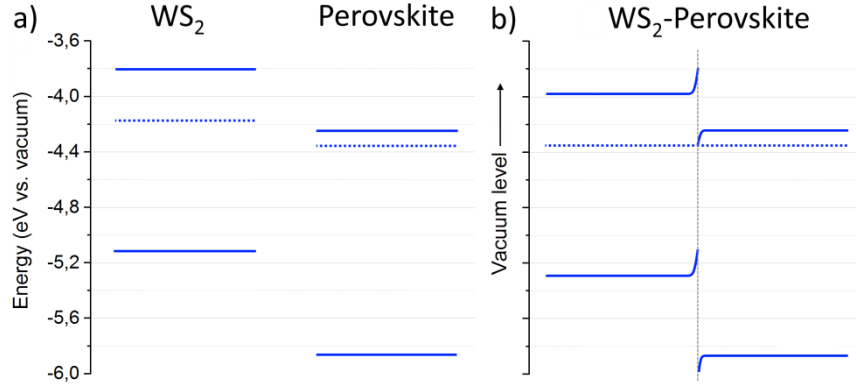


Figure 7.7: UPS characterization of WS₂ and perovskite films. A band structure of a standalone neat WS₂ and the perovskite layer (a) and the predicted band alignment after the formation of the WS₂-Perovskite interface (b). The heterojunction is presented in an arbitrary energy position with respect to the vacuum level.

The UPS results of the standalone WS₂ and the perovskite film revealed a large valence band offset between the two semiconductors (Figure 7.7a). By taking into account the known optical gaps of both semiconductors we can deduce that the WS₂ and the perovskite form a staggered type heterojunction. This type of a heterojunction promotes the hole and blocks the electron transport from the perovskite to the WS₂ layer. The heterojunction sketch in Figure 7.7b takes into account a spontaneous electron transfer upon contact as a result of Fermi level equilibration and consequently the band bending at the interface. There are, however, other processes that could influence the band structure at the interface, such as the appearance of new interface states or passivation of perovskites' mobile ionic species at the interface, which are not considered in this simplified scheme.

7.4 Conclusions

In this chapter I presented the first application of exfoliated WS₂ as a standalone specific charge selective layer in perovskite solar cells, applied by a robust and scalable deposition under normal atmosphere without affecting the quality of the light harvesting layer. In the final optimized solar cell WS₂ turned out as a sufficient hole transporting layer showing stabilized power conversion efficiency of up to 6%. These preliminary results suggest that the novel inorganic layer possesses charge selectivity properties as suggested by the supporting photoluminescence measurements and by the determination of basic band alignment properties.

Chapter 8

Thiol Click Chemistry on Gold-Decorated MoS₂: Elastomer Composites and Structural Phase Transitions

This chapter contains a published paper entitled *Thiol click chemistry on gold-decorated MoS₂: elastomer composites and structural phase transitions* [252]. In this work we demonstrated a homogeneous incorporation of metallic MoS₂ nanosheets synthesized by a chemical exfoliation of pristine MoS₂ powder. Highly defective exfoliated nanosheets were subsequently exploited for spontaneous growth of gold particles on sulfur vacancies. Gold-decorated MoS₂ were later used in conjunction with thiol-terminated polymer chains forming a homogeneous composite as a result of a strong thiol-based interaction between the MoS₂ nanosheets and the polymer. Subsequent phase transition from metallic to semiconducting phase of the MoS₂ was induced by laser-induced heating. The presented work was published in the *Nanoscale* journal (Impact factor: 7.76).

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8.1 Abstract

We show that gold decorated MoS₂ flakes are amenable to thiol chemistry by blending them with a cross-linkable thiolated polysiloxane (PMMS). PMMS prevents restacking of dispersed MoS₂ when transforming the metallic to the semiconducting phase.

Cross-linking PMMS yields an elastomer of good optical quality, containing individual, mostly single-layer MoS₂ flakes.

8.2 Introduction

Research on layered semiconducting transition metal dichalcogenides is growing rapidly, driven by the wide gamut of possible applications such as field-effect transistors [253], photodetectors [254], photovoltaic elements [255], saturable absorbers [256], catalysts for hydrogen evolution [257], and sensors for DNA detection [258]. Mono- and few-layer TMDs can be obtained either bottom-up via CVD [259] or colloidal synthesis [260], or top-down via mechanical exfoliation [122], chemical exfoliation in liquid via ion or molecular intercalation [261]–[263], exfoliation in liquid using ultrasound [137], or high-shear mixing [136]. Chemical exfoliation using *n*-Butyllithium (*n*-BuLi) allows the exfoliation of comparatively large amounts of material and stands out from the other methods in that it largely transforms semiconducting TMDs from their stable 2H into the metallic 1T phase. This metastable phase can be transformed back to 2H through heating.

Thiol chemistry drives progress in areas ranging from molecular electronics to biosensors [264]. In particular, thiol-ene click chemistry [265] enables tunable polysiloxane-based elastomers, such as poly[(mercaptopropyl)methylsiloxane] (PMMS) [266], whose cross-linking can be activated photochemically or thermally. A thiol group at each repeating unit along the backbone allows for strong cross-linking, while the high molecular weight (ca. 47 kgmol⁻¹) eliminates the traditional odor problems of thiols.

Here we show that thiol click chemistry can be performed on gold nanoparticle (GNP) decorated single- and few-layer MoS₂ flakes. GNP decoration has previously been shown for MoS₂ flakes used as electrocatalysts [267] and for WS₂ nanotubes and fullerene-like WS₂ [268]. Furthermore, GNP decorated MoS₂ flakes have shown great promise as substrates for surface enhanced Raman scattering [269], electrodes for rechargeable batteries [270] as well for optical and electrochemical sensing [271]. In our case, upon the addition of HAuCl₄·3H₂O to a dispersion of MoS₂ flakes in water, GNPs nucleate on defects introduced to the flakes by chemical exfoliation in water using *n*-BuLi. PMMS serves as a surfactant for dispersing both metallic and semiconducting MoS₂ flakes in the same solvent, such as chloroform, and prevents their restacking. This way, the predominantly metallic MoS₂ flakes resulting from chemical exfoliation can be transformed into their semiconducting phase in solution via heating. Cross-linking the PMMS forms an elastomeric film filled with MoS₂ flakes that can be transformed either globally via heating or selectively via laser irradiation. Upon layering PMMS with an immiscible solvent such as ethanol, the affinity of thiol groups towards GNPs and defects on the flakes drags the flakes dispersed in ethanol into PMMS. The efficiency and speed of this process increases with increased GNP or defect content of the flakes as well as with increased thiol content of PMMS. We show that the interaction between the GNPs and the thiol groups is the driving force behind this process and predict some applications this will enable.

8.3 Experimental Methods

8.3.1 Lithium intercalation

Intercalation of MoS₂ with lithium was initiated by mixing 100 mg of MoS₂ with 1 ml of 1.6 M *n*-Butyllithium. The mixture was left in a glovebox at room temperature for 48 h

to complete the intercalation. The obtained powder was washed with anhydrous hexane and dried.

8.3.2 Exfoliation of Li-intercalated MoS₂

100 ml of Milli-Q water was poured over the dried intercalated powder and mildly sonicated for 30 min. The obtained colloid was centrifuged at 2,500 rpm for 30 min to sediment larger unexfoliated particles. The supernatant was then centrifuged at 11,000 rpm for 60 min. The acquired sediment was successively washed with Milli-Q water three times, repeating the centrifugation step while discarding the supernatant each time.

8.3.3 Decoration with Au nanoparticles

Solution of HAuCl₄·3H₂O in Milli-Q water (0.2 mgml⁻¹) was added dropwise to Li:MoS₂ colloid (1 mgml⁻¹) during constant stirring to obtain 10 wt.% Au decoration. Decorated Li:MoS₂-Au was again washed following the procedure described in the exfoliation paragraph. In the last centrifugation step absolute ethanol was used instead of Milli-Q water in order to obtain ethanol colloidal solution.

8.3.4 Fabrication of polymeric nanocomposites

We used mercaptopropyl methylsiloxane homopolymer (Gelest SMS992) as a backbone and tri(ethylene glycol) divinyl ether (Sigma Aldrich) as a cross-linking agent. The thiol-ene polymerization was performed with 1 wt.% of thermal free radical initiator 1,1'-azobis(cyclohexanecarbonitrile) (Sigma Aldrich). The polymer and the crosslinker were mixed in 1:0.4 stoichiometric ratio and left for 20 h at 80°C in a Teflon mold. The obtained sample was transparent and brittle. For samples of polymeric nanocomposites we switched the pure polymer for the one with layered nanomaterial already attached to the polymeric backbone; all other parameters were the same. The mixture of polymer and nanomaterial were centrifuged before use to eliminate aggregates. The obtained nanocomposites were tinted due to the content of semiconducting moiety. No aggregates were visible under an optical microscope (Figure 8.1f). To obtain samples with metallic phase nanoplatelets, which are sensitive to heat, we changed the initiator to a UV sensitive one (BASF Darocur 1173), preparation of the mixture stayed the same, for cross-linking we used a 365 nm UV-LED (800 mW) with exposure time 30 s.

8.3.5 Raman spectroscopy

Raman spectroscopic characterization of MoS₂ was performed with an NT-MDT NTEGRA SPECTRA confocal Raman microscope in backscattering geometry with spectral resolution of 0.7 cm⁻¹. We used the excitation line at 632.8 nm (He-Ne laser) focused onto a spot size of 40 microns with a laser power of 1.5 mW and 4 h exposure time. The Raman signals were detected with a CCD array at -70°C.

8.3.6 X-ray photoelectron spectroscopy

XPS analyses of surface composition were carried out on the PHI-TFA XPS spectrometer produced by Physical Electronics inc. The analyzed area was 0.4 mm in diameter and the analyzed depth was about 3-5 nm. Sample surfaces were excited by X-ray radiation from monochromatic Al source at photon energy of 1486.6 eV.

8.4 Results and Discussion

Chemical exfoliation yields micron-sized flakes (Figure 8.1a) that tend towards restacking upon drying. By adding H₂AuCl₄·3H₂O to the dispersions of exfoliated flakes, Au nucleates on the flake surfaces and forms nanoparticles of roughly spherical shape (Figure 8.1b) [270]. These have a narrow size distribution with almost all GNPs below 5 nm diameter and the most frequent diameters around 2 nm as presented in a histogram in Figure 8.1b. They cover approximately 20% of the flake surface. The distance between the lattice plane determined in Figure 8.1e is 2.35 ± 0.05 Å, typical of Au 111 planes. Additional characterization of both the as-exfoliated and the GBP-decorated flakes is reported in the Appendix C. A recent study proposed that on WS₂ nanotubes and fullerenes AuCl₄⁻ ions preferentially bind to sulfide-terminated surface defects, i.e. unsaturated S atoms [272] and that some defects are already active at room temperature, while the majority needs to be activated by heating the solvent to 100°C. Our method yields a large number of small GNPs already at room temperature. We assume that the chemical exfoliation using *n*-BuLi introduces a larger amount of defects that are already active at room temperature. Similar to earlier results on Mo₆S₈I₂ molecular wires [273], the MoS₂ surface itself provides a sufficiently reducing environment for the gold nucleation, eliminating the need for the addition of reducing agents.

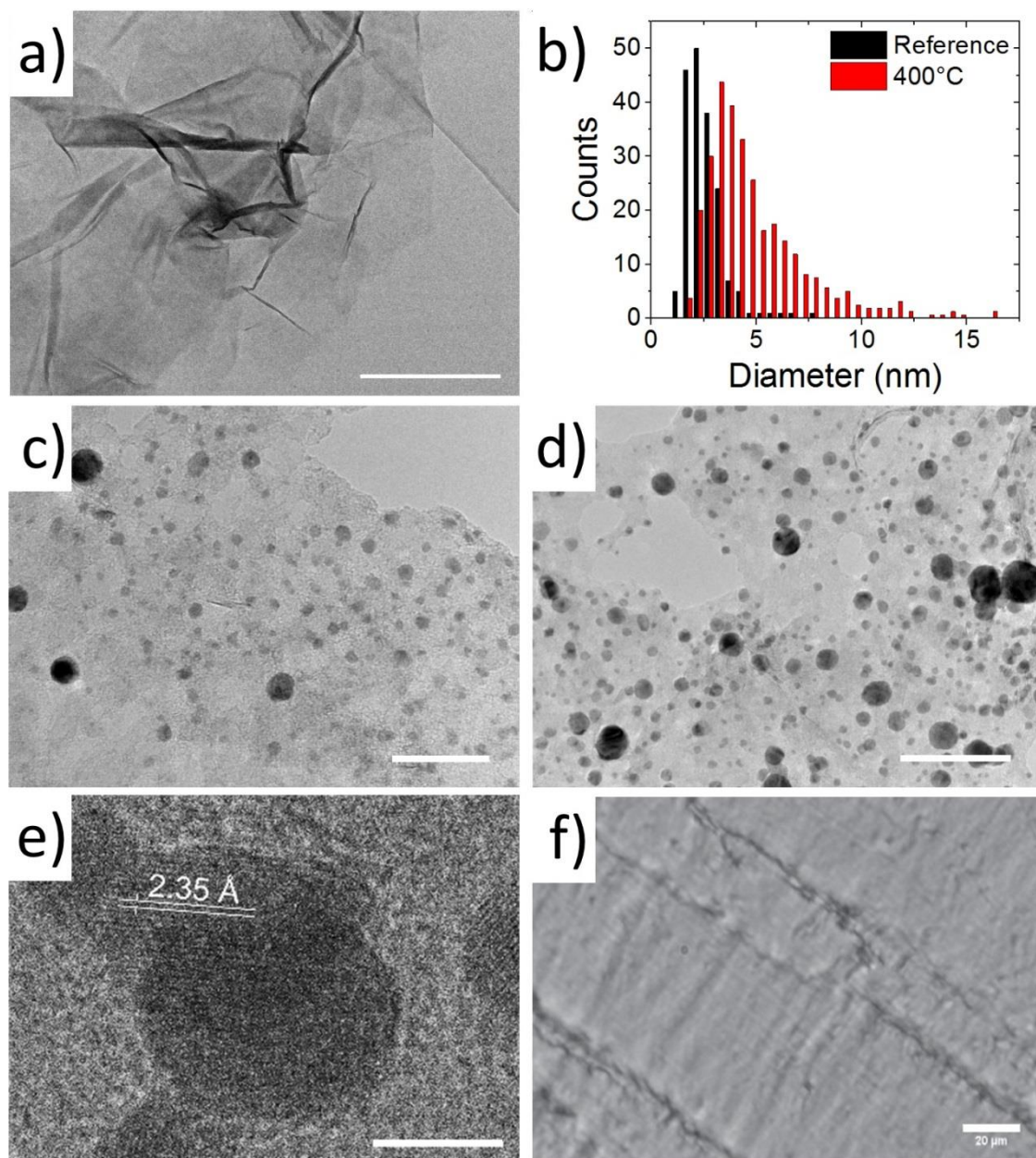


Figure 8.1: TEM characterization of MoS₂ and GNP decorated MoS₂. a) MoS₂ flakes upon cleaning and dispersion in ethanol [scale bar 0.5 μm]. b) Histogram of Au particle size counts for thermally untreated and 400°C treated sample. c) Gold decorated MoS₂ flakes [scale bar 20 nm]. d) Gold decorated MoS₂ flakes – thermally treated at the temperature of 400°C for 1 h in Ar atmosphere [scale bar 50 nm]. e) Gold particles decorating MoS₂ flakes [scale bar 5 nm] with indication of the Au lattice plane distance. f) Optical microscopy image of a PMMS/MoS₂ composite.

Upon annealing at 400°C, some GNPs coalesce, shifting the most frequently occurring diameter towards 4-5 nm (Figure 8.1d), with a tail in the distribution extending beyond 10 nm (Figure 8.1b). The surface coverage remains approximately 20%. The stability of the GNPs against annealing at temperatures as high as 400°C makes GNP-decorated TMDs ideally suited for further thermal processing.

MoS₂ flakes from Li exfoliation are predominantly in the metastable metallic 1T phase [143], [262], while most applications are based on the semiconductor properties of the stable 2H phase. The transformation from 1T to 2H can be performed simply by heating. Successful transformation can be easily identified by the absorption spectrum, which is nearly featureless in the 1T case, while the 2H phase shows characteristic excitonic resonances, in particular two peaks at 670 and 610 nm, customarily labelled A and B [274].

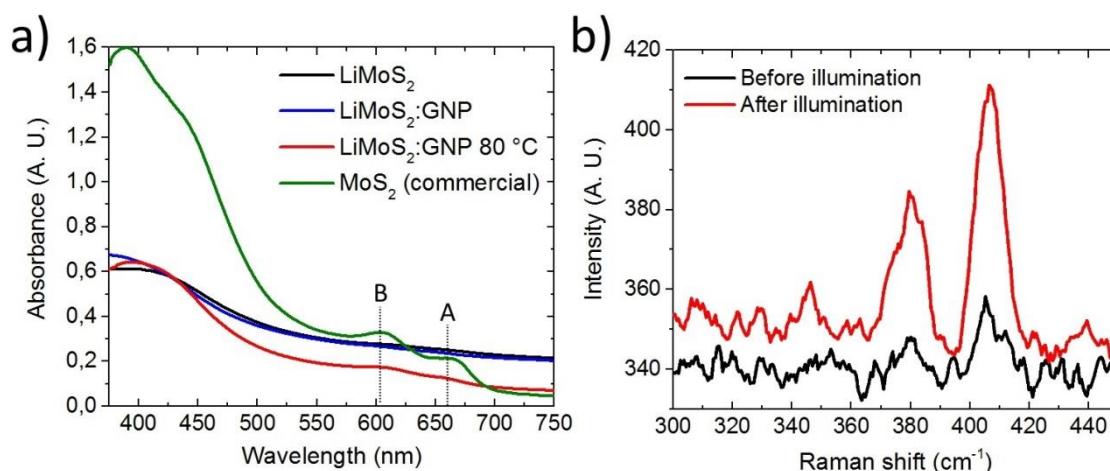


Figure 8.2: Optical absorption and Raman spectra of pristine and transformed MoS₂. a) Absorbance of various MoS₂ samples before and after annealing. b) Raman spectra of the elastomeric composite containing GNP-decorated MoS₂ flakes before and after laser-induced transformation from the metallic 1T to the semiconducting 2H phase.

We now assess the viability of using GNP-decorated flakes together with PMMS to produce elastomeric composite films. In a first step, we disperse the flakes in a mixture of chloroform and PMMS with 99% of all monomer units containing a thiol group. Neither pristine nor GNP-decorated MoS₂ flakes disperse in chloroform; the stable dispersion here is enabled by PMMS. MoS₂ flakes from Li exfoliation are predominantly in the metallic 1T phase, as is confirmed by the almost complete absence of the A and B exciton peaks around 2 eV in the extinction spectra of both pristine and decorated flakes (Figure 8.2a). Annealing for 12 hours at 80°C restores these exciton resonances and hence the semiconducting 2H phase for both types of flakes. Such conversion in liquid usually results in precipitation and restacking of the semiconducting flakes for several reasons [275]. The 1T and 2H phases have different solubilities and different preferred solvents; only in the 1T phase restacking is prevented because the flakes are charged; and heating increases Brownian motion, which is the driving force of aggregation. The strong binding of PMMS to GNPs prevents all these complications.

In alternative to transforming all flakes in a composite sample from the metallic to the semiconducting phase by heating, the transformation can also be performed selectively by focusing a laser on the desired spot of the sample [276]. Figure 8.2b shows the Raman spectrum of the sample containing mostly metallic flakes. Subsequently, a spot of about 40 μm is illuminated for 4 h at 1.5 mW at 633 nm. In a second measurement only at the illuminated spot, the double peak around 400 cm⁻¹, characteristic of the semiconducting phase, is clearly enhanced.

To verify the strong affinity of thiolated PMMS for MoS₂, we first fill vials with a bottom layer of PMMS (99%). As a top layer we add a dispersion of MoS₂ flakes in

ethanol (Figure 8.3a, (I) before heating). Since ethanol is immiscible with PMMS, the ethanol phase stays on top of the PMMS phase. Upon heating to 60°C, the GNP decorated flakes transfer completely to the polymer within 1 h, as is shown in Figure 8.3a by the dark color of the polymer while the ethanol evaporated during heating. For the pristine flakes the analogous result is obtained after 12 h, for a control sample of flakes dispersed in ethanol from ultrasonic or shear-exfoliation (obtained from Graphene Supermarket™) the process requires 72 h. Additionally, for GNP decorated flakes, the process runs even at 4°C, lasting 12 h rather than 1 h. We assume that the thiol groups of PMMS interact strongly with the GNPs, and, to a lesser extent, with defects on the pristine flakes, of which the Li-exfoliated flakes have more than the ultrasonically or shear-exfoliated ones.

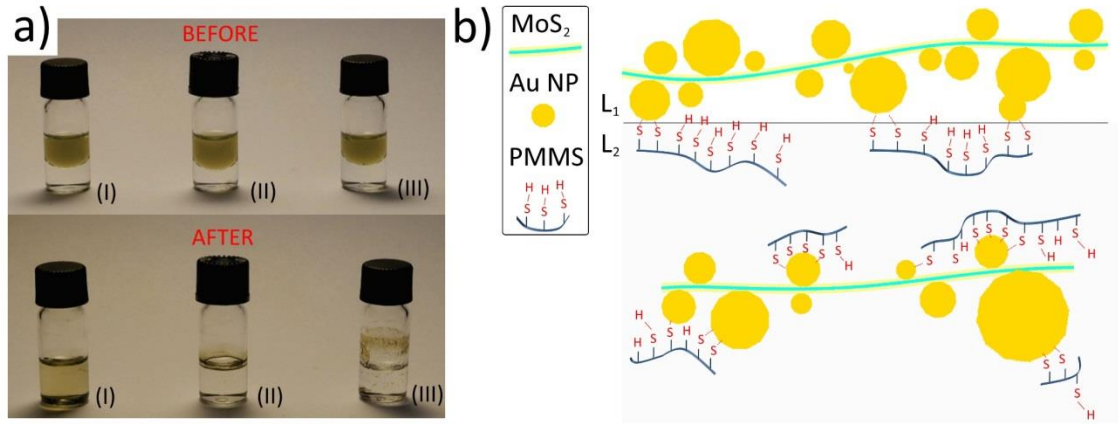


Figure 8.3: Interaction mechanism of PMMS and GNP decorated MoS₂. a) Picture of vials filled with immiscible ethanol and chloroform containing GNP decorated MoS₂ and PMMS respectively before and after the heating at 60°C. (I), (II) and (III) denote variants of PMMS containing 99, 4 and 0% of thiol group within the monomers respectively. b) Illustration of the interactions between the PMMS and GNP decorated MoS₂ at the ethanol-chloroform interface. The strongest interaction is the one between the thiol group and Au nanoparticles attached to the surface of MoS₂.

To test this hypothesis, we repeated the experiment using GNP-decorated MoS₂ with different variants of PMMS, where only 4%, and 0% of all monomer units contain a thiol group. During the heating of PMMS with 4% of thiol groups, a thin dark layer of GNP decorated MoS₂ forms on top of the polymer (Figure 8.3, (II) after heating), indicating insufficient interaction on the flakes to induce transport over the interface. For the 0% variety, no transfer occurs. The efficiency of the transfer hence scales with both the number of thiol groups and the number of GNPs or defects (with GNPs being much more efficient than defects), confirming the thiol-gold interaction as the driving force behind this process.

8.5 Conclusions and Outlook

We have shown a procedure for decorating MoS₂ flakes from chemical exfoliation with GNPs. TEM images confirm the crystal structure of gold and show that the GNPs, with typical diameters around 2 nm only slightly coalesce upon thermal treatment at up to 400°C. Subsequently, we have found that PMMS enables to disperse both metallic and semiconducting flakes in the same solvent, and used optical absorption and Raman spectroscopy to show transformation from the metallic to the semiconducting phase

without restacking both in dispersion and as fillers of an elastomer nanocomposite. Finally, by using different flakes (decorated and undecorated, different defect content) and PMMS with different degrees of thiolation, we identified the interaction between the thiol groups and the GNPs as the driving force for the nanocomposite formation.

Based on our findings, we may preview possible applications of the produced decorated flakes, dispersions and nanocomposites. Restacking prevention is especially beneficial for TMD deposition via ink-jet printing [277], [278], where the GNPs will likely enhance the inter-flake contact [279]. The thermal stability of the gold nanoparticles and of PMMS makes this approach ideally suited for thermal processing. The excellent optical quality of the transparent elastomeric composites of MoS₂ in PMMS shows promise for non-linear optical applications, such as saturable absorbers [256] or optical limiters [280].

Having identified the GNP-thiol interaction as the driving force in the nanocomposite formation, we can envisage a vast range of applications for GNP decorated TMD flakes based on thiol chemistry. In chemical and biochemical sensing, GNP-decorated TMD flakes provide a biocompatible [281] nanocarrier platform that can be loaded with many thiolated signal molecules to amplify the sensor response and enhance its sensitivity. Functionalized TMDs have already been used for electrochemical DNA detection [282], [283], chemiresistive gas sensors (using a thiolated ligand) [284], and electrochemical aptamer sensors [285]. Since GNPs are much more reactive towards thiol groups than the defects in bare TMDs, all these designs will be much more efficient using GNP-decorated flakes. The easy charge transfer across the GNPs should additionally enhance the sensor response [286]. We envisage further aptamer-, antibody-, or other biomolecule-based sensors analogous to those built from GNP-decorated graphene [287], carbon nanotubes [288], or from sulfur terminated molecular wires [289]. Besides sensing, our approach also allows the synthesis of novel donor-acceptor structures [290] for light harvesting applications in order to efficiently use the exceptionally strong light-matter interaction of TMDs [291].

Chapter 9

General Conclusions and Future Prospects

To conclude, I have presented my work in the fields of metal halide perovskites and layered transition metal dichalcogenides focusing in majority on addressing or solving specific problems related to their use in real applications. In the first part I presented a novel lead-halide-based perovskite particle synthesis based on an environmentally friendly approach. Since these particular perovskite-based materials hold great promise for light harvesting applications, transition to an industrial scale production is expected in the near future. Thus, new low-cost and non-hazardous synthetic approaches are strongly sought for and the one presented here takes a step forward in various aspects, such as simplicity, scalability and control over the size of the resulting material. Very general future guidelines originating from the reported synthesis can be proposed. Particularly, controlling the shape and dimensionality of the precursor PbI_2 is the most important parameter to have control over. Controlled two-dimensional PbI_2 growth could be adopted from the growth techniques of other more widespread layered materials, either by a large area slow growth or other solution-processed techniques, such as hydrothermal synthesis. This would lead to a complete regulation of the size and uniformity of formed perovskite particles down to a few nanometer-sized particles (approaching the limit of a PbI_2 monolayer). Furthermore, the presented thermal treatment using solvent vapors as recrystallization mediator turned out as a promising experimental pathway towards creating large perovskite grains or quasi single crystals on arbitrary substrates. This processing could potentially become a bridge between the single crystal and thin film growth by forming thicker films with less surface retaining the beneficial optoelectronic properties of organolead halide perovskites. In addition, less surface with a reduced amount of grain boundaries would reflect in a lower amount of detrimental surface trap states and inhibit degradation of the perovskite layer upon exposure to humidity [292], [293].

In the second part I presented the work on self-assembled functionalized fullerene monolayers used as an electron transporting material in perovskite solar cells. We have reached close to state of the art performance by minimizing the material consumption using a straightforward, self-governed deposition method which in contrast to spin coating has no size limitations. High performing devices with such ultrathin layers is a remarkable outcome on its own, since it shows that charge selectivity can be achieved on a nanometric scale. Semiconducting layers with a charge-selective function inside the solar cell should exhibit limited parasitic absorption to allow a maximum number of photons to reach the light harvesting layer. Self-assembled monolayers are a perfect platform for application in tandem or any other multijunction solar cells, where

intermediate charge-selective layers between distinct light harvesting layers are needed and every reduction of the parasitic absorption impacts the overall performance. Another potential use of siloxane functionalized fullerenes could be a direct assembly directly on the surface of the perovskite forming the charge-selective layer in an inverted structure. Hydrophobicity of the layer could contribute an additional barrier towards moisture ingress, reducing the perovskite degradation process in the presence of water molecules in the environment.

The third part was dedicated to the application of WS₂ as a hole transporting layer in PSCs, connecting two large material science fields. The problem of perovskite degradation and deposition in air was solved by using a more resilient light harvesting layer and a solvent for WS₂ deposition which does not extensively cause the dissolution of the perovskite layer. Furthermore, although devices incorporating WS₂ showed average performance, they showed a stabilized power output, which has not been demonstrated in the literature before. However, in order to probe the performance limits of WS₂ (or other TMDs) in perovskite solar cells additional steps are needed. Colloidal particles should be replaced by a controllably grown WS₂ subsequently transferred on top of the perovskite layer. In this configuration the performance dependence on the number of WS₂ layers could be accurately determined. These films would not pose a limitation in particle-to-particle conduction as in the case of films prepared from colloidal suspension.

General motivation behind the research and future use of layered materials in perovskite solar cells is based on their superior properties in comparison to conventional “3D” materials and the possibility to deposit them in the form of nanometric thin films. Ultrathin films of layered materials can minimize the parasitic absorption of the layers inside a solar cell when used in the form of transparent electrodes (graphene), as charge-selective layers, or as a barrier for ion migration. Nanometric thin layers can also significantly reduce the series resistance of a complete device, which is an important aspect defining the final solar cell performance. On behalf of their mechanical properties layered materials could be an ideal replacement for fragile organic layers conventionally used in PSCs [250]. Most commonly used layered materials express high resistance to stretching before they break [124], [294] and in addition they can slide against each other under shear stress [295]. Thus films composed of layered materials should be highly resistant to mechanical stress, as was already demonstrated in the case of graphene-based electrodes applied in flexible solar cells [296], [297]. Lastly, it has been demonstrated that layered materials with perfect, no defect containing structure act as ideal encapsulants for various gases, including water vapor [298]-[300]. This implies that in the future, when layered materials are controllably grown and transferred to arbitrary surfaces without forming structural defects, they could exhibit a dual role, electronic as well as encapsulating.

The last part of the dissertation was dedicated to chemical exfoliation of MoS₂ and its homogeneous incorporation in elastomers. This was achieved by exploiting the defective surface of 2D MoS₂ nanosheets working as a reductant for auric acid, promoting the formation of gold nanoparticles on their surface, which then interacted with polymers through thiol-gold interaction. In a broader context, the ability of nanosheet functionalization opens a path towards selective interaction to specific functional groups, which could be used to manipulate inorganic and organic structures of various sizes. One of the direct possibilities stemming from the presented work is to transform the metastable metallic phase of MoS₂ into a semiconducting phase inside an electrically active polymer (i.e. with a bandgap in the optical part of the spectrum) forming a homogeneous bulk heterojunction. In addition, the procedure is most likely not limited to MoS₂ alone, thus the presented protocol could extend to a broad compositional variation of transition metal dichalcogenides.

Appendix A

Synthesis of MAPbI₃ Sub-Micrometer Particles

A.1 Supporting Results

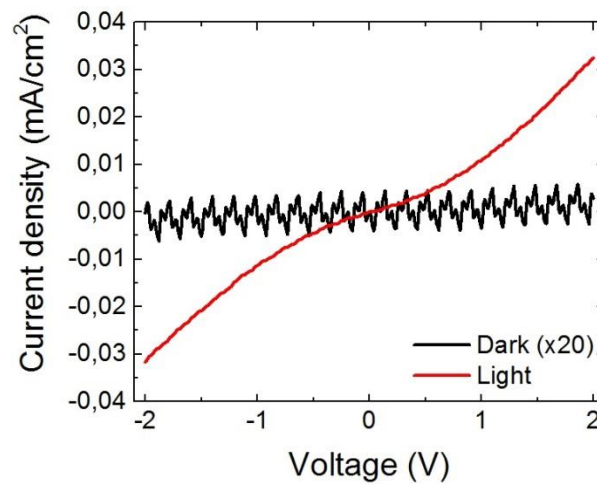


Figure A.1: As measured $I - V$ curves (linear scale) of MAPbI₃ particles. The film was bar coated on top of a gold patterned interdigitated electrode showing nonlinear behavior typical for a metal-semiconductor Schottky barrier.

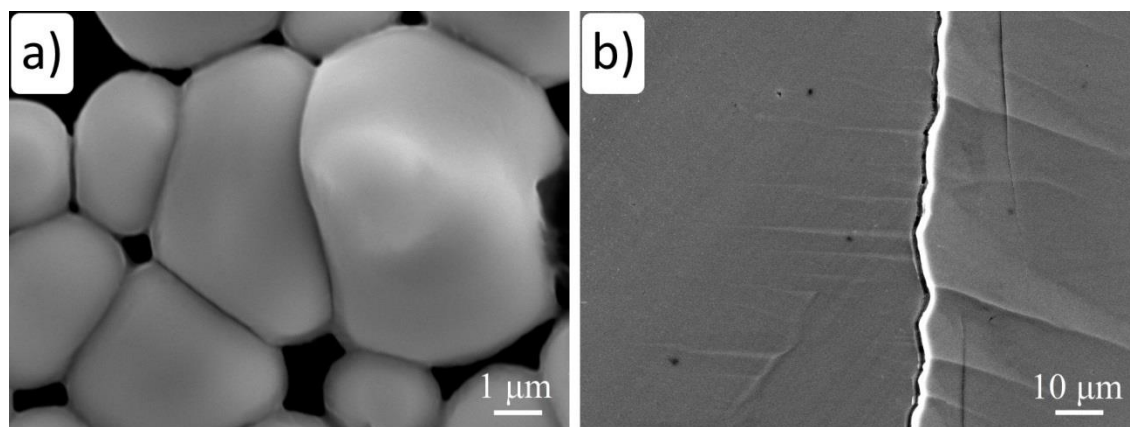


Figure A.2: Additional SEM images of solvent-annealed films. Higher magnification SEM image of solvent-annealed films with two distinct regions, polycrystalline (a) and monocrystalline (b).

Appendix B

Self-Assembled Siloxane Functionalized Fullerene Layers in Perovskite Solar Cells

B.1 Sil-C60 Synthesis

Sil-C60 preparation. All reagents and solvents were purchased from Sigma Aldrich and used as received. C₆₀ was purchased from BuckyUSA (98%).

The synthesis of Sil-C60 molecule has been described previously [294] but is here reported again with slight modifications for the sake of clarity. *N*-[3-(triethoxysilyl)propyl]-2-carbomethoxyaziridine was also prepared following the procedure reported previously [294].

N-[3-(Triethoxysilyl)propyl]-2-carbomethoxy-3,4-fulleropyrrolidine (Sil-C60). C60 (200 mg, 0.28 mmol) was added to degassed chlorobenzene (200 ml) under a nitrogen atmosphere. After stirring for 10 min, *N*-[3-(triethoxysilyl)propyl]-2-carbomethoxyaziridine (340 mg, 1.13 mmol) was added and the resulting mixture was heated up to 130°C for 48 h. After cooling down to room temperature, the solvent was evaporated and the residue was purified through column chromatography on silica gel, eluting initially with toluene to eliminate unreacted C60 and then with toluene:ethyl acetate (8:2) to isolate the product. The combined fractions containing the product were concentrated to 5 ml and acetonitrile (20 ml) was added, inducing the precipitation of a brown solid. The dispersion was centrifuged (1500 rpm, 20 min) and the supernatant was removed. Fresh acetonitrile (20 ml) was added and, after sonication, the same centrifugation procedure was repeated. The brown solid at the bottom of the centrifugation vessel was dried in vacuo, resulting in 116 mg of pure Sil-C60 (40%).

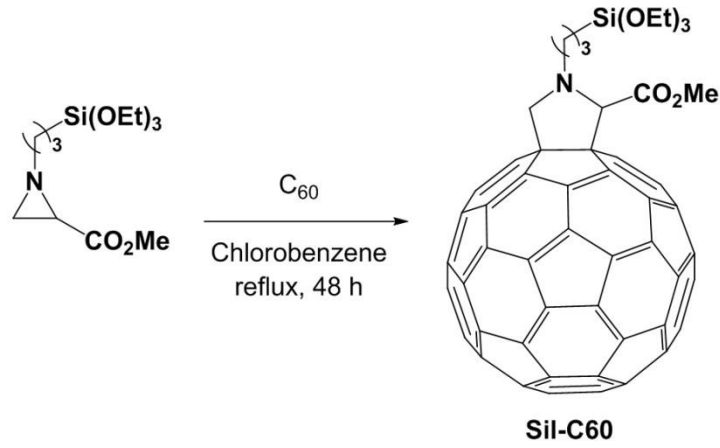


Figure B.1: Synthesis of Sil-C60.

B.2 Supporting Results

Table B.1: Summary of fitted data for Sil-C60 SAM sample using equivalent circuit model in Figure 6.3b. CPEs are used instead of ideal capacitances for increasing the quality of the fitting ($\chi^2 < 0.03$)

Sample	R_s (Ohm)	R_{po} (Ohm)	C_c (nF)	R_{ct} (kOhm)	Q_{dl} (uMho)
Sil-C60 SAM	137 (1%)	733 (9%)	649 (3%)	90.9 (1.5%)	1.46 (4%) / N=0.876 (0.90%)
Sil-C60 SAM after DMF	132 (2%)	383 (17%)	675 (5%)	80.0 (2.4%)	2.62 (5%) / N=0.829 (1%)

Table B.2: Summary of fitted data for bare FTO sample using a Randles modified cell [295] equivalent circuit model in Figure 6.3b. CPE is used instead of ideal capacitance (Q_{dl}) and Warburg element (Q_w) for increasing the quality of the fitting ($\chi^2 = 0.023$)

R_s (Ohm)	R_{ct}^{FTO} (kOhm)	Q_{dl} (uMho)	Q_w (mMho)
138 (0.7%)	309 (2%)	7.02 (10%) / N = 0.85	6.06 (4.4%) / N=0.44

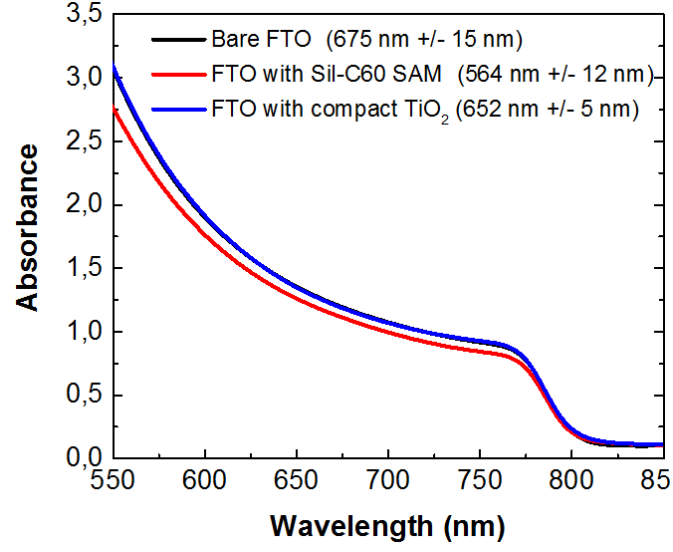


Figure B.2: Optical absorption of perovskite films obtained on various substrates. The legend contains film thickness values measured by a profilometer.

a) O₂ plasma treated FTO, 2° ± 0.2°



b) cTiO₂, 21° ± 2°



Figure B.3: Wettability measurements of a) plasma treated FTO and b) compact TiO₂.

$$d = \frac{\varepsilon_0 \varepsilon_i A}{C}, \quad (\text{B.1})$$

Where d is the thickness of the coating, C is the coating capacitance calculated using fitted values in Table B.1, ε_0 is the permittivity of free space, ε_i is the dielectric constant of the coating ($3.9 < \varepsilon_i < 4.5$) and A is the area of the electrode [208].

$$\Gamma = 1 - \frac{R_{ct}^{FTO}}{R_{ct}^{SAM}}, \quad (\text{B.2})$$

Where Γ is the surface coverage, R_{ct}^i are the charge transfer resistance fitted values tabulated in Table B.1 and Table B.2.

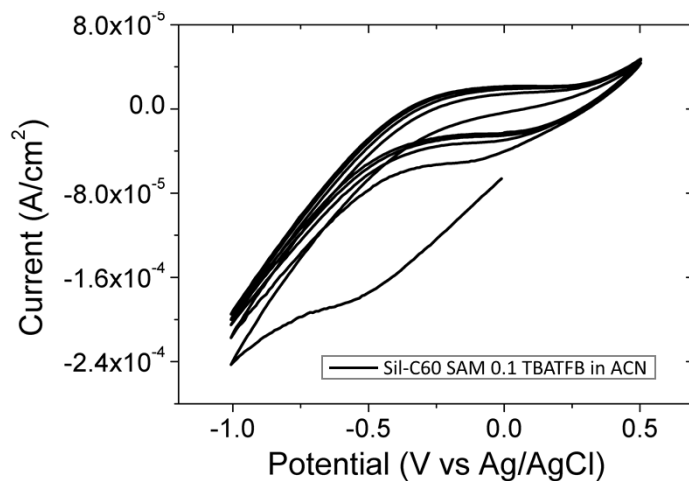


Figure B.4: Stability test of a Sil-C60 SAM sample. Scan rate: 0.1 Vs⁻¹.

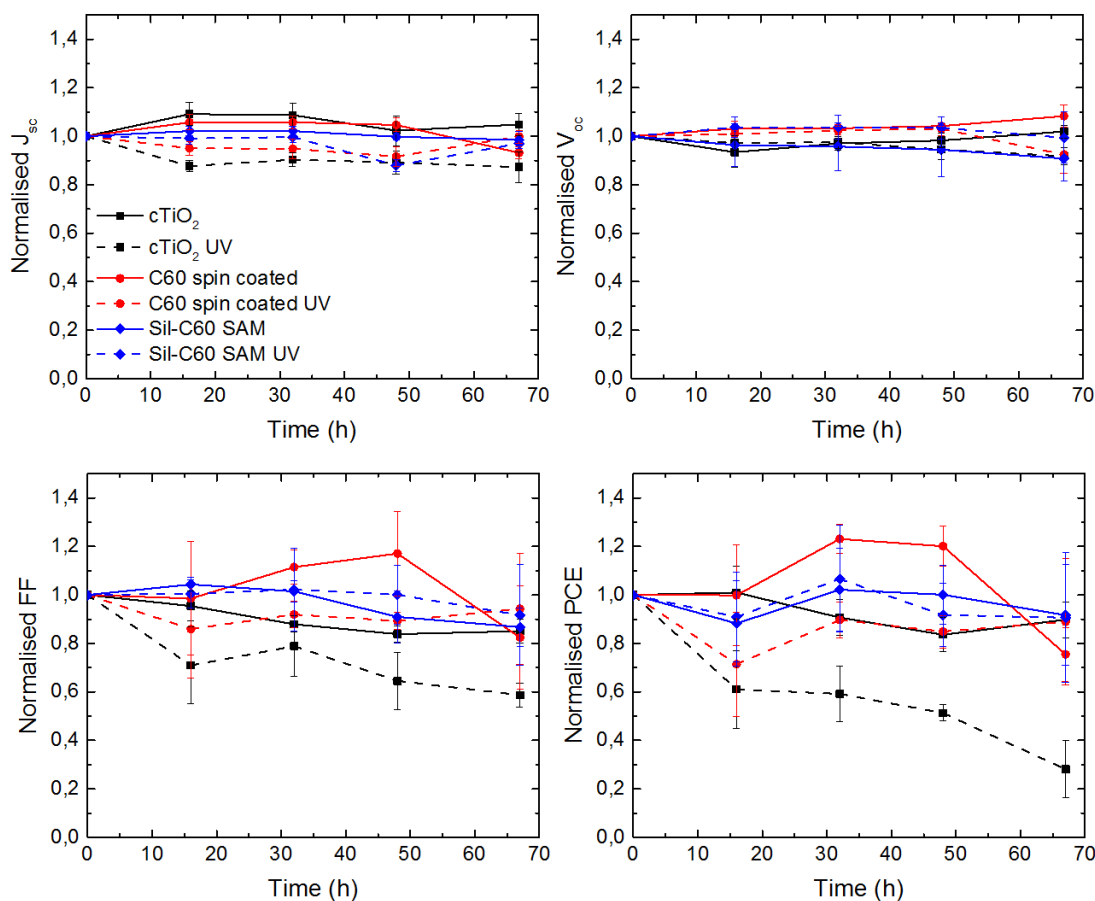


Figure B.5: Time dependence of normalized solar cell parameters (backward scan). Results were obtained by averaging values of 6-8 pixels on each substrate employing various electron transport layers (control and UV exposed), taking only backward scans (open circuit to short circuit).

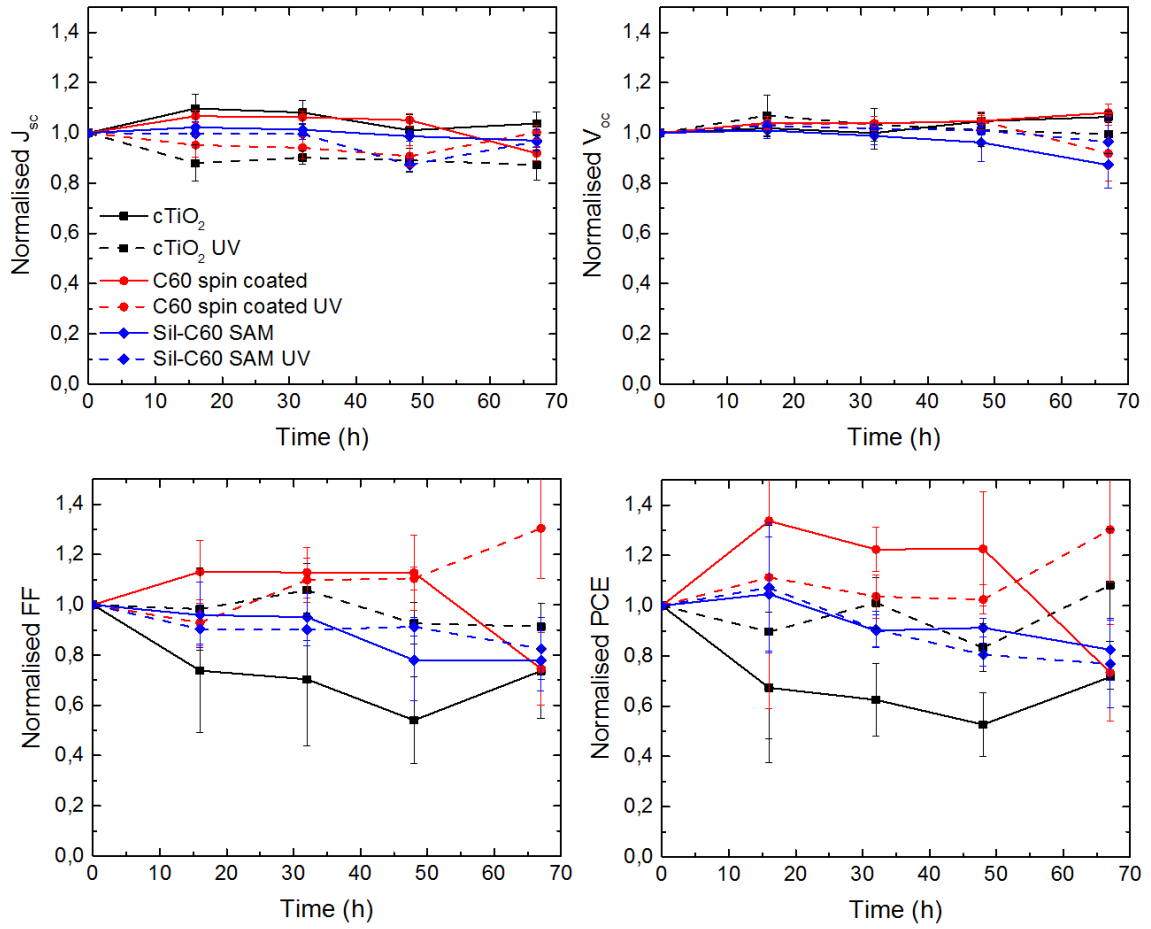


Figure B.6: Time dependence of normalized solar cell parameters (forward scan). Results were obtained by averaging values of 6-8 pixels on each substrate employing various electron transport layers (control and UV exposed), taking only forward scans (short circuit to open circuit).

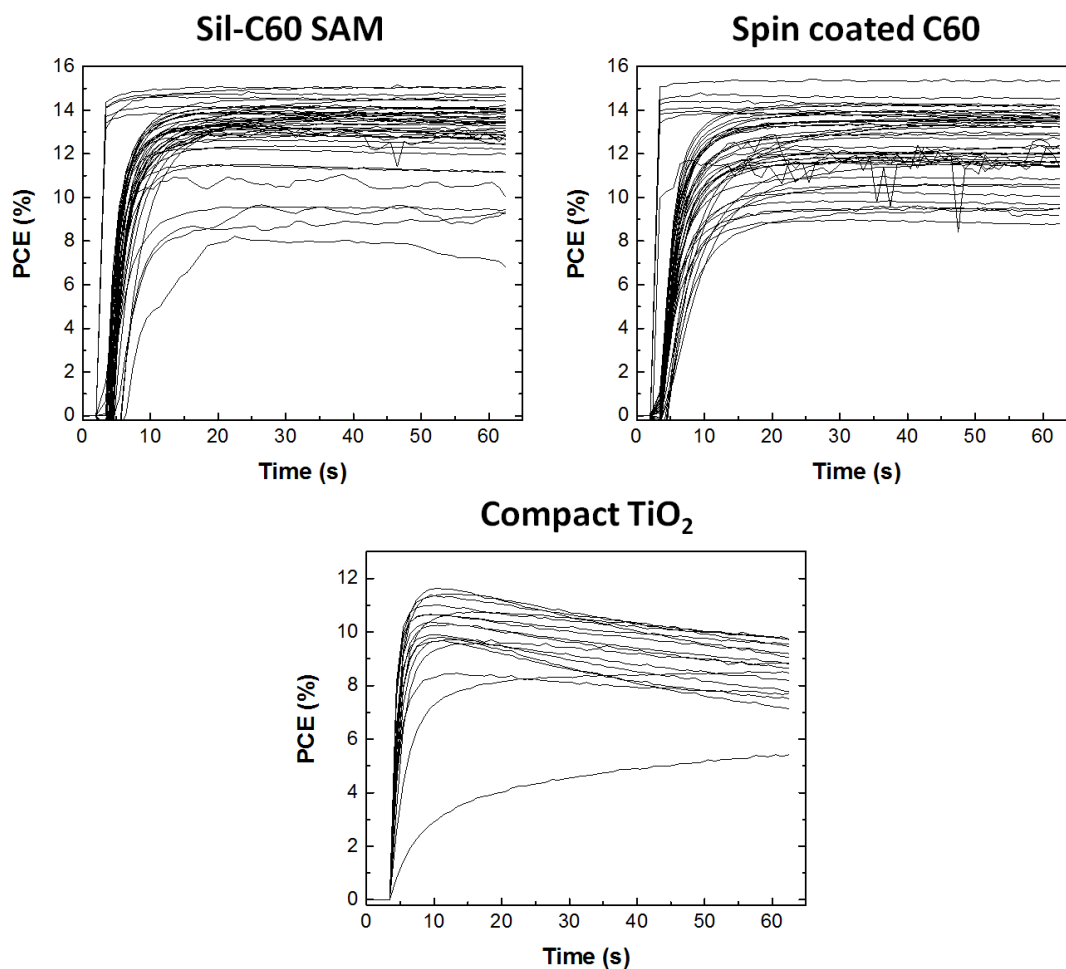


Figure B.7: Stabilization curves of all tested devices. Time dependent PCEs obtained with solar cells employing Sil-C60 SAM, spin-coated C60 and compact TiO₂ as ETL.

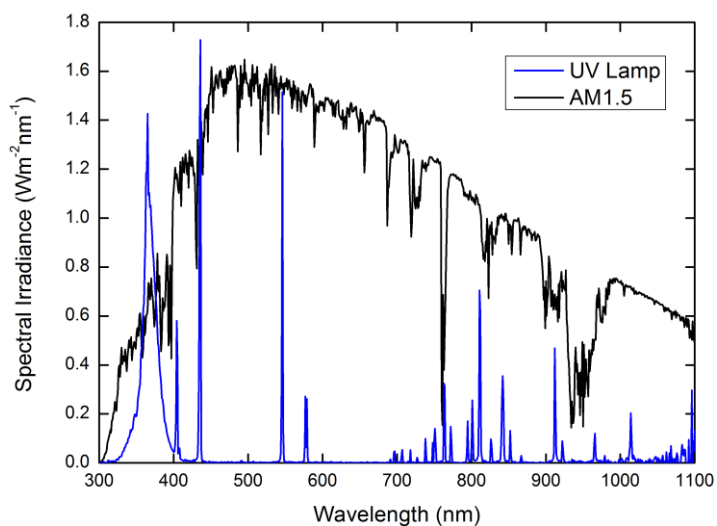


Figure B.8: Spectral irradiance of the UV lamp compared to AM1.5 solar spectrum.

Appendix C

Nano-Thin WS_2 Films as a Hole Transporting Layer in PSCs

C.1 Supporting Results

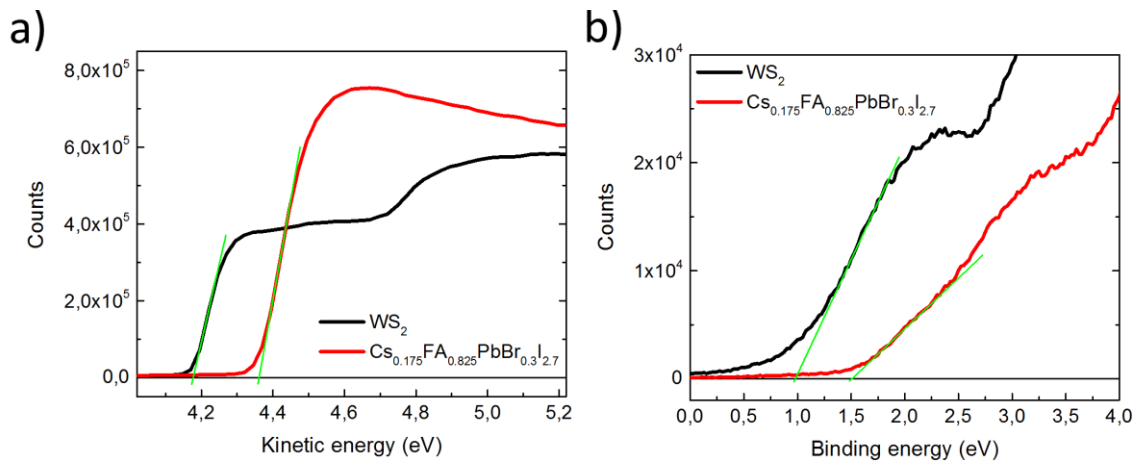


Figure C.1: UPS raw data acquired on the WS_2 and the perovskite. a) Photoemission onset of the secondary electrons determining the Fermi level of both semiconductors. b) Low binding energy part of the spectrum of both semiconductors, defining the position of the VBM below the Fermi level.

Appendix D

Thiol-Click Chemistry on Gold-Decorated MoS₂: Elastomer Composites and Structural Phase Transitions

D.1 Supporting Results

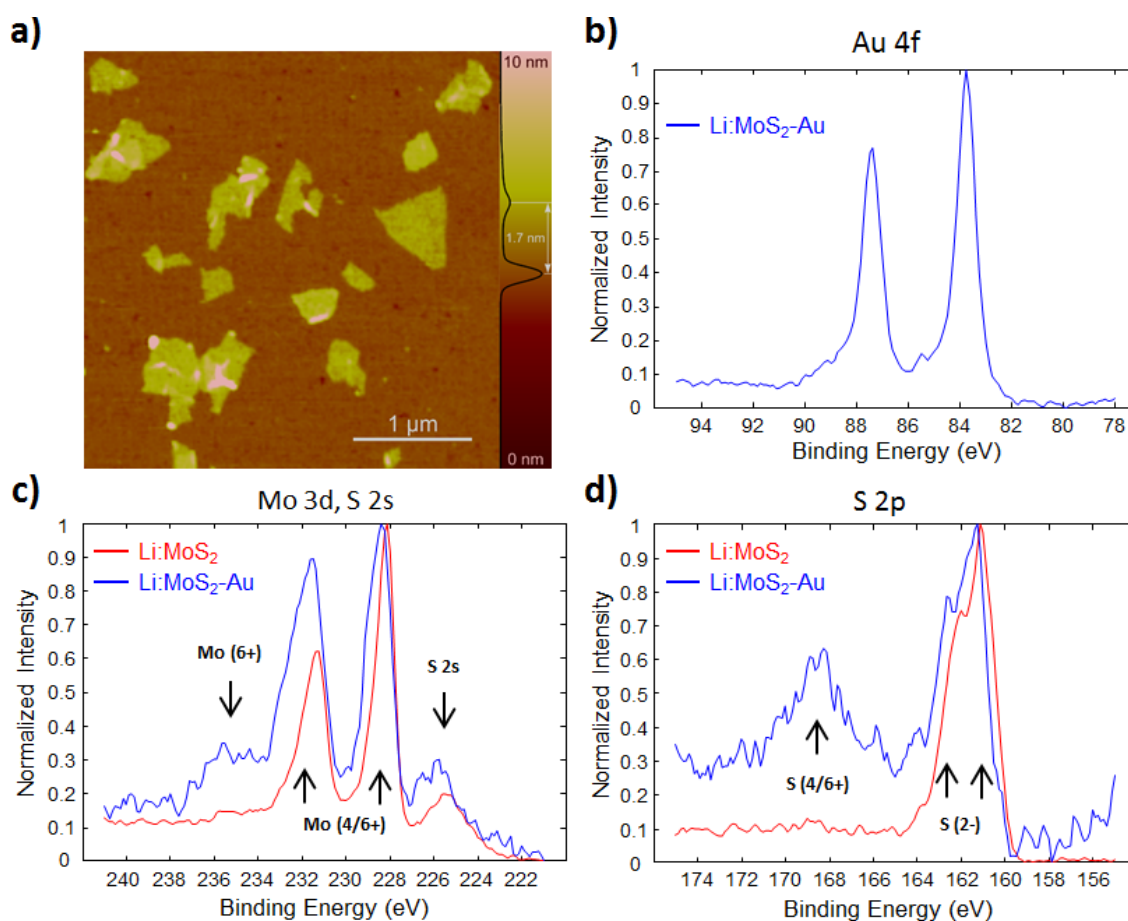


Figure D.1: AFM image of as-exfoliated MoS₂ flakes. The color code bar contains a height histogram showing two main peaks ascribed to the substrate and the flakes.

Detailed XPS spectra of Au 4f (b), Mo 3d and S 2s (c), and S 2p (d) signals of lithium intercalated and exfoliated MoS₂, undecorated (red) and gold decorated (blue) samples.

The exfoliated flakes have typical lateral sizes of a few 100 nm (Figure D.1a) and uniform thicknesses of 1.7 nm. While mechanical exfoliation yields step heights of 0.7 nm, consistent with the crystal structure of MoS₂, chemical exfoliation typically yields monolayers with thicknesses exceeding 1 nm [253]. This discrepancy may be explained by surface corrugation due to distortions as well as adsorbed or trapped molecules. The AFM height profile shows that all flakes have the same thickness and no steps, suggesting they all have the same number of layers.

The XPS spectra of as-exfoliated (undecorated) and gold-decorated flakes are shown in Figure D.1b-d. While the as-exfoliated sample shows sulphur only in the oxidation state S²⁻, upon GNP decoration some of the sulphur is oxidized to S⁴⁺ and/or S⁶⁺. Additionally, the decorated flakes show a gold doublet (Figure D.1b), which points towards a significant presence of both gold atoms bound to sulphur in the flakes and gold atoms bound only to other gold atoms within a GNP. These results confirm the invoked nucleation of GNPs proceeding via the reduction of HAuCl₄ and oxidation of MoS₂.

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Publications Related to the Thesis

Journal Articles

- P. Topolovsek, F. Lamberti, T. Gatti, A. Cito, J. M. Ball, E. Menna, C. Gadermaier and A. Petrozza, "Functionalization of transparent conductive oxide electrode for TiO₂-free perovskite solar cells," *Journal of Materials Chemistry A*, 2017, DOI: 10.1039/C7TA02405C.
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Biography

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