

Carbon Nanotube Thin Film Electrodes and Optical Spectroscopy of Graphene Nanoribbons and FAPbI_3 Single Crystals



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To my parents
for their never-ending love and encouragement

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Abstract

Carbon nanomaterials are a promising class of materials for optoelectronics with low environmental impact. However, dark states limit their photoluminescence (PL) efficiency and thus applicability. In this thesis, hitherto-unrecognised twilight states in graphene nanoribbons are identified, where inter-valley mixing produced by periodic edge modulation and strong electron-phonon coupling are key mechanisms that make conventionally-dark states at least four times brighter, resulting in a 7.7% PL quantum yield. Strong vibron-electron coupling is revealed by the high spectral definition, with the bandgap modulated by coupling to the radial breathing-like mode. Unexpectedly, the predominant phonon modes affect absorption and emission differently, due to the simultaneous presence of Herzberg-Teller and Franck-Condon couplings. The achievement of efficient light emission from carbon nanostructures, both in solutions and thin films, opens the path to their integration into electro-optical circuits, and to the optical investigation and manipulation of topological states in graphenoids. Further, a detailed study of carbon nanotube–ethylene-vinyl acetate (CNT-EVA) transparent conductive films (TCFs) and the connection between processing and optoelectronic film properties is presented, leading to a 100-fold improvement of the electrical conductivity at the same transmittance. The dispersion technique and polymer removal steps are established as crucial steps for improving TCF performance. Changing the composition of the EVA copolymer allows tuning the mechanical and chemical resilience of CNT-EVA films and the films perform well in flexible applications. CNT-EVA films are chemically p-doped with halogenated metals and low-cost dopants identified. The improved CNT-EVA films perform well in transparent touch-sensitive devices and as transport layer in perovskite photovoltaic (PV) devices, highlighting the potential of hybrid transport layers and opening a pathway for the large-scale application of low-cost CNT-EVA conductive films. Finding ways to stabilise perovskites under ambient conditions is the main challenge to overcome before they can be applied on a large scale. Substantial stability improvement is demonstrated for the perovskite formamidinium lead iodide (FAPbI₃) in single crystals by the addition of methylenediammonium dichloride (MDACl₂). This is quantified by Raman spectroscopy which is established as a powerful tool for the characterisation of FAPbI₃ by devising the defocused Raman spectroscopy method. The MDACl₂ additive reduced the trap density and increased the excited carrier lifetime significantly, whereas the band gap at room temperature appears unaffected by the addition of MDACl₂.

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List of Abbreviations

AFM		atomic force microscopy
AGNR		armchair graphene nanoribbon
CCVD		catalytic chemical vapour deposition
CNT		carbon nanotube
CoMoCAT		cobalt-molybdenum catalyst
DOS		density of states
E_F		Fermi level
E_G		band gap energy
EVA		ethylene-vinyl acetate
FA		formamidineum
FC		Franck–Condon
FF		fill factor
FoM		figure of merit
FTO		fluorine-doped tin oxide
FWHM		full width at half maximum
GHG		greenhouse gas
GNR		graphene nanoribbon
HiPCO		high-pressure carbon monoxide disproportion
HMTA		hexamethylenetetramine
HT		Herzberg–Teller
HTL		hole transport layer
IPCC		international panel on climate change
ITO		indium doped tin oxide
J_{SC}		short-circuit current density
Li-TFSI		lithium bis(trifluoromethanesulfonyl)imide

MA	mehtylammonium
MDACl₂	methylenediammonium dichloride
MI	melt index
MWCNT	multi-walled carbon nanotube
NOMI	<i>N-n</i> -octadecylmaleimide
NMR	nuclear magnetic resonance
P3HT	poly(3-hexylthiophene)
PCE	power conversion efficiency
PDOS	projected density of states
PEDOT:PSS	poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
PV	photovoltaic
PL	photoluminescence
PLE	photoluminescence excitation
PLQE	photoluminescence quantum efficiency
PMMA	poly(methyl methacrylate)
PS	polystyrene
RBM	radial breathing mode
RBLM	radial breathing-like mode
SANS	small-angle neutron scattering
SEM	scanning electron microscope
SFM	shear force mixing
spiro-OMeTAD	2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene
SWCNT	single-walled carbon nanotube
TA	transverse acoustic
TCF	transparent conductive film
TRPL	time-resolved photoluminescence
VA	vinyl acetate
V_{MPP}	maximum power point voltage
V_{OC}	open circuit voltage
ZGNR	zigzag graphene nanoribbon
ZPL	zero-phonon line

List of Publications

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Conference Presentations

Tuning Optical Transmittance and Electrical Conductivity of Low-Cost Solution-Processed Carbon Nanotube–Ethylene-Vinyl Acetate Films, *NT19: International Conference on the Science and Application of Nanotubes and Low-Dimensional Materials*, 21-26 July 2019, Würzburg, Germany, poster presentation.

Transparent Conductive Carbon Nanotube–Ethylene-Vinyl Acetate Films, *CDT-PV Showcase*, 02-03 September 2021, Sheffield, UK, oral presentation.

Improving performance of fully scalable, flexible transparent conductive films made from carbon nanotubes and ethylene-vinyl acetate, *Multi-CDT Conference on Clean Energy and Sustainable Infrastructure*, 05-06 April 2022, Sheffield, UK, oral presentation.

Brightly Fluorescent States in Graphene Nanoribbons, *Final CDT-PV Showcase*, 11 November 2022, Westminster, London, UK, oral presentation.

1

Introduction

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1.1 Climate Change & Renewable Energies

The emission of greenhouse gases (GHGs) by human activity has led to a surge in the atmospheric concentration of the primary GHG carbon dioxide (CO_2) to 415 ppm, a concentration which has been unmatched on Earth for at least two million years [1]. The main driver for these emissions was industrialisation in the late 19th and 20th centuries and the connected rise in fossil fuel usage. The annual global CO_2 emissions, shown since 1850 in Fig. 1.1a, have grown dramatically in this period, which led to a sharp increase in global temperatures since the 1950s. The global surface temperature reached 1.1°C above 1850-1900 levels in 2011-2020 [1] (Fig. 1.1a) and the last decade was warmer than any period for 125,000 years [1]. The Intergovernmental Panel on Climate Change's (IPCC) Sixth Assessment Report (AR6), finds that human influence has unequivocally caused

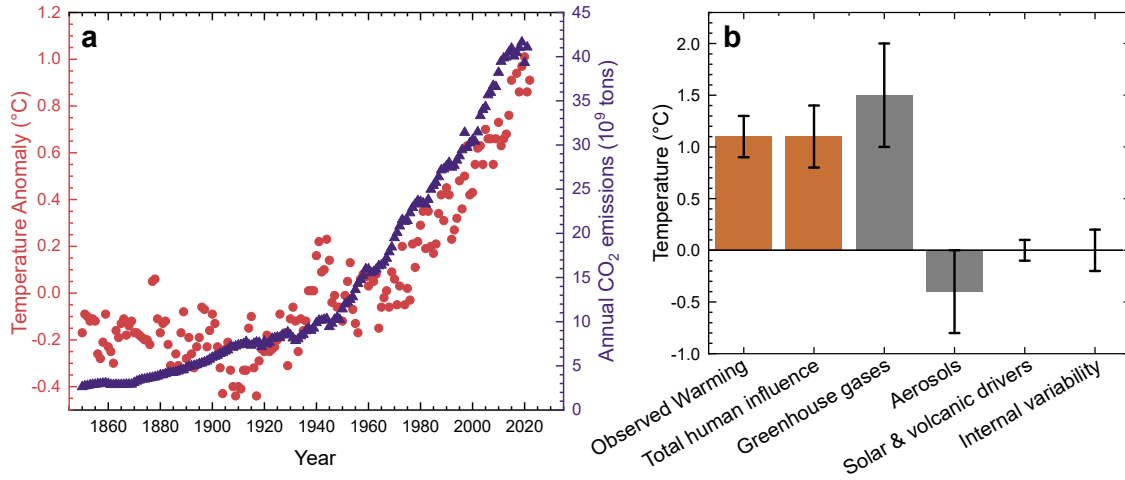


Figure 1.1: Global surface temperature anomaly and CO₂ emissions since 1850. **a)** Global annual surface temperature relative to the 1901-2000 average (red) and annual carbon dioxide (CO₂) emissions (blue). Data reproduced from National Center for Environmental Information at NOAA [2] and under a CC BY 4.0 license from [3]. **b)** Observed warming and contributing factors, reproduced from IPCC AR6 2023 [1].

the warming of 1.1°C observed in 2010-2019 relative to 1850-1900 [1], see Fig. 1.1b. The contribution from greenhouse gases (mainly CO₂, methane, nitrous oxide and fluorinated gases) is paramount while the contributions of solar and volcanic drivers as well as the internal variability are negligible.

Without immediate efforts to reduce GHG emissions, the global temperature is predicted to keep rising. The effects of this change in climate are catastrophic and can already be observed today with more extreme weather events, rising sea levels, and biodiversity loss among the immediate consequences threatening life on Earth [4, 5]. In an effort to limit global warming to well below 2°C, the Paris Agreement was signed at the United Nations Climate Change Conference in 2015 [6].

Since about 70% of GHG emissions are caused by the energy sector, replacing fossil fuels with renewable energy sources like wind and solar is one of the key challenges facing humanity in the 21st century. The IPCC report 2023 finds that solar energy is not only the mitigation option with the highest potential contribution to net emission reduction, it is also the cheapest (Fig. 1.2) with solar energy already being cheaper than burning fossil fuels in many scenarios today [1, 7]. Solar energy is also the most evenly distributed energy source available on Earth. As little as

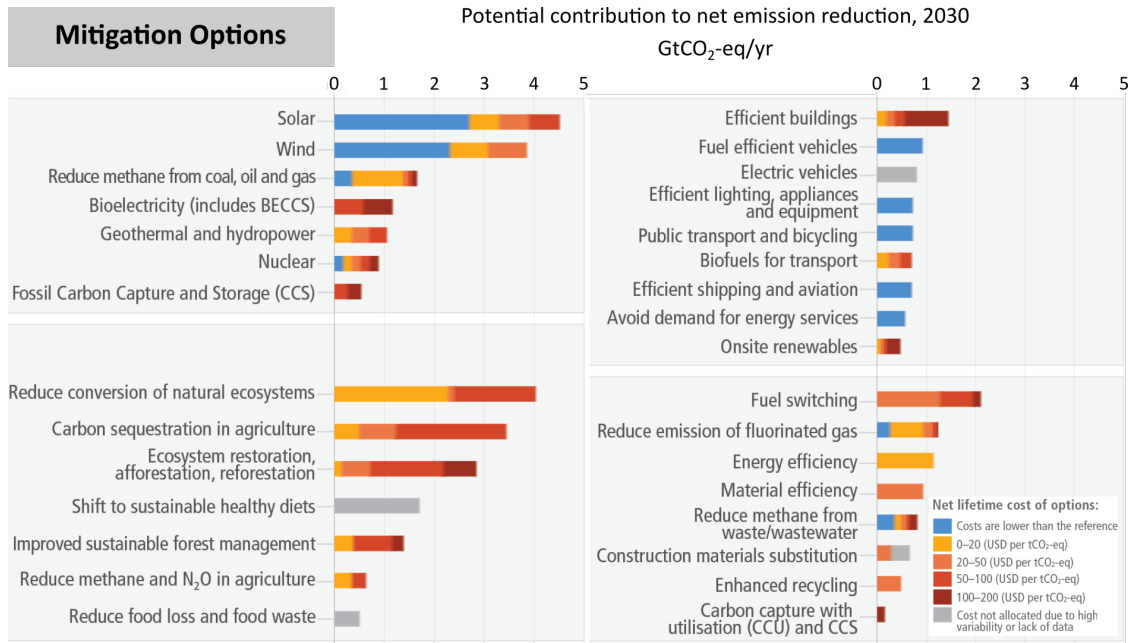


Figure 1.2: Mitigation options for climate change. A list of key mitigation options to reduce greenhouse gas emissions and their potential contribution to net emission reduction. The colour of the bars indicates the net lifetime cost of options. Data reproduced from IPCC AR6 2023 [1].

0.02% of the incoming solar energy is sufficient to satisfy the global demand [8], making solar energy a critical factor in the mitigation of climate change.

1.2 Perovskite Solar Cells

An emerging contender as absorber material in photovoltaic devices is a class of materials called perovskites. Having risen from single digits to 25.7% power conversion efficiency within a decade of research, perovskites are a promising material in many regards [9–12].

Their low fabrication cost and ease of processing together with an adjustable band gap, high carrier mobility, long carrier lifetime and high diffusion length [13, 14] make them a promising candidate not just for photovoltaic devices but also for field-effect transistors [15], light emitting diodes [16], photodetectors [17], and lasers [18, 19]. However, the main caveat of the material remains its instability under ambient conditions, making further research necessary.

1.3 Carbon Nanomaterials

For solar cells and most other optoelectronic devices alike, transparent conductors are a key component.

Current standard materials for transparent conductive films such as indium tin oxide (ITO) need to be replaced for two reasons: on the one hand, conventional materials cannot keep up with the ever-expanding requirement profile of modern optoelectronics including being flexible, lightweight and low-cost. On the other hand, conventional conductive films are made from scarce metals or even rare elements such as indium, which have limited supply and are increasingly costly to mine [20].

Carbon nanomaterials such as carbon nanotubes or graphene nanoribbons offer a promising route forward. The ability to synthesize these materials from readily available sources of carbon at a low cost makes them a low environmental impact alternative to existing technology and addresses the drawbacks listed above. Recent advances in CNT synthesis have demonstrated that carbon nanotubes can not only be made from traditional carbon sources (e.g. ethylene) but also from plastic waste [21] or directly from CO₂ [22].

In combination with their outstanding mechanical strength and versatile electronic properties, which can be tuned via edge structures and the resulting quantum confinement, this makes carbon nanomaterials an exciting material for next-generation optoelectronics.

1.4 Thesis Outline

- Chapter 2 introduces the fundamentals of semiconductors and photovoltaic devices.
- Chapter 3 provides an overview of the characteristics of carbon nanotubes and graphene nanoribbons derived from the description of graphene.
- In chapter 4, the materials and methods deployed in this thesis are introduced.

- Chapter 5 investigates the optical and electronic properties of a new type of soluble graphene nanoribbon with a particular focus on the role of electron-phonon coupling.
- In chapter 6, several approaches to improve the performance of transparent conductive films made from carbon nanotubes and the polymer ethylene-vinyl acetate are presented.
- Chapter 7 demonstrates how these films can be applied in touch-sensitive thin films or as transport layers in FAPbI₃ perovskite photovoltaic devices.
- Chapter 8 analyses the effect of the additive methylenediammonium dichloride on the phase stability and optoelectronic properties of FAPbI₃ perovskite single crystals.
- Finally, chapter 9 provides a summary of the presented results and an outlook over possible future implications and research.

2

Theory of Semiconductors and Solar Cells

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This chapter briefly introduces the concepts and fundamental principles of semiconductors and photovoltaic devices. The description is based on *The Physics of Solar Cells* by JENNY NELSON, 2003, Imperial College Press [23], and *Physics of Solar Cells* by PETER WÜRFEL, 2016, Wiley [24].

2.1 Optical Properties of Semiconductors

2.1.1 Introduction

Bulk materials can be classified by the size of their band gap E_g . The band gap typically describes the energy difference between the top of the valence band and the bottom of the conduction band. Valence and conduction bands are the bands right below and above the Fermi energy E_F , which is defined as the energy up to which electronic states are occupied at zero temperature. In between these two bands, no electronic states exist and the density of states (DOS), the number of electronic states per unit of energy, is zero. If the energy gap is significantly larger than the thermal energy $E_g \gg k_B T$, the material system is considered a semiconductor. Materials without an appreciable band gap $E_g < k_B T$ around E_F are called metals, while for insulators the band gap is typically larger than 4 eV. This definition is chosen to reflect the fact that in semiconductors the thermal energy at room temperature is sufficient to excite a small fraction of electrons from the valence into the conduction band, while for insulators the band gap is too large to be overcome by absorbing thermal or even visible radiation.

2.1.2 Light Absorption and Charge Carrier Excitation

Absorption of light requires two states separated by an energy gap with the lower (ground) state occupied and the higher (excited) state unoccupied initially. In a semiconductor, this condition is met for ground states in the valence band and excited states in the conduction band.

Another condition for light absorption is that the photon energy $h\nu$ needs to exceed the band gap. A photon can then be absorbed by an electron in the ground state, transferring it to a higher energy level, see Fig. 2.1a.

The excess energy $h\nu - E_g$ is quickly released by the electron through thermal vibrations until it reaches the band edge. This process is called thermalisation and typically occurs within femtoseconds. In contrast, interband relaxation from

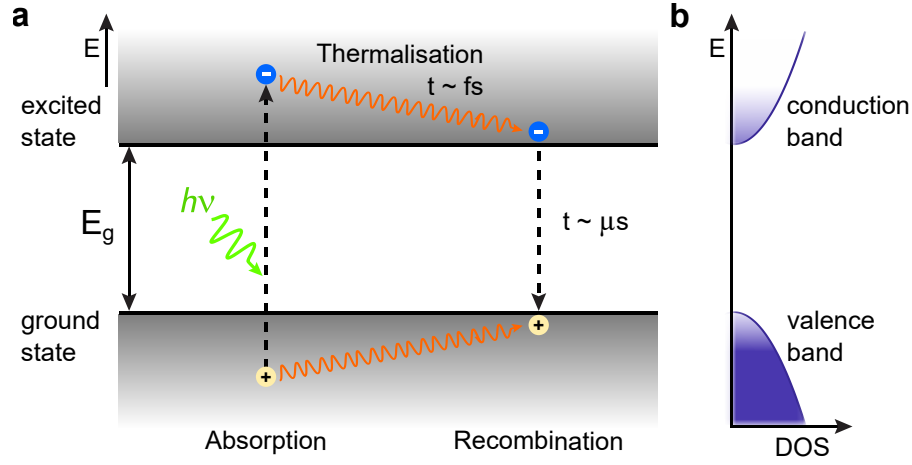


Figure 2.1: Photon absorption, thermalisation, consecutive recombination and density of states. **a)** Excited and ground states are separated by a band gap energy E_g . While the thermalisation of excited charge carriers occurs within femtoseconds, lifetimes at the band edge are typically in the microsecond range for absorber materials. **b)** Density of states (DOS) for a 3-dimensional semiconductor with band gap E_g . The shading of the fill colour indicates an exemplary occupation of states.

the excited state band edge back to the ground state happens on the timescale of microseconds.

The density of states for a 3-dimensional semiconductor with band gap E_g is shown in Fig. 2.1b. While states in the valence band are predominantly occupied, the conduction band is nearly empty. This allows photons with energy $E > E_g$ to be absorbed.

2.1.3 Absorption and Reflection of Crystalline Semiconductors

When a photon impinges the surface of a crystal, it can be reflected or transmitted. Upon transmission into the crystal, the photon can undergo scattering processes and, if it has sufficient energy, be absorbed by exciting an electron as described above. The excited electrons will eventually relax to their ground state in the valence band. The timescale and photon energy of the relaxation process provides insights into the structure and defects of the crystal.

Absorption and reflectivity characteristics of a crystalline semiconductor are described by the dielectric tensor $\varepsilon_{ij}(\omega)$, which determines the response to an external

electric field $E(\mathbf{q}, t)$ with wavevector $\mathbf{q}$ and frequency ω . This tensor ε_{ij} is defined by

$$D_i(\mathbf{q}, \omega) = \varepsilon_0 \varepsilon_{ij}(\omega) \cdot E_j(\mathbf{q}, \omega) \quad (2.1)$$

where $D(\mathbf{q}, \omega)$ is the Fourier transform of the electric displacement vector $D(\mathbf{r}, t)$. $D_i(\mathbf{q}, \omega)$ and consequently $\varepsilon_{ij}(\omega)$ are complex, with the real part (ε_r) describing the reflectivity, the imaginary component (ε_i) the absorption of the crystal.

The imaginary and complex components of ε can be connected by the *Kramers-Kronig relations*. These relate two equations by employing a contour integral in the upper plane

$$\begin{aligned} \chi_i &= \frac{\mathcal{P}}{\pi} \int_{-\infty}^{\infty} \frac{\chi_r(\omega')}{\omega' - \omega} d\omega' \\ \chi_r &= -\frac{\mathcal{P}}{\pi} \int_{-\infty}^{\infty} \frac{\chi_i(\omega')}{\omega' - \omega} d\omega', \end{aligned} \quad (2.2)$$

with a normalisation constant $\mathcal{P}$ and the electric susceptibility χ_{ij} defined as $\chi_{ij}(\mathbf{q}, \omega) = \varepsilon_{ij}(\mathbf{q}, \omega) - 1$. Using these relations, it is sufficient to know either ε_r or ε_i to calculate the other [25], see Fig. 2.2.

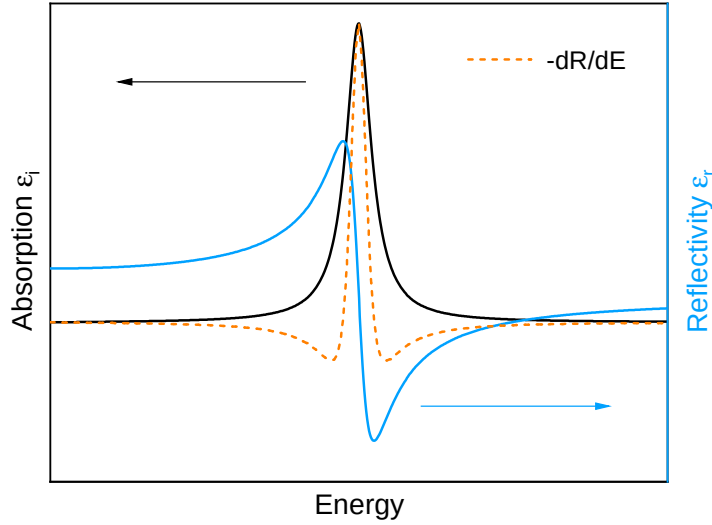


Figure 2.2: The Kramers-Kronig relation of absorption and reflection. The absorption (black) can be calculated from the reflectivity (blue) via the Kramers-Kronig relations (Eq. 2.2). The position of a given absorption peak can thus be described well by $-\frac{dR}{dE}$.

For crystals of sufficient thickness, strong absorption and scattering make accurate transmission measurements impossible. In these situations, the Kramers-Kronig relations prove useful, allowing the determination of the absorption from the

reflectivity. This can be a powerful tool to determine the band gap of crystalline semiconductors. Even in the case of incomplete data for ε_r (note the ∞ bounds in Eq. 2.2), a good approximation of the spectral transmission can be made with the energy derivative $-\frac{dR}{dE}$ of the reflectivity R . This is shown exemplarily in Fig. 2.2.

2.2 Photovoltaic Devices

2.2.1 Definition

A photovoltaic (PV) device converts photons into electric power. Upon absorption of electromagnetic waves in the active layer of the device, the photon energy is transferred to electrons, lifting them into an excited state of higher energy. To extract power from the photovoltaic device, the photochemical potential energy of the excited electrons needs to be extracted into an external electric circuit. The first step of charge extraction consists of separating the charges of opposite polarity, electrons and holes before they recombine. Once charges are extracted, they can be extracted into an external circuit and perform work on a load. The details of the steps involved in the conversion of radiation energy to electric energy will be described in the following sections.

2.2.2 Charge Carrier Generation and Recombination

The discrepancy in lifetimes between short-lived vibrational levels and states at the conduction band edge (see Fig. 2.1a) allows excited charges to be extracted at the band edge energy following absorption. The photon energy in excess of the band gap is lost to thermalisation. Consequently, the size of the band gap manifests a trade-off between the absorbable photon energy range, corresponding to the current in a photovoltaic device, and the energy that can be extracted per electron-hole pair, corresponding to the voltage. The size of the band gap is optimal when the product of voltage and current, equalling the electric power, is maximised.

Consequently, the theoretical maximum power conversion efficiency (PCE) depends on the incident photon flux. For terrestrial applications, the solar emission and absorbance from the atmosphere have to be considered, leading to the AM 1.5

photon flux reference spectrum shown in Fig. 2.3a. Shockley and Queisser demonstrated that a maximum power conversion efficiency (PCE) of 33.7% exists for an absorber with a band gap of 1.34 eV, referred to as the *Shockley Queisser limit* [26], while the PCE quickly decays for band gaps below 1 eV or above 1.5 eV (Fig. 2.3b).

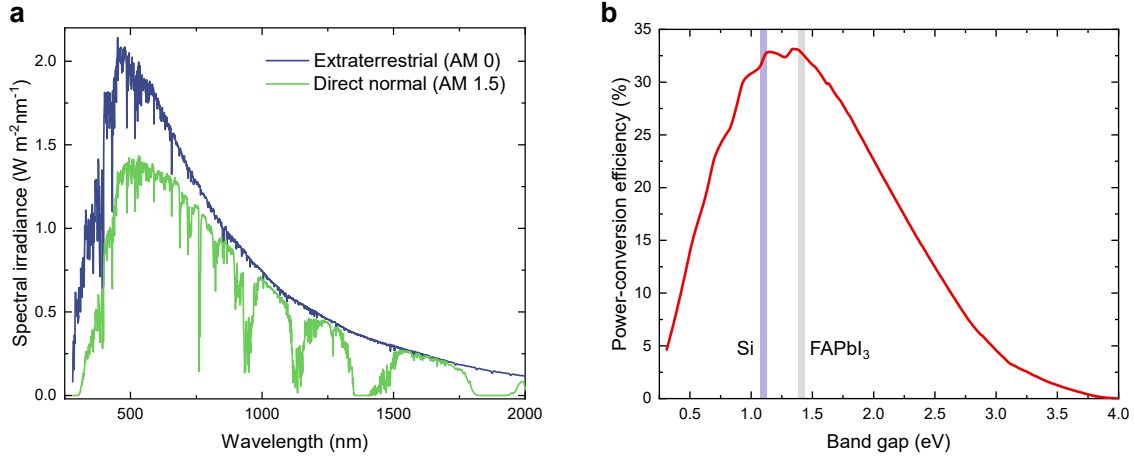


Figure 2.3: Spectral irradiance on Earth and Shockley-Queisser limit. **a)** Extraterrestrial and direct normal spectral irradiance caused by the black-body radiation of the sun. Spectra are ASTM G-173 standards provided by NREL. **b)** Maximum theoretical power-conversion efficiency (Shockley-Queisser limit) for different band gaps under AM1.5 illumination with no concentration and at 25° C [27]. The band gaps of the industry standard Silicon (Si) [28] and the perovskite FAPbI₃ [29] investigated in this thesis are highlighted.

Once a material with an adequate band gap has been chosen, the absorption depends on the layer thickness and interference effects. While thicker layers allow for more photons to be absorbed, the generated charges also have to travel further to be extracted, which gives rise to recombination losses. Materials with higher charge mobility and longer diffusion lengths are thus favourable, allowing faster carrier extraction with fewer scattering events. Typically, three types of recombination losses are distinguished, Radiative, Auger and defects, see Fig. 2.4.

Radiative recombination describes the time-inverted process of absorption, an electron in the conduction band recombines spontaneously with a hole in the valence band under the emission of a photon. Spontaneous recombination is a material-specific intrinsic property and therefore sets a limit to the overall efficiency of photovoltaic materials.

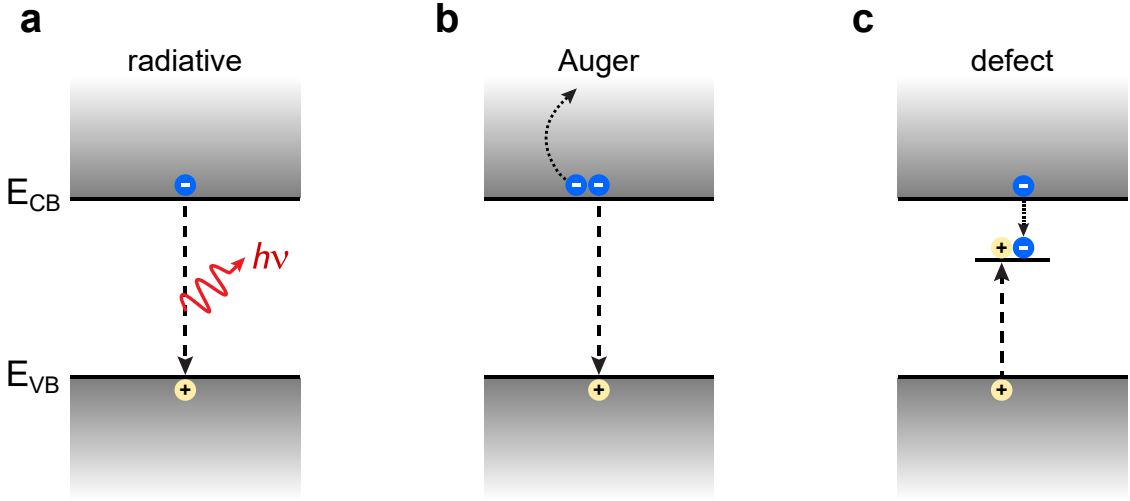


Figure 2.4: Recombination mechanisms. a) Radiative interband recombination b) non-radiative Auger recombination c) non-radiative trap-assisted recombination.

In a spontaneous recombination event of an electron and a hole, the energy can also be transferred to another electron in the conduction band via collision, lifting it to a higher energy state in the conduction band, before thermalising back to the conduction band edge. Such processes are referred to as *Auger recombination* and are most relevant in semiconductor materials with high carrier densities due to the higher probability of carrier collisions.

The most important loss mechanism in real devices is commonly *defect recombination*, caused by impurities and defects in the absorber layer. These imperfections lead to localised states inside the band gap capturing excited charge carriers. When a second charge carrier of opposite polarity relaxes into the same trap, the two charges recombine and the energy is released non-radiatively in form of heat. Such defects are referred to as recombination centres and the dominant loss mechanism in most real-world materials.

2.2.3 Charge Carrier Separation and Extraction

When a photon is absorbed, its energy excites an electron into the conduction band, generating a hole in the valence band. These two charge carriers possess opposite polarity and therefore electrostatic Coulomb attraction. Depending on the dielectric environment of the material this attraction can be significantly larger than

the thermal energy at room temperature and thus prevent spontaneous separation of the electron-hole pair. In this case, the pair of charges can be treated as a quasi-particle and is called an exciton. As long as the pair are bound together, the two charges can not be extracted to perform work in a circuit.

To overcome this issue, photovoltaic devices have a built-in asymmetry driving electrons and holes in opposite directions, and leading to a net current in the absorber layer. Two types of currents are distinguished via the type of driving force behind the asymmetry. *Diffusion currents* are caused by differences in charge carrier density, while *drift currents* are the result of an electric field in the absorber layer. This can be realised by bringing two materials with different work functions, electron affinity or band gaps in contact. Details will be discussed in the following.

2.2.4 Semiconductor Junctions and Contacts

Contacts between two semiconductors as well as between semiconductors and metals play a crucial role in photovoltaic devices and equally in carbon nanotube networks, see Sec. 4.1.2. We have previously defined semiconductors as materials with a band gap $k_B T \ll E_g < 4 \text{ eV}$. The occupation of electronic states in a semiconductor follows the Fermi-Dirac distribution

$$f(E, T) = \frac{1}{\exp(\frac{E - E_F}{k_B T}) + 1} \quad (2.3)$$

with the Boltzmann constant k_B and the Fermi level E_F . The Fermi-Dirac distribution describes the probability of a given state at energy E to be occupied at temperature T .

This allows a more elegant definition of the Fermi level as the energy at which $f = 0.5$ which also includes cases where E_F is located inside the band gap. In intrinsic semiconductors, E_F is at the centre of the band gap. At zero temperature, all states up to E_F are filled and all states above are empty. To make E_F comparable between different materials, we introduce the *work function* Φ which is defined as

$$\Phi = E_{vac} - E_F \quad (2.4)$$

relative to the vacuum energy E_{vac} . In metals, the work function is equivalent to the *electron affinity* χ which describes the change of energy upon moving an electron from the vacuum level to the lowest unoccupied state, typically the conduction band edge.

Doping shifts the Fermi level of a material and consequently the work function. For n-doping, the Fermi level shifts towards the conduction band and thus reduces the work function, while p-doping has the opposite effect, such that $\Phi_n < \Phi_i < \Phi_p$.

If two materials are brought in contact, a junction is formed and the Fermi levels align to one constant energy level. If the work functions of the two materials differ, there will be a gradient in the vacuum levels causing an electrostatic field across the junction.

Metal-semiconductor contacts

A metal-semiconductor junction is illustrated in Fig. 2.5 for an n-type semiconductor with a smaller work function than the metal. Since the Fermi level must be constant

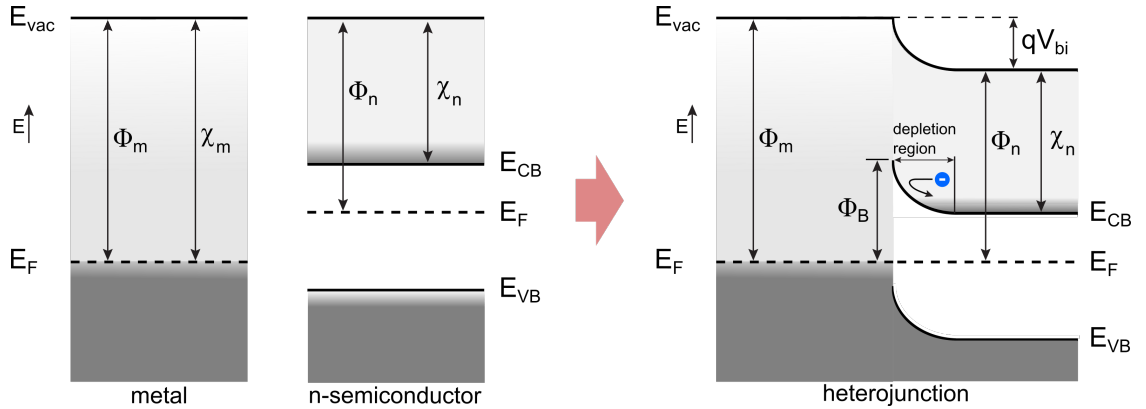


Figure 2.5: Formation of a metal-semiconductor junction for an n-type semiconductor. Upon contact, the Fermi levels (E_F) align which results in a shift of the vacuum level (E_{vac}) and band bending in the semiconductor, while the work functions (Φ_m, Φ_n) and electron affinities (χ_m, χ_n) remain unaffected. In the process of aligning the Fermi levels, electrons flow to the metal, leaving behind a positively charged depletion region in the semiconductor. The bending of the conduction band creates a barrier (Φ_B) preventing electrons from entering the metal from the semiconductor, while the transport of holes into the metal is favourable.

after contacting the layers and $\Phi_n < \Phi_m$, electrons will flow from the semiconductor to lower-lying states in the metal, leaving behind immobile positively charged ions in

the semiconductor. This process continues until the built-up space charge is strong enough to halt the charge exchange and equilibrium between the layers is reached.

The electron affinities and the band gap of the semiconductor are material properties and remain unchanged when the two layers are brought in contact. Therefore, aligning the Fermi levels results in a difference between the vacuum levels of the two materials. This gives rise to a gradient in the electrostatic potential in the proximity of the interface. Most of this potential difference is dropped in the semiconductor since its higher dielectric constant means it has a higher capacity to store charge. Conduction and valence bands bend in the same manner as the vacuum level and the magnitude of the band bending is given by qV_{bi} where V_{bi} is the built-in potential caused by the space charge.

The bending of the conduction band results in an energetic barrier Φ_B preventing electrons from moving from the semiconductor to the metal. This is also referred to as *Schottky barrier*. By contrast, the band bending drives holes from the semiconductor to the energetically favourable states in the metal. Far away from the junction, the vacuum level reaches its intrinsic value and the bands become flat. At this point, the electric field is zero and no electrons have been drained from the semiconductor. The region up to this point is thus called *depletion region*.

Overall, the built-in electric field at the interface of the described junction drives electrons into the semiconductor and holes into the metal, presenting a mechanism to separate charges. This type of junction has a high resistance for electrons entering the metal and is also called *Schottky junction*.

In analogy to the above, for a p-type semiconductor, a Schottky junction is formed if $\Phi_m < \Phi_p$. In this case, the bands bend downwards inside the semiconductor and thus create a barrier preventing the majority carriers, this time holes, from entering the metal, while electrons can transfer into the metal freely.

However, not all metal-semiconductor junctions are Schottky junctions. If the work function of an n-type semiconductor is larger than that of the metal ($\Phi_n > \Phi_m$), or smaller for p-type materials, the bands bend in the opposite direction. This enables the majority carriers to transfer into the metal but impedes the transport of

the minority carriers. These junctions possess a low resistance and display Ohmic behaviour. They are thus referred to as *Ohmic contacts*.

Semiconductor pn-junctions

Junctions between p-type and n-type semiconductors (*pn-junctions*) are classified into homojunctions and heterojunctions, depending on whether the two layers consist of the same semiconductor material or not.

Mostly, homojunctions of the same material are being used, where one component is heavily p-doped and the other heavily n-doped, see Fig. 2.6.

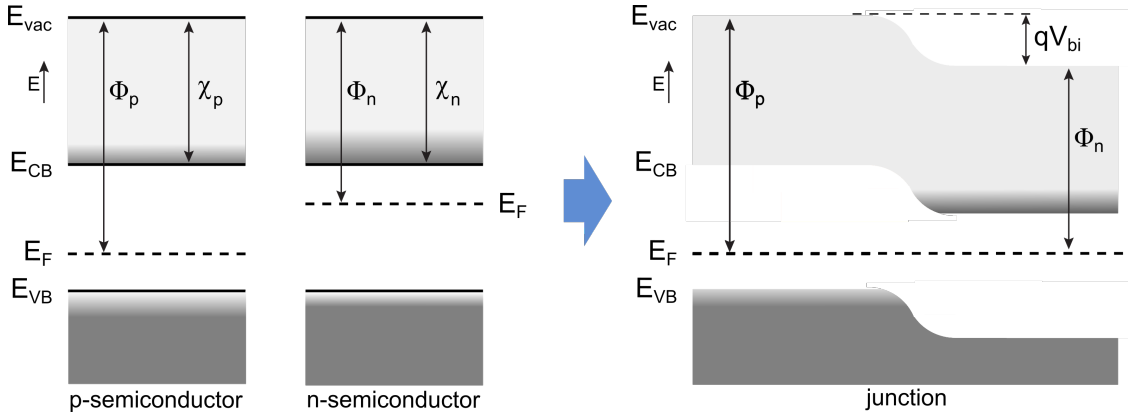


Figure 2.6: Formation of a pn-junction between two semiconductors of the same material. A homojunction is characterised by two materials with the same electron affinity ($\chi_p = \chi_n$) but different work functions ($\Phi_p > \Phi_n$). Upon contact, this causes a gradient in the vacuum levels and band bending which occurs in equal parts in both materials. In the process of matching the Fermi levels, mobile majority carriers flow into the opposite side and recombine, leaving behind ionised dopant atoms which manifest a space charge.

The lower work function of the n-doped material results in a similar band bending to the one observed in Schottky junctions when the materials are brought in contact and the Fermi levels equilibrate. Since both materials have the same dielectric environment, the band bending is now shared between the p- and n-side.

The electrostatic potential is lower on the n-side, resulting in an electric field across the junction. In the process of matching the Fermi levels, mobile majority carriers flow into the opposite side, electrons into the p-side and holes into the n-side, where they recombine. The majority carriers leave behind immobile minority carriers

in the form of ionised donor or acceptor atoms, which manifest a space charge with polarity opposite the doping type. The electrostatic field of this space charge causes a drift current of minority carriers across the junction. Equilibrium is reached when the drift current of minority carriers matches the diffusion current of majority carriers.

2.3 Solar Cell Characterisation

Solar cells are characterised by the work they perform on a load per unit of time t .

$$P = \frac{Q \cdot V}{t} = I \cdot V \quad (2.5)$$

Therefore, both current I and voltage V need to be generated by a photovoltaic device. If the two terminals of a device are connected without a load, the voltage is zero and the device operates at the *short-circuit current* I_{sc} . This property depends on the band gap, the intensity of incident light and in a perfect cell scales linearly with the active area A of the device. Therefore, the short circuit current is commonly given as current density $J_{sc} = I_{sc}/A$.

If a load is added to the circuit, a potential difference exists between the terminals. This results in a light-independent current called *dark current* described by the Shockley equation

$$J_{dark} = J_0 \left[\exp \left(\frac{qV}{k_B T} \right) - 1 \right]. \quad (2.6)$$

The constant $J_0 \propto \exp(-E_g/k_B T)$ is the saturation current. The direction of the dark current is opposite to the photogenerated current. The difference between the two currents characterises the current-voltage behaviour of an ideal diode in the *ideal diode equation*

$$J = J_{sc} - J_0 \left[\exp \left(\frac{qV}{k_B T} \right) - 1 \right]. \quad (2.7)$$

The JV curve of an ideal diode is plotted in Fig. 2.7. The inset provides the equivalent circuit of an ideal photovoltaic device.

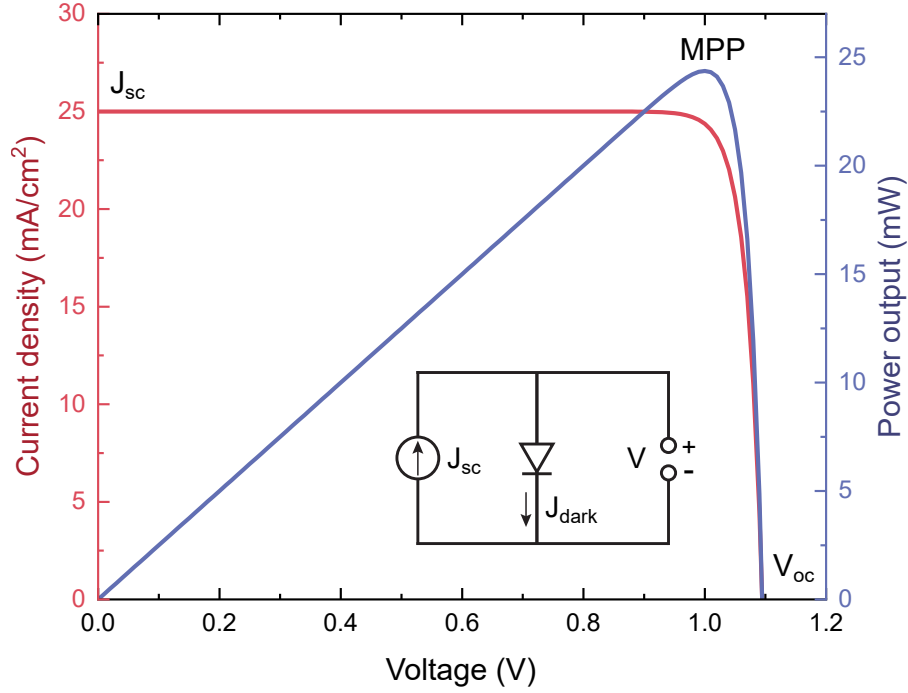


Figure 2.7: Current-voltage characteristics of an ideal photovoltaic cell. An ideal JV-curve (red) with short-circuit current (J_{sc}) and open-circuit voltage (V_{oc}). The power output (purple) of a 1 cm^2 cell as a function of the operating voltage is maximised at the maximum power point (MPP). The inset depicts the equivalent circuit of an ideal photovoltaic cell.

In an open circuit, the current is zero and the voltage has its maximum value, the *open-circuit voltage* V_{oc} . This situation corresponds to the dark current matching the photogenerated current and we find

$$V_{oc} = \frac{k_B T}{q} \ln \left(\frac{J_{sc}}{J_0} + 1 \right). \quad (2.8)$$

The operation range of a solar cell is between 0 and V_{oc} . The maximum power is generated when the product of current and voltage is maximised. This *maximum power point* voltage V_{MPP} is the operating point of a solar cell, see Fig.2.7. The ratio of the power generated at V_{MPP} and the product of J_{sc} and V_{oc} is called the *fill factor* FF

$$FF = \frac{J_{MPP} \cdot V_{MPP}}{J_{sc} \cdot V_{oc}}. \quad (2.9)$$

The fill factor provides a measure of the achieved power output compared to the idealised power output in the absence of internal losses.

In absolute terms, the power output of a solar cell is described by the *power conversion efficiency* PCE , which is given as a fraction of the power of incident light P_{light}

$$PCE = \frac{P_{MPP}}{P_{light}} = \frac{J_{MPP} \cdot V_{MPP}}{P_{light}} = \frac{J_{sc} \cdot V_{oc} \cdot FF}{P_{light}}. \quad (2.10)$$

In real-world devices, two types of parasitic resistances exist that reduce the generated power. The *series resistance* R_s is the sum of all contact resistances throughout the device and affects the JV curve by reducing the magnitude of the slope at $V > V_{MPP}$, see Fig. 2.8. The *shunt resistance* R_{sh} of a device should

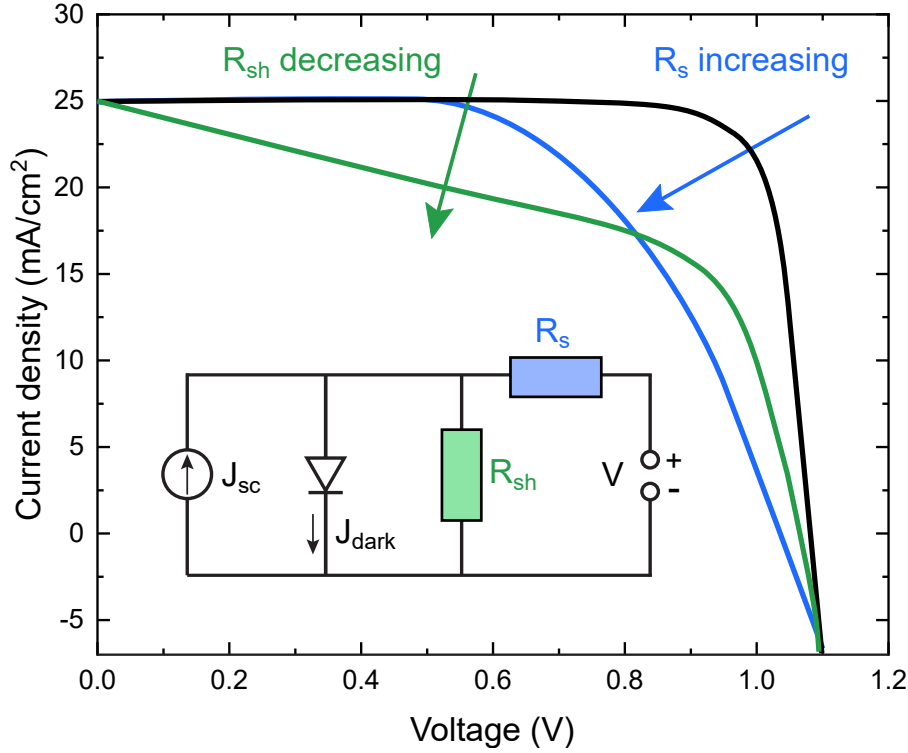


Figure 2.8: Current-voltage curve of a solar cell with parasitic resistance losses. An ideal JV -curve (black) has a nearly square shape following the ideal diode equation with $R_s = 0$ and $R_{sh} \rightarrow \infty$. For increasing series resistances (R_s), the magnitude of the slope of the JV -curve at $V > V_{MPP}$ is reduced. For decreasing shunt resistances (R_{sh}), the slope of the JV curve is reduced at $V < V_{MPP}$.

ideally be infinite and is reduced by leakage currents i.e. if contacts of opposite polarity come into direct contact. Lower shunt resistances reduce the slope of the JV curve at $V < V_{MPP}$ (Fig. 2.8).

The two parasitic resistances can be included in the diode equation

$$J(V) = J_{sc} - J_0 \left[\exp \left(\frac{q(V + JAR_s)}{k_B T} \right) - 1 \right] - \frac{V + JAR_s}{R_{sh}} \quad (2.11)$$

where A is the area of the device. The equivalent circuit is shown as inset in Fig. 2.8.

2.4 Perovskite Solar Cells

2.4.1 Perovskite Crystal Structure (FAPbI₃)

Perovskite solar cells are characterised by having an active layer material in the ABX₃ perovskite crystal structure. Perovskites are composed of a monovalent cation at the A site, a divalent metal cation at the B site and a halogen anion at the X site. The B- and X-site moieties form BX₆ octahedra with B at the centre, while the A species is located in the gaps between the octahedra, see Fig. 2.9. This crystal configuration of a three-dimensional perovskite is only possible for

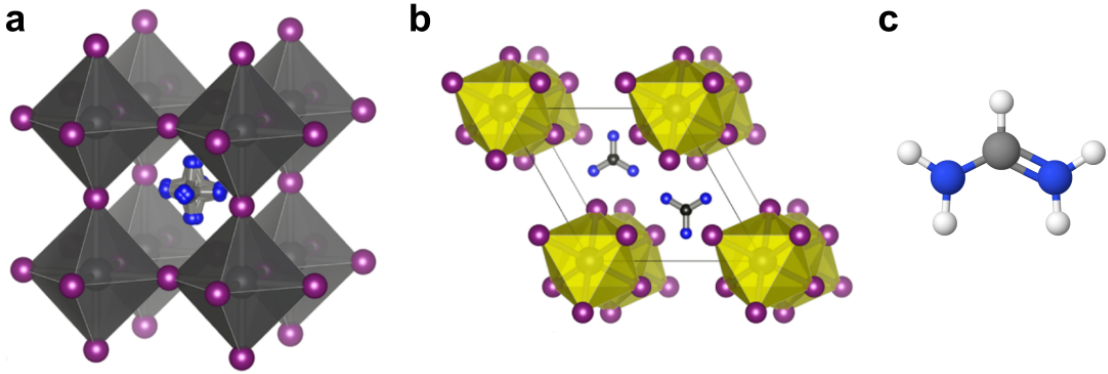


Figure 2.9: Crystal structure of the ABX₃ perovskite compound FAPbI₃. The B- (Pb²⁺, grey) and X-site (I⁻, purple) ions form BX₆ octahedra (black, yellow), the A-site cations (FA⁺, blue and grey) are located in between these octahedra. **a)** Crystal structure of the three-dimensional cubic α -FAPbI₃. **b)** Crystal structure of the hexagonal δ -FAPbI₃. Adapted from [30]. **c)** Molecular structure of the A-site cation formamidinium (FA).

certain combinations of ions, depending on their respective sizes. This can be predicted by the Goldschmidt tolerance factor t

$$t = \frac{R_X + R_A}{\sqrt{2}(R_X + R_B)} \quad (2.12)$$

where R_i describes the ion radii of the corresponding sites [31, 32].

In a perfectly cubic perovskite structure $t = 1$. This condition appears relaxed in practice and three-dimensional cubic perovskite structures can be formed in the range of $0.9 \leq t \leq 1$. At lower values, $0.7 \leq t \leq 0.9$ the perovskite will deviate from the ideal cubic structure and lower-symmetry structures such as hexagonal, tetragonal, orthorhombic or rhombohedral will be assumed.

This condition limits the number of elements eligible for the ABX_3 perovskite structure. The metal cation at the B-site can be occupied by any divalent metal ion such as lead (Pb), tin (Sn) or germanium (Ge). Any halide can in principle occupy the X-site anion, most studies so far have focused on iodide (I), bromide (Br) or chloride (Cl) [33–35]. Among these combinations, lead iodide perovskites have shown to be the most promising for single-junction photovoltaic cells [36]. Cations with the appropriate size for the A-site include the inorganic caesium (Cs) and the organic methylammonium (MA, CH_3NH_3^+) and formamidinium (FA, $\text{CH}(\text{NH}_2)_2^+$, see Fig. 2.9c) [36].

Initially, MAPbI_3 has been the dominant material system but has now been replaced by FAPbI_3 due to its higher thermal stability and favourable narrower band gap ($E_g = 1.4\text{ eV}$) [29], compare Fig.2.3b. Thus, FAPbI_3 is the material we study in both PV devices and single crystals.

2.4.2 Crystal Phases and Stability of FAPbI_3

The main challenge with FAPbI_3 is improving the phase stability of the cubic α -phase ($\text{Pm}\bar{3}\text{m}$ space group). α -phase crystals are thermodynamically unstable at ambient conditions and tend to transform into the photo-inactive hexagonal δ -phase with $\text{P6}_3\text{mc}$ space group [37]. This phase transition is kinetically inhibited and thus occurs within time frames of hours up to weeks, allowing a metastable α - FAPbI_3 to exist. Increased α -phase stability can be achieved by A-site cation mixing with smaller A-site cations such as MA^+ [38, 39] and the alkali-metal Cs^+ [40, 41]. This is often done in combination with I^- , Br^- or Cl^- X-site alloying.

In addition to the phase stability, improving chemical stability poses another key challenge for perovskites. The hygroscopic nature of the organic cation makes them highly sensitive to moisture which can penetrate films via grain boundaries even at relative humidities as low as 10% [42]. This requires the perovskite absorber layer to be encapsulated within a PV device.

In a typical n-i-p stack, electrons are collected by the transparent electrode which is protected by a thick layer of glass. The ingress of moisture is thus expected through the hole-transport layer on the opposite side of the perovskite. This has spurred efforts to design charge-selective contacts that resist the penetration of moisture [43, 44]. In particular, the common hole-transporting material 2,2',7,7'-tetrakis-(N,N-di-p-methoxyphenylamine)9,9'-spirobifluorene (spiro-OMeTAD) suffers from poor barrier properties that are worsened by the hygroscopic bis(trifluoromethane)sulfonimide lithium salt (Li-TFSI) dopant it requires. Therefore, a focus has been put on replacing the hygroscopic dopant or adding thin inert barrier layers between the absorber and the hole-transport layers [45–47]. We shall employ a similar approach here.

3

Graphene and Related Carbon Nanostructures

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This chapter provides a brief overview of the characteristics of carbon nanotubes and graphene nanoribbons. Since both material systems are closely related to graphene, the description of graphene will serve as a useful starting point.

3.1 Graphene

3.1.1 Lattice Structure of Graphene

Real Space

Graphene is a two-dimensional carbon-based material with a honeycomb crystal structure. The honeycomb structure corresponds to a hexagonal Bravais lattice with a two-atom basis, A and B , at each lattice point, see Fig. 3.1a.

In a Cartesian coordinate system with x and y axes in the plane of the graphene sheet, the primitive lattice vectors of the hexagonal Bravais lattice $\mathbf{a}_1$ and $\mathbf{a}_2$ can be expressed as

$$\mathbf{a}_1 = \left(\frac{\sqrt{3}}{2}, \frac{1}{2} \right), \quad \mathbf{a}_2 = \left(\frac{\sqrt{3}}{2}, -\frac{1}{2} \right), \quad (3.1)$$

where $|\mathbf{a}_1| = |\mathbf{a}_2| = a_0 = 0.246 \text{ nm}$ is the lattice constant of graphene corresponding to the distance between unit cells. The distance between adjacent carbon atoms is given by carbon-carbon bond length $a_{CC} = a_0/\sqrt{3} = 0.142 \text{ nm}$ [48].

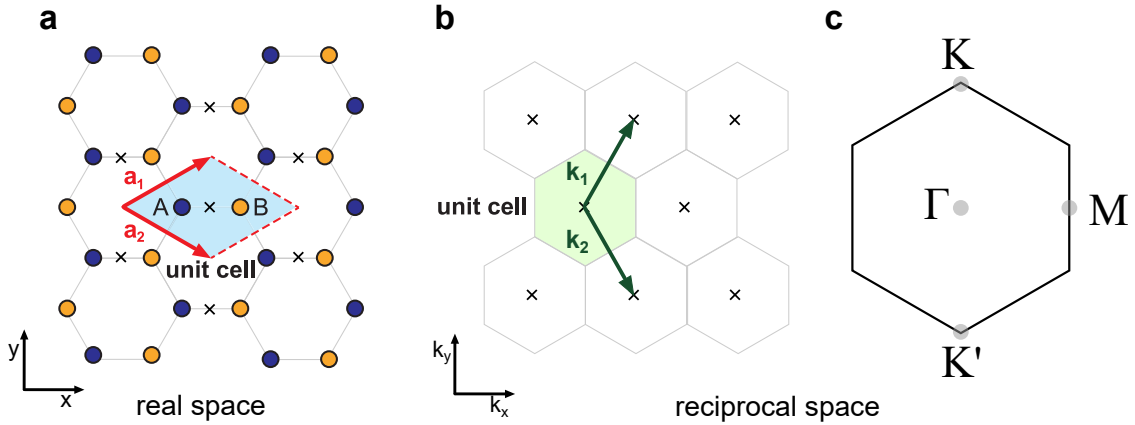


Figure 3.1: Lattice vectors and unit cell of graphene. Honeycomb crystal structure of graphene (grey) with black crosses marking the lattice points of the hexagonal Bravais lattices. **a)** Real space lattice with red arrows indicating the primitive lattice vectors $\mathbf{a}_1$ and $\mathbf{a}_2$ with length equal to a , the lattice constant. The light blue rhombus highlights the size of a unit cell containing two atoms at sites A (blue) and B (yellow). **b)** Lattice of graphene in reciprocal space with reciprocal lattice vectors $\mathbf{b}_1$ and $\mathbf{b}_2$ (dark green) and the first Brillouin zone (light green). **c)** Symmetry points Γ , K and M of the first Brillouin zone.

Reciprocal Space

With the real space unit cell defined, its counterpart in reciprocal space, the first Brillouin zone, can now be calculated. The first Brillouin zone contains all allowed lattice vectors and is thus an important tool in the description of a material's band structure. The reciprocal lattice of a hexagonal honeycomb structure is again a hexagonal lattice. The primitive reciprocal lattice vectors $\mathbf{k}_1$ and $\mathbf{k}_2$ need to satisfy $a_i \cdot k_j = 2\pi\delta_{ij}$ and are thus given by

$$\mathbf{k}_1 = \left(\frac{2\pi}{\sqrt{3}a}, \frac{2\pi}{a} \right) = \frac{4\pi}{\sqrt{3}a_0} \left(\frac{1}{2}, \frac{\sqrt{3}}{2} \right) \quad (3.2)$$

$$\mathbf{k}_2 = \left(\frac{2\pi}{\sqrt{3}a}, -\frac{2\pi}{a} \right) = \frac{4\pi}{\sqrt{3}a_0} \left(\frac{1}{2}, -\frac{\sqrt{3}}{2} \right). \quad (3.3)$$

The length of the reciprocal lattice vectors is given by $k_0 = |\mathbf{k}_1| = |\mathbf{k}_2| = \frac{4\pi}{\sqrt{3}a_0}$. The reciprocal lattice is shown in Fig. 3.1b with the first Brillouin zone indicated in light green. The symmetry points Γ, K and M of the first Brillouin zone are illustrated in Fig. 3.1c.

3.1.2 Electronic Properties of Graphene

Atomic Orbitals of Carbon and Graphene

Each carbon atom has six electrons occupying the $2s, 2p_x, 2p_y$ and $2p_z$ orbitals. The configuration of a free carbon atom, $\frac{\uparrow\downarrow}{1s} \frac{\uparrow\downarrow}{2s} \frac{\uparrow}{2p_x} \frac{\uparrow}{2p_y} \frac{\uparrow}{2p_z}$, rearranges for the 2D honeycomb structure of graphene due to the sp^2 hybridisation of the $2s$ orbital with the in-plane $2p$ orbitals, $2p_x$ and $2p_y$. This orbital mixing results in three sp^2 orbitals and the electron configuration is $\frac{\uparrow\downarrow}{1s} \frac{\uparrow}{sp^2} \frac{\uparrow}{sp^2} \frac{\uparrow}{sp^2} \frac{\uparrow}{2p_z}$.

The three electrons in the sp^2 orbitals form strong covalent σ bonds with the three neighbouring carbon atoms. The electrostatic repulsion between the electrons in the sp^2 orbitals leads to a maximised in-plane angle of 120° between them, producing the well-known honeycomb structure (see Fig. 3.1). The corresponding bonding(σ) and antibonding (σ^*) bands have a large separation that is responsible for the mechanical properties of graphene.

The remaining $2p_z$ orbitals are oriented perpendicular to the graphene plane and do not couple to the σ orbitals due to their symmetry. They overlap slightly with the $2p_z$ orbitals of adjacent carbon atoms to form delocalised π orbitals. In contrast to the σ orbitals, the bonding (π) and antibonding (π^*) bands of the π orbital are located in the vicinity of the Fermi level E_F and thus responsible for the electronic properties of graphene. In fact, the bonding π bands make up the highest occupied band, the valence band, and the anti-bonding π^* bands form the conduction band. Since the small sideways overlap between p_z orbitals leads to much weaker coupling to neighbouring orbitals, the p_z orbitals keep much of their atomic orbital characteristics.

The Tight-Binding Model

Since the π bands make up both valence and conduction bands and coupling to neighbouring atoms is weak, the band structure of graphene can be described with a tight-binding model for the π electrons as originally shown by Wallace [49]. Within this model, the dispersion relation of graphene is given by

$$E_{2D}^{\pm} = \frac{\epsilon_{2p} \mp \gamma_0 \sqrt{f(\mathbf{k})}}{1 \mp s_0 \sqrt{f(\mathbf{k})}} \quad (3.4)$$

where E_{2D}^+ (E_{2D}^-) denotes the conduction (valence) band of graphene, ϵ_{2p} the site energy of the $2p_z$ orbitals, γ_0 the transfer integral and s_0 the overlap integral between two adjacent carbon atoms.

The function $f(k)$ is given by

$$f(\mathbf{k}) = 3 + 2 \cos(\mathbf{k} \cdot \mathbf{a}_1) + 2 \cos(\mathbf{k} \cdot \mathbf{a}_2) + 2 \cos[\mathbf{k}(\mathbf{a}_1 - \mathbf{a}_2)] \quad (3.5)$$

and can be expressed in terms of the coordinates k_x and k_y as

$$f(k_x, k_y) = \sqrt{1 + 4 \cos\left(\frac{\sqrt{3}k_x a_0}{2}\right) \cos\left(\frac{k_y a_0}{2}\right) + 4 \cos^2\left(\frac{k_y a_0}{2}\right)}, \quad (3.6)$$

where a_0 is again the carbon-carbon bond length of graphene. The resulting band structure is displayed in Fig. 3.2 for energies close to the Fermi level.

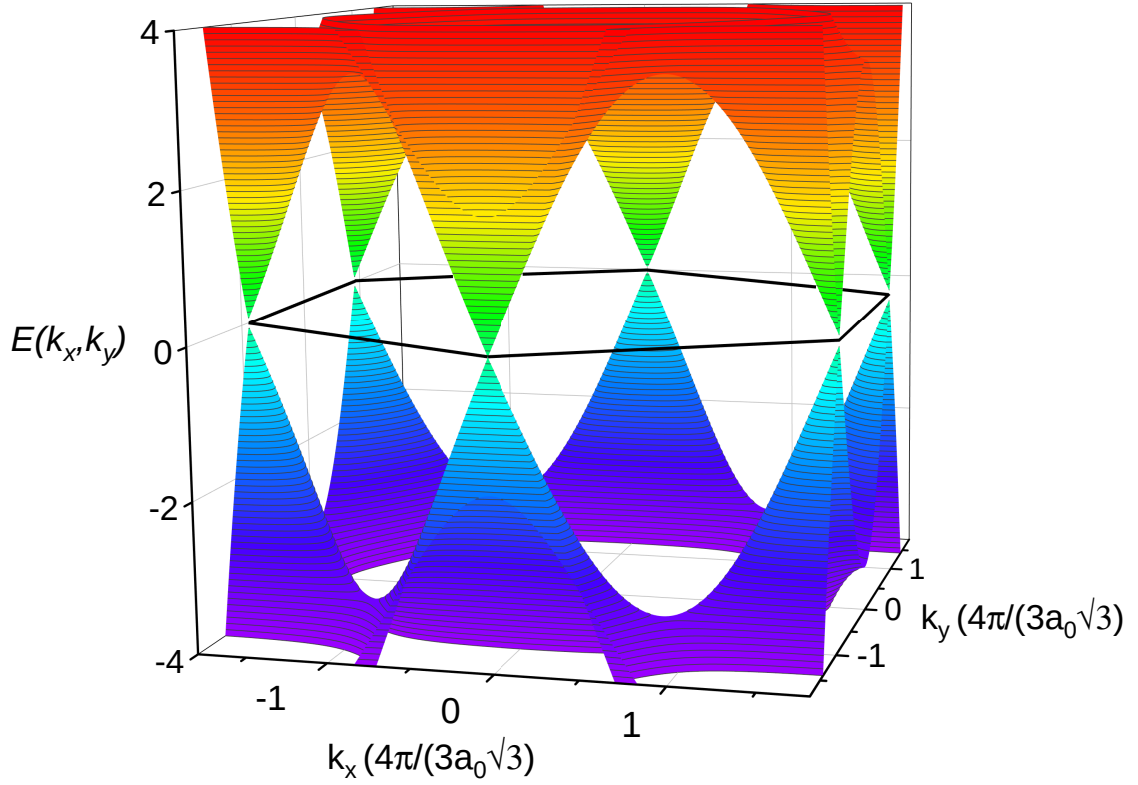


Figure 3.2: Electronic band structure of graphene. $E_{2D}^{\pm}$ bands for graphene were calculated with the tight-binding model after eq. 3.4. The first Brillouin zone is indicated by a black hexagon. Bonding (π , blue) and antibonding (π^* , green-red) bands cross over at the K points, demonstrating semimetallic behaviour due to the absence of a band gap. The Fermi level is located at $E = 0$.

With one p_z electron per atom included in the model, the valence band is fully occupied, whereas the conduction band is empty. The two bands touch at the K and K' symmetry points. The Fermi level E_F is chosen as the zero-energy reference in Fig. 3.2. With occupied and unoccupied bands crossing over at the corners of the first Brillouin zone, graphene can be classified as semi-metallic or a zero-gap semiconductor. Starting from this description, the properties of carbon nanotubes and graphene nanoribbons will be described in the following sections.

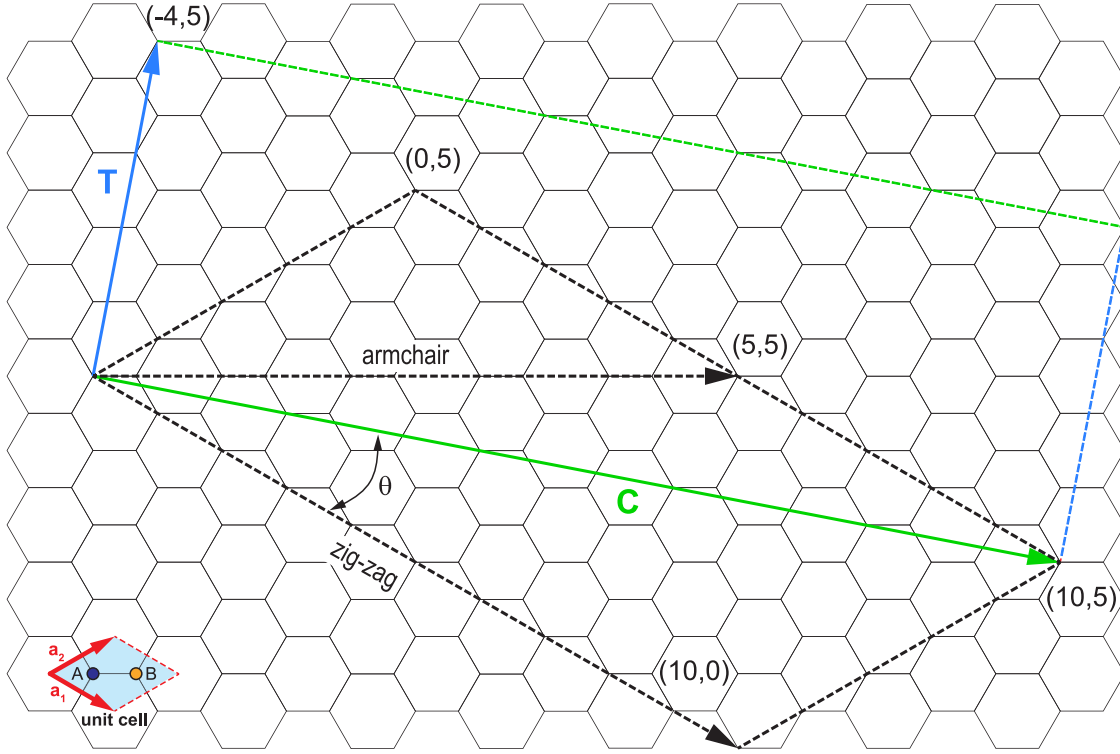


Figure 3.3: Construction of a (10,5) SWCNT from graphene. Schematic display of how a graphene sheet can be rolled up into different chirality SWCNTs. Chirality vector $\mathbf{C}$ and translational vector $\mathbf{T}$ can be expressed in terms of the basic lattice vectors $\mathbf{a}_1$, $\mathbf{a}_2$ and define the points to be connected in the roll-up and the nanotube's long axis, respectively.

3.2 Carbon Nanotubes

3.2.1 Lattice Structure of Carbon Nanotubes

Real Space

Carbon nanotubes (CNTs) are cylindrical carbon allotropes that can be envisioned as rolled-up sheets of graphite. The number of atomic layers in the graphite sheet corresponds to the number of walls of the CNT. Accordingly, rolling up a monoatomic layer of graphite, which is graphene, results in a single-walled carbon nanotube (SWCNT). The manner in which the graphene layer is rolled up can be described by two numbers, the chiral indices (n_1, n_2) . These define how many graphene basic lattice vectors $\mathbf{a}_1, \mathbf{a}_2$ (see eq. 3.1) are required to describe one SWCNT circumference, shown as chirality vector $\mathbf{C}$ in Fig. 3.3.

The vector $\mathbf{C} = n_1\mathbf{a}_1 + n_2\mathbf{a}_2$ defines the two points in the lattice that will be connected when the graphene sheet is rolled up to form the circumference of a nanotube. Further, the diameter of the nanotubes can be found from the chiral indices via

$$d = \frac{|\mathbf{C}|}{\pi} = \frac{a_0}{\pi} \sqrt{n_1^2 + n_2^2 + n_1n_2} = \frac{a_0}{\pi} \sqrt{N} \quad (3.7)$$

using the norm of the basic lattice vectors $a_0 = \|\mathbf{a}_1\| = \|\mathbf{a}_2\| = 2.46\text{\AA}$ and $N = n_1^2 + n_2^2 + n_1n_2$. The chirality can also be expressed in terms of the chiral angle θ , the angle between $\mathbf{C}$ and $\mathbf{a}_2$, which describes the orientation of carbon hexagons in the tube walls and can be calculated via

$$\theta = \arccos\left(\frac{\mathbf{C} \cdot \mathbf{a}_2}{|\mathbf{C}| \cdot |\mathbf{a}_2|}\right) = \arccos\left(\frac{n_1 + 2n_2}{2N}\right). \quad (3.8)$$

A unique characteristic of carbon nanotubes is that there are infinite possible ways to roll up a layer of graphene into a tube, corresponding to a vast number of possible combinations for the chiral indices. The six-fold rotational symmetry of the hexagonal lattice of graphene means that the range from 0° to 60° suffices to describe all tubes with unique chirality. Further, for each tube in the range from 0° to 30° , there exists a tube with equivalent chirality within 30° to 60° , the only difference being the handedness of the graphene lattice helix. As a consequence, all unique cases of chirality can be described within the chiral angle range of $0^\circ \leq \theta \leq 30^\circ$ or in terms of chiral indices $n_1 \geq n_2 \geq 0$.

When considering the chiral angle, two special cases of nanotubes arise. Nanotubes with chiral angle $\theta = 0^\circ \equiv (n_1, 0)$ are called *zig-zag* tubes, tubes with $\theta = 30^\circ \equiv (n, n)$ are referred to as *armchair* tubes. The names originate from the orientation of the graphene lattice along the circumference of the tubes as can be seen in Fig. 3.4. The $\mathbf{C}$ vectors of the tubes shown there are also given in Fig. 3.3.

To determine the unit cell of a carbon nanotube, we define the translational vector $\mathbf{T} = t_1\mathbf{a}_1 + t_2\mathbf{a}_2$ that is perpendicular to $\mathbf{C}$ and points along the long axis of the tube. $\mathbf{T}$ can easily be found from the condition $\mathbf{C} \cdot \mathbf{T} = 0$, which yields

$$\mathbf{T} = -\frac{2n_2 + n_1}{m_R}\mathbf{a}_1 + \frac{2n_1 + n_2}{m_R}\mathbf{a}_2 \quad (3.9)$$

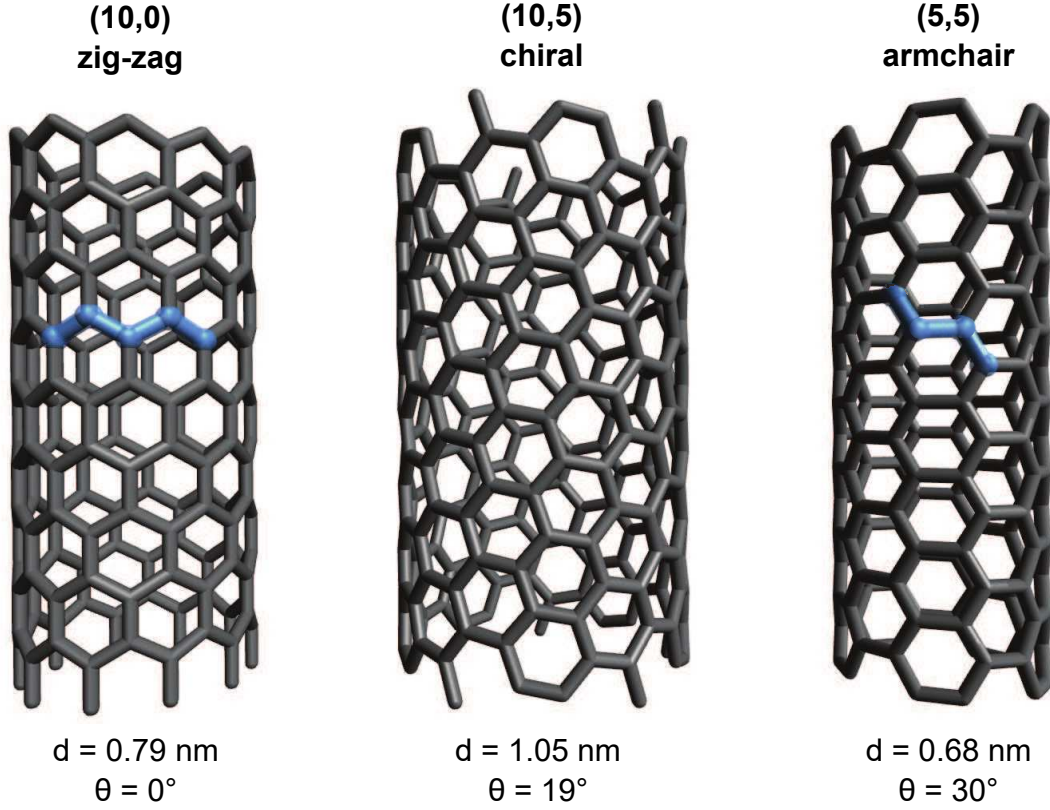


Figure 3.4: Schematic of SWCNTs with different chiralities. A (10,0) zig-zag tube, a (10,5) chiral tube and a (5,5) armchair tube are shown with their respective diameters and chiral angles. The bonds providing the names of zig-zag and armchair tubes are indicated in blue and highlight the orientation of the chiral angle relative to the horizontal plane. All chiral tubes possess chiral angles in between those two.

where m_R is the greatest common divisor of $2n_1 + n_2$ and $2n_2 + n_1$. The length T of the translational vector $\mathbf{T}$ is

$$T = |\mathbf{T}| = a_0 \cdot \frac{\sqrt{3(n_1^2 + n_2^2 + n_1 n_2)}}{m_R} = \sqrt{3} \cdot a_0 \cdot \frac{\sqrt{N}}{m_R} \quad (3.10)$$

and defines the smallest translational period, or in other words the length of the nanotube unit cell, alongside its axis. As an example, $\mathbf{C}$ and $\mathbf{T}$ are given for a (10,5) nanotube in Fig. 3.3. The rectangle spanned by the two vectors $\mathbf{C}$ and $\mathbf{T}$ then establishes the unit cell of the carbon nanotube. The area of the unit cell can be found via

$$A_{CNTuc} = |\mathbf{C} \times \mathbf{T}| = \sqrt{3} \cdot a_0^2 \cdot \frac{N}{m_R}. \quad (3.11)$$

The number of carbon atoms per unit cell q can now be derived by dividing the area of the nanotube unit cell by the area of the graphene unit cell

$$q = \frac{A_{\text{CNT uc}}}{A_{\text{graphene uc}}} = \frac{\sqrt{3} \cdot a_0^2 \cdot \frac{N}{m_R}}{\frac{\sqrt{3}}{2} \cdot a_0^2} = \frac{2N}{m_R} \quad (3.12)$$

Since there are 2 carbon atoms per graphene unit cell and q graphene unit cells fit into one nanotube unit cell, the total number of carbon atoms in a carbon nanotube unit cell is

$$N_C = 2q = \frac{4N}{m_R} \quad (3.13)$$

Reciprocal Space

In analogy to the description of graphene in Sec. 3.1.1, the unit cell in reciprocal space, the first Brillouin zone, can be found from the unit cell in real space. Since the nanotube unit cell in real space is characterised by the vectors $\mathbf{C}$ and $\mathbf{T}$, converting these vectors into reciprocal space leads us directly to the first Brillouin zone.

The translational vector $\mathbf{T}$ is oriented in parallel to the long axis of the tube and we thus label its reciprocal counterpart $\mathbf{k}_T \equiv \mathbf{k}_{\parallel}$. The length of this vector is $|\mathbf{k}_{\parallel}| = 2\pi/T$ and since the nanotubes can be considered infinitely long, there are no boundary conditions for $\mathbf{k}_{\parallel}$. This means $\mathbf{k}_{\parallel}$ is continuous and the Brillouin zone along the nanotube axis is located in the interval $[-\pi/T, \pi/T]$.

A different situation arises for the orthogonal wave vector $\mathbf{k}_C \equiv \mathbf{k}_{\perp}$ which is derived from the circumferential vector in real space $\mathbf{C}$. Here, the Born-von Karman boundary condition of a standing wave along the circumference of a tube $\phi(x+c) = \phi(x) \iff m \cdot \lambda = |\mathbf{C}| = \pi d$, requires $\mathbf{k}_{\perp}$ to be discrete. This condition can be derived from Bloch's theorem $\psi(\mathbf{r} + \mathbf{C}) = e^{i\mathbf{k} \cdot \mathbf{C}} \cdot \psi_{\mathbf{k}}(\mathbf{r}) = \psi(\mathbf{r})$ which is only satisfied for phase shifts that are a multiple of 2π as all other phase shifts vanish due to destructive interference.

Consequently, only discrete wavelengths are allowed which imposes the following condition on $\mathbf{k}_{\perp}$

$$m \cdot \lambda = |\mathbf{C}| = \pi \cdot d \iff k_{\perp, m} = \frac{2\pi}{\lambda} = \frac{2}{d} \cdot m \quad (3.14)$$

where m is an integer. The perpendicular wave vector $k_{\perp,m}$ is therefore quantized with $2m$ nodes around the nanotube circumference. To elucidate the possible values of m , we project all carbon atoms in the unit cell onto the circumferential vector $\mathbf{C}$, shown as red lines for a (10,5) tube in Fig. 3.5.

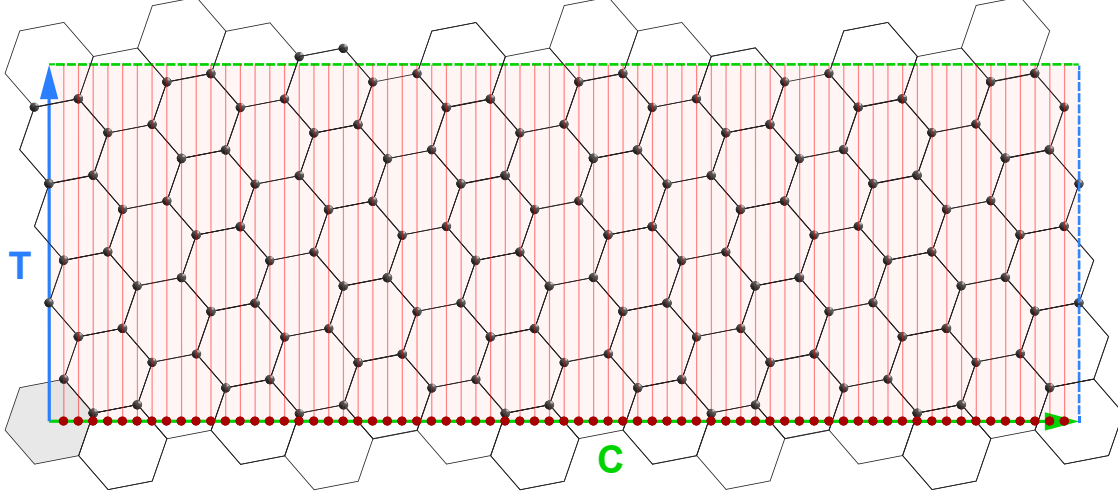


Figure 3.5: Projection of all carbon atoms within the unit cell onto the circumferential vector $\mathbf{C}$ for a (10,5) tube. There are two carbon atoms on every projected red line, which means there are q pairs of carbon atoms within the unit cell. The translational vector $\mathbf{T}$ points along the long axis of the tube.

Every red line projects two carbon atoms onto $\mathbf{C}$. Since there are $N_C = 2q$ carbon atoms in the unit cell, this means that there are q pairs of carbon atoms that all have equidistance in direction of $\mathbf{C}$.

This implies that $|m| \leq q/2$, meaning the number of nodes is limited by the number of atoms in the unit cell. The quantization number m can therefore take integer values in the interval $]-q/2, q/2]$ and wave vectors $\mathbf{k}_{\perp}$ exist as discrete lines with a separation of $2/d$. Since the parallel wave vector $\mathbf{k}_{\parallel}$ is continuous, the nanotube Brillouin zone consists of q lines in parallel to the long axis of the nanotube. The lines have a length of $2\pi/T$ and are spread out over a distance $2q/d$ in $\mathbf{k}_{\perp}$ direction. With the relation $a_i k_j = 2\pi \delta_{ij}$ between unit cell vectors

in real and reciprocal space we find

$$\mathbf{k}_\perp = \frac{2n_1 + n_2}{q \cdot m_R} \mathbf{k}_1 + \frac{n_1 + 2n_2}{q \cdot m_R} \mathbf{k}_2 \quad (3.15)$$

$$\mathbf{k}_\parallel = -\frac{n_2}{q} \mathbf{k}_1 + \frac{n_1}{q} \mathbf{k}_2. \quad (3.16)$$

For illustration, the allowed wave vectors of the three carbon nanotubes previously discussed are given in Fig. 3.6.

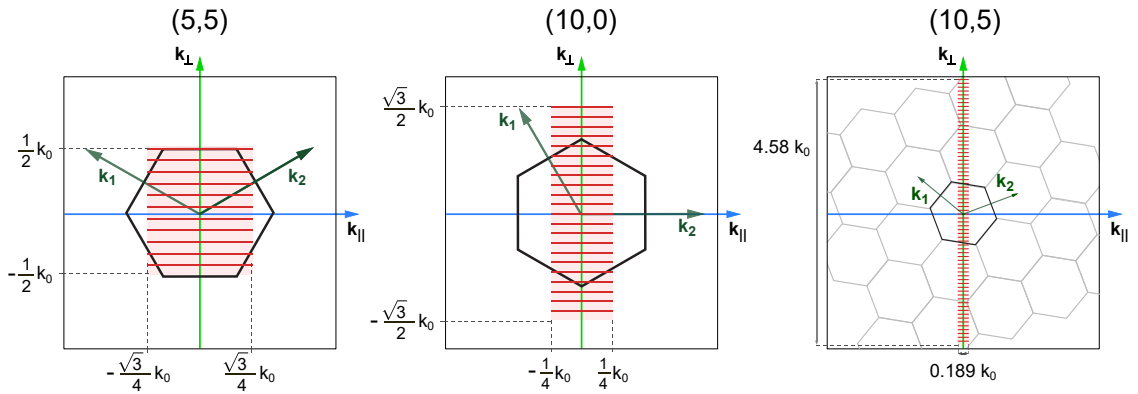


Figure 3.6: Brillouin zone of carbon nanotubes with different chiralities. The chiralities are denoted on top of each subfigure. The reciprocal lattice vectors of graphene, $\mathbf{k}_1, \mathbf{k}_2$ are given in dark green, the lattice vectors of the nanotubes in blue ($\mathbf{k}_\parallel$) and light green ($\mathbf{k}_\perp$). The allowed wave vectors (red) are segments in parallel to $\mathbf{k}_\parallel$ due to the quantization in direction of $\mathbf{k}_\perp$.

3.2.2 Electronic Properties of Carbon Nanotubes

Band Structure

To describe the band structure of carbon nanotubes, we start from the description of graphene (Sec. 3.1.2) and apply the results of the last section. We have derived that the $\mathbf{k}$ -states are quantized in $\mathbf{k}_\perp$ direction, which means the allowed states are confined to discrete lines in parallel to the long axis of the tube. In the *zone-folding approximation*, the nanotube band structure is assumed to be equal to the energies of graphene on these discrete lines in the Brillouin zone. The states on these discrete k lines are referred to as subbands. The subbands of a (6,6) SWCNT are provided as an example in the next section in Fig. 3.14.

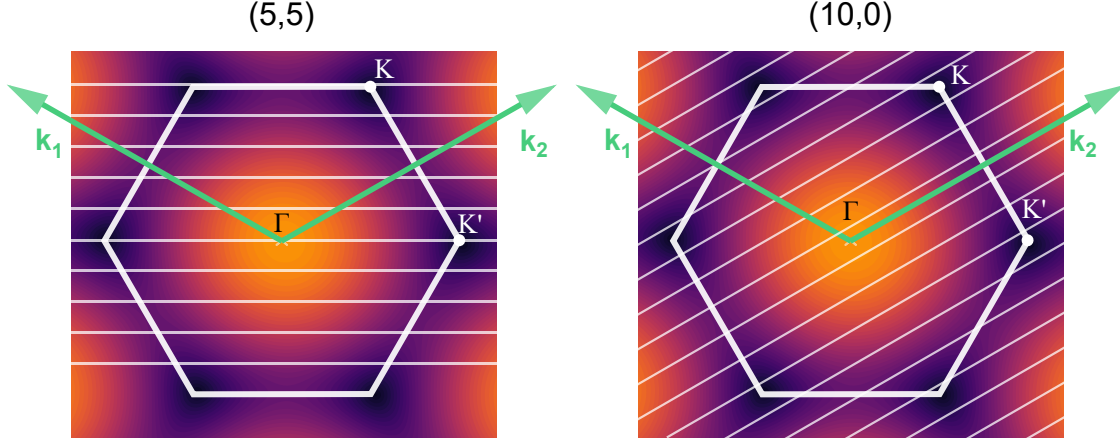


Figure 3.7: Brillouin zone of graphene with allowed $\mathbf{k}$ states for two nanotube species. The white hexagons highlight the size of the graphene Brillouin zone. The underlying false colour maps indicate the band structure of graphene calculated with eq. 3.4. Allowed $\mathbf{k}$ states of the (5,5) and (10,0) nanotubes are indicated by white lines. If the allowed states coincide with the K point, the tube is metallic, otherwise semiconducting.

As we have seen in the previous section, the chiral indices of the nanotube determine the position and number of the subbands in the Brillouin zone. This has far-reaching consequences for the electronic properties of nanotubes. If the K point of the Brillouin zone coincides with a sub-band, allowed states exist at the K point and the conduction and valence band intersect; the nanotube is metallic. If, however, no allowed states are present at the K point, the nanotube has a band gap and is semiconducting. These two scenarios are illustrated in Fig. 3.7 together with the energy landscape of graphene calculated after eq. 3.4.

The dispersion relation of metallic nanotubes close to the K point can be found via a second-order perturbation of the general dispersion relation [50]. Similar to graphene, this yields a linear band dispersion in the vicinity of the Fermi level

$$E(k) = \pm \frac{3a_0}{2} \gamma_0 |\mathbf{k} - \mathbf{K}| \quad (3.17)$$

where $\gamma_0 = 2.9 \text{ eV}$ [51] is again the transfer integral between first-neighbour π orbitals. From this equation, we find the Fermi velocity as $v_F = \frac{3}{2\hbar} \gamma_0 a_0 \approx 8 \cdot 10^5 \text{ ms}^{-1}$.

For semiconducting nanotubes, we find the dispersion relation with a similar procedure. For the subbands closest to the K point, a low-energy expansion yields

$$E(k_{\parallel}) \cong \pm \frac{3a_0}{2} \gamma_0 \sqrt{\left(\frac{2\pi}{|\mathbf{C}|}\right)^2 \left(q \pm \frac{1}{3}\right)^2 + k_{\parallel}^2} \quad (3.18)$$

where q counts the number of available subbands and $k_{\parallel}$ describes the continuum of k states in one subband in direction of the tube's long axis. This leads to the opening of a band gap at the Fermi level, where $q = k_{\parallel} = 0$, described by

$$\Delta E_g = E_{q=0}^+(k_{\parallel} = 0) - E_{q=0}^-(k_{\parallel} = 0) = \frac{2\pi a \gamma_0}{\sqrt{3}|\mathbf{C}|}. \quad (3.19)$$

Since the nanotube diameter is per definition proportional to the length of the circumferential vector $|\mathbf{C}|$, the band gap is inversely proportional to the diameter $\Delta E \propto 1/d$.

The condition for a metallic nanotube is that the K point has to coincide with an allowed k state $\mathbf{K} \cdot \mathbf{C} = 2\pi \cdot m$ with $m \in \mathbb{N}$. This can be used to derive an expression determining the electronic type from the chiral indices of a tube. The two vectors can be expressed in terms of unit vectors as $\mathbf{K} = \frac{1}{3}(\mathbf{k}_1 - \mathbf{k}_2)$ and $\mathbf{C} = n_1 \mathbf{a}_1 + n_2 \mathbf{a}_2$. Together with the previously used relation between the unit vectors $\mathbf{a}_i \cdot \mathbf{k}_j = 2\pi \delta_{ij}$ this converts to the condition $n_1 - n_2 = 3m$ for metallic tubes, which can be summarized as [48]

$$(n_1 - n_2) \mod 3 = \begin{cases} 0 & \text{metallic} \\ 1, 2 & \text{semiconducting.} \end{cases} \quad (3.20)$$

Consequently, 2/3 of the possible chiralities correspond to semiconducting SWCNTs and 1/3 to metallic. A non-selective synthesis process will therefore result in a 1 : 2 ratio of metallic to semiconducting tubes.

An illustration of the nanotube subbands and how their position determines whether nanotubes are metallic or semiconducting is given in Fig. 3.8.

Multi-walled carbon nanotubes (MWCNTs) consist of multiple concentric layers of graphene. The number of walls N_w can be estimated from the diameter d of the nanotube $d(\text{nm}) \approx N_w + 1$ [52]. As soon as one of the walls is metallic, the whole MWCNT is metallic. It is fair to assume that all MWCNTs used in this

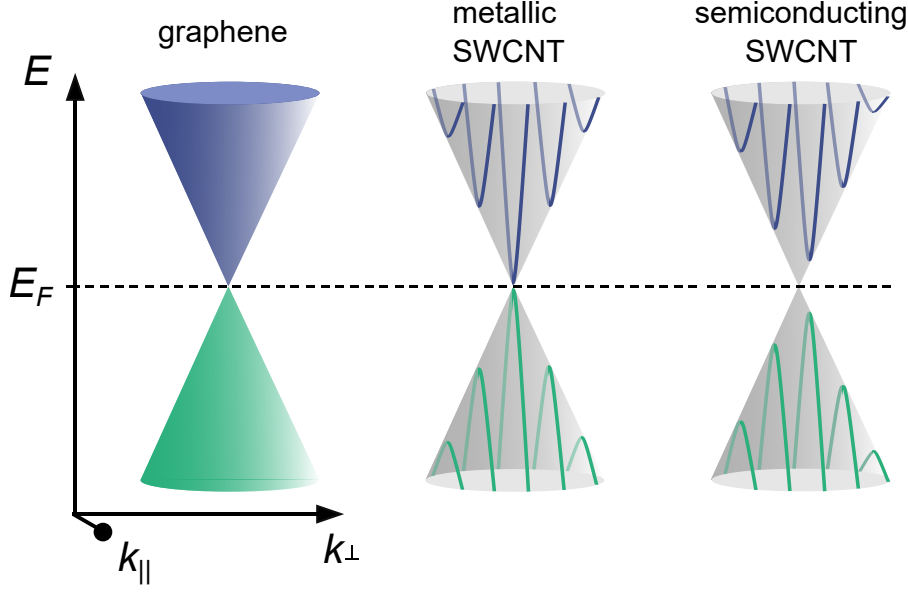


Figure 3.8: Dispersion relation of graphene, metallic and semiconducting SWCNTs. The dispersion relation for graphene can be used to describe the band structure of metallic and semiconducting SWCNTs. The positions of allowed states are derived from the chirality with the zone-folding approximation.

work are metallic since their diameters are typically $d \geq 10$ nm, meaning they consist of $N_w \geq 9$ concentric tubes.

Density of States

The density of states (DOS) describes the number of states available for electrons per unit of energy. A general expression for the DOS of carbon nanotubes was derived by Mintmire *et al.* [53]

$$n(E) = \frac{2}{Q|\mathbf{k}_{\parallel}|} \sum_j \int dk_{\parallel} \delta(k_{\parallel} - k_j) \left| \frac{\partial E^{\pm}(k_{\perp}, k_{\parallel})}{\partial k_{\parallel}} \right|^{-1} \quad (3.21)$$

where k_j is given by $E - E^{\pm}(k_{\perp}, k_{\parallel}) = 0$ and $Q|\mathbf{k}_{\parallel}| = \frac{3\pi^2 d}{\sqrt{3}a_0^2}$. The DOS for $\mathbf{k}$ values near the Fermi level can be calculated by expanding the dispersion relation of graphene (eq. 3.4)

$$E^{\pm} \approx \pm \frac{\sqrt{3}}{2} a_0 \gamma_0 |\mathbf{k} - \mathbf{K}|. \quad (3.22)$$

Any given distance between $\mathbf{k}$ to the nearest $\mathbf{K}$ point can be expressed as

$$|\mathbf{k} - \mathbf{K}| = \sqrt{\Delta k_{\perp}^2 + \Delta k_{\parallel}^2}. \quad (3.23)$$

As described in Sec. 3.2.1, $\Delta k_{\parallel}$ takes continuous values while $\Delta k_{\perp}$ is quantized and given by the projection of $(\mathbf{k} - \mathbf{K})$ onto $\mathbf{k}_{\perp}$:

$$\Delta k_{\perp} = \left| (\mathbf{k} - \mathbf{K}) \cdot \frac{\mathbf{k}_{\perp}}{|\mathbf{k}_{\perp}|} \right| = \frac{2}{3d} |3i - q|, \quad (3.24)$$

where q is defined in eq. 3.27 and i takes integer values.

The derivative term in eq. 3.21 can thus be written as

$$\left| \frac{\partial E^{\pm}(k_{\perp}, k_{\parallel})}{\partial k_{\parallel}} \right|^{-1} = \left| \frac{\sqrt{3}}{2} a_0 \gamma_0 \frac{\partial \sqrt{\Delta k_{\perp}^2 + \Delta k_{\parallel}^2}}{\partial k_{\parallel}} \right|^{-1} = \left(\frac{2}{\sqrt{3} a_0 \gamma_0} \right) \frac{|E^{\pm}|}{\sqrt{(E^{\pm})^2 - E_i^2}}, \quad (3.25)$$

where

$$E_i = \frac{\sqrt{3}}{2} a_0 \gamma_0 \Delta k_{\perp} = |3i - q| \frac{a_0 \gamma_0}{\sqrt{3}d}. \quad (3.26)$$

By inserting this result for E_i into eq. 3.21 and integrating over $k_{\perp}$, we find

$$n(E) = \frac{4a_0}{\pi^2 d \gamma_0} \sum_{i=-\infty}^{\infty} g(E, E_i), \quad g(E) = \begin{cases} \frac{|E|}{\sqrt{E^2 - E_i^2}}, & |E| > |E_i| \\ 0, & |E| < |E_i|. \end{cases} \quad (3.27)$$

This shows that the DOS diverges at $E = E_i$, the so-called *van Hove singularities*.

The position of these singularities is given by $E_i = \frac{ia_0\gamma_0}{\sqrt{3}d}$ with $i = 0, 3, 6, \dots$ for metallic and $i = 1, 2, 4, 5, 7, \dots$ for semiconducting nanotubes. Consequently, the band gap for semiconducting nanotubes is

$$E_{11} = 2E_1 = 2 \frac{a_0 \gamma_0}{\sqrt{3}d}. \quad (3.28)$$

The DOS and band structure of a metallic (5,5) and a semiconducting (10,0) nanotube is depicted in Fig. 3.9. The figure demonstrates that metallic tubes have states available at any energy, whereas semiconducting tubes possess a band gap.

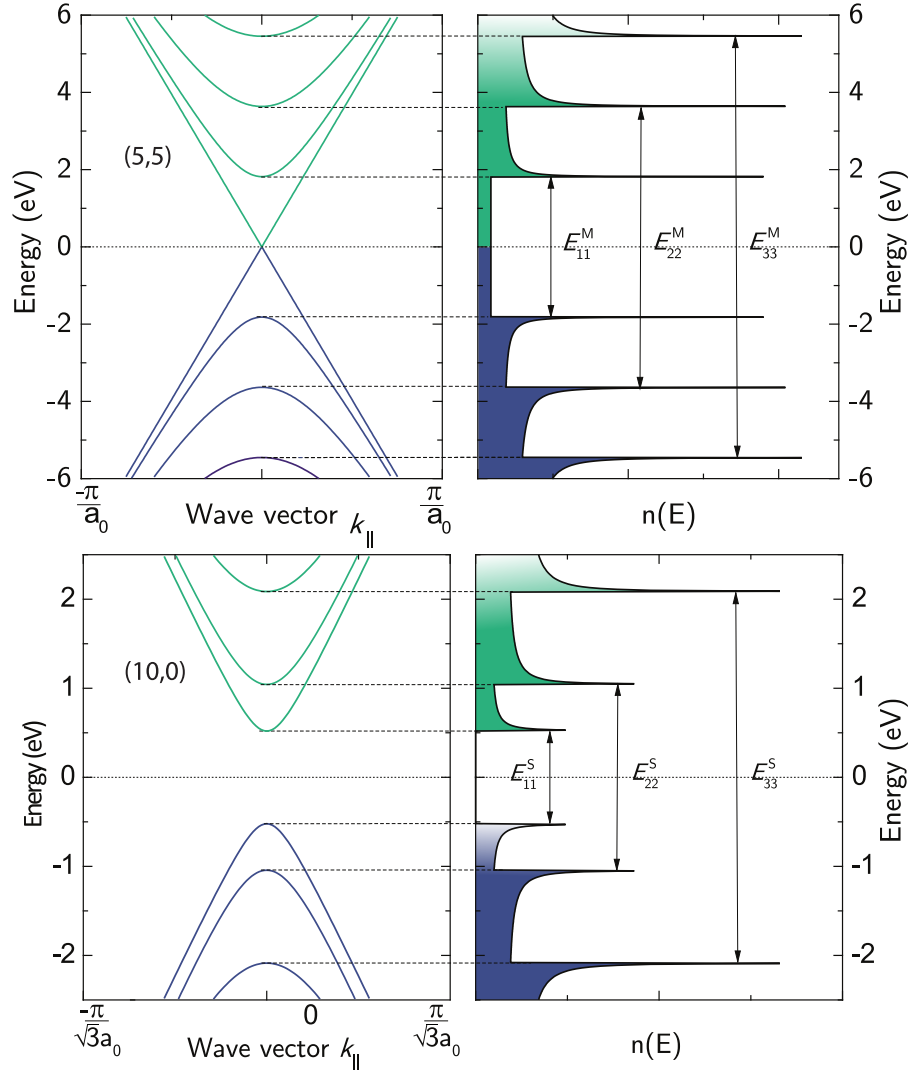


Figure 3.9: Carbon nanotube band structure and density of states. The band structure (left) and density of states (right) are given for a metallic (5,5) nanotube (top) and a semiconducting (10,0) nanotube (bottom). The metallic tube has a non-zero density of states at the Fermi energy, whereas the semiconducting nanotube has a band gap. The band structure was calculated with the tight-binding approximation.

Doping Induced Carrier Concentration

Doping is a common method to increase the number of free charge carriers in a semiconductor. This is accompanied by a shift in the Fermi level. In semiconducting carbon nanotubes, the presence of multiple subbands allows us to estimate the Fermi level position by observing the bleaching of these subband transitions in absorbance measurements. We will thus derive a relationship between the Fermi level shift and the underlying change in carrier concentration.

The carrier concentration N of a p-doped semiconductor can be calculated via [54]

$$N = \int_{-\infty}^{E_v} n(E) f(E) dE \quad (3.29)$$

where $n(E)$ is the density of states, $f(E)$ is the Fermi–Dirac distribution given in eq. 2.3 and E_v is the energy of the valence band edge.

Together with the density of states derived in the previous section, this leads to

$$N = \frac{8a_0}{\pi^2 d \gamma_0} \sum_{i=-\infty}^0 \int_{-\infty}^{E_{v_i}} E (E^2 - E_{v_i}^2)^{-1/2} (1 + e^{E-E_F})^{-1} dE. \quad (3.30)$$

This integral is not straightforward to solve and Marulanda *et al.* have provided approximate solutions under two limits [55]. With $\eta = (E_v - E_F)/k_B T$, the carrier density can be approximated as

$$N = \begin{cases} N_v I e^{\frac{E_v - E_F}{k_B T}}, & \eta \ll -1 \\ N_v I \frac{\sqrt{E_v^2 - E_F^2}}{k_B T}, & \eta \gg 1, \end{cases} \quad (3.31)$$

where I is an extensive polynomial expression depending only on E_v, E_F and T [55]. Now, if the doping-induced Fermi level shift is known, the induced carrier concentration can be calculated.

3.3 Graphene Nanoribbons

Graphene nanoribbons (GNRs) are another class of graphene-based nanostructures and can be understood as cut and unrolled carbon nanotubes. GNRs are similar to carbon nanotubes in many ways, the key difference, however, is the presence of edges in nanoribbons. To allow simple theoretical treatment, all dangling bonds on GNR edges are typically assumed to be passivated with hydrogen. This sustains the aromaticity and sp^2 hybridisation of the carbon lattice. We will follow this assumption and further consider GNRs as one-dimensional structures with lengths sufficiently greater than their width.

Since we have derived the properties of carbon nanotubes extensively in the previous sections of this chapter and only one specific type of graphene nanoribbon is relevant for this work, this section will merely provide a short introduction to

GNRs focused on comparison with CNTs. The interested reader may be referred to chapter 9 of the book *Graphene Nanoelectronics* by Hassan Raza [56] for a more detailed discussion.

3.3.1 Lattice Structure of Graphene Nanoribbons

A structural classification of GNRs in accordance with CNTs based on two indices was proposed by Ezawa *et al.* [57]. However, the larger diversity of possible GNR edge structures that arises from not having to roll up the ribbons into a tube makes this system less intuitive than for CNTs and a simpler description based on ribbon width and chiral angle θ will suffice for our purposes.

The chiral angle defines the orientation of the nanoribbon within the graphene sheet and, similarly to CNTs, is defined in the range $0^\circ \leq \theta \leq 30^\circ$. The two extreme cases are again labelled as *zigzag* and *armchair*, only that for GNRs this refers to the shape of the carbon bonds along the ribbon edges rather than perpendicular to it, as is the case for CNTs, which means the labelling is inverted. Consequently, *zigzag* GNRs possess a chiral angle of $\theta = 30^\circ$ and *armchair* GNRs have $\theta = 0^\circ$, see Fig. 3.10. Chiral angles intermediate between those two are possible with different edge structures (green in Fig. 3.10). The resulting nanoribbons are called *chiral* GNRs. Finally, if the edge structure is more complex and only repeats over a larger area, we call the ribbon *superlattice* GNR. An example of *superlattice* GNR is the cove-edged GNR, shown in blue in Fig. 3.10. Cove edges are *zigzag* edges with an additional carbon hexagon present in every third spot on both sides. This is the type of GNR we will investigate in this work and the consequences of the edge structure on the electronic properties will be discussed in detail in the following.

3.3.2 Electronic Properties of Graphene Nanoribbons

Armchair and Zigzag Nanoribbons

For the simplest GNR structures, armchair (AGNRs) and zigzag GNRs (ZGNRs), we obtain a good representation of the band structure by projecting the allowed $\mathbf{k}$ states on the bands of graphene, as we have done for carbon nanotubes. In this context, the

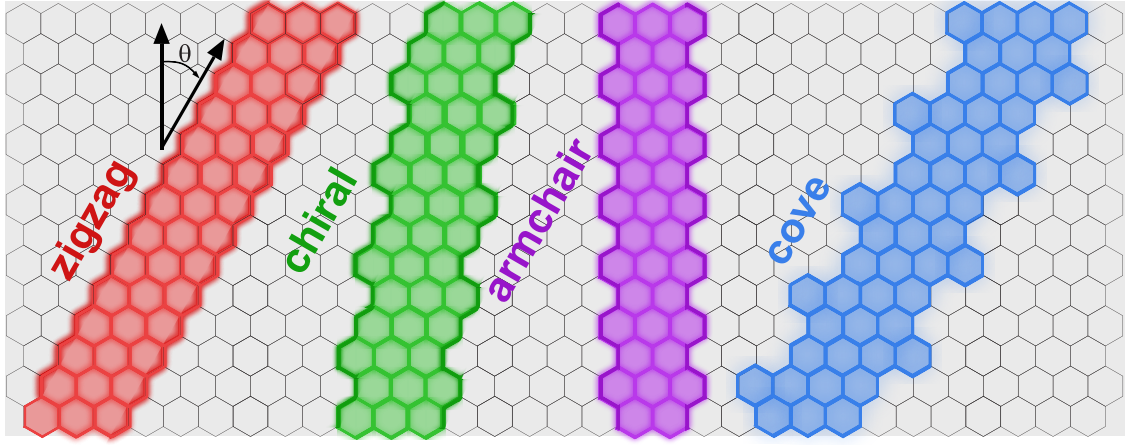


Figure 3.10: Structure of different graphene nanoribbons. Labels arise from the edge shape and are related to the chiral angle of the GNR. Zigzag GNRs have $\theta = 30^\circ$ (red), chiral GNRs $0^\circ < \theta < 30^\circ$ (green), armchair GNRs $\theta = 0^\circ$ (purple) and cove-edged GNRs have zigzag edges with only every third carbon hexagon present in the outermost layer (blue).

nanoribbon width w is defined by the number of carbon dimer bonds across the width of the ribbon N , as depicted in Fig. 3.11a,c. N is often prefixed to the GNR name.

For armchair GNRs we find the width as

$$w_{AGNR} = \frac{1}{2}(N - 1)a_0 \quad (3.32)$$

and for zigzag GNRs accordingly

$$w_{ZGNR} = \frac{\sqrt{3}}{2}(N - 1)a_0 \quad (3.33)$$

with the graphene lattice constant a_0 . From the ribbon width, we can derive the allowed wave vectors. While the parallel wave vector $\mathbf{k}_{\parallel}$ is again continuous, the perpendicular wave vector $\mathbf{k}_{\perp}$ only allows standing waves perpendicular to the ribbon's long axis and thus induces the boundary condition

$$n \cdot \lambda_{\perp,n} = 2w_{ribbon} \iff k_{\perp,n} = \frac{n \cdot \pi}{w_{ribbon}} \quad (3.34)$$

where n is an integer, leading to a quantized wave vector.

For AGNRs, the translational vector along the ribbon's long axis has the length $|\mathbf{T}| = \sqrt{3}a$ in real space. The size of the 1D Brillouin zone in $k_{\parallel}$ direction is then $2\pi/\sqrt{3}a$.

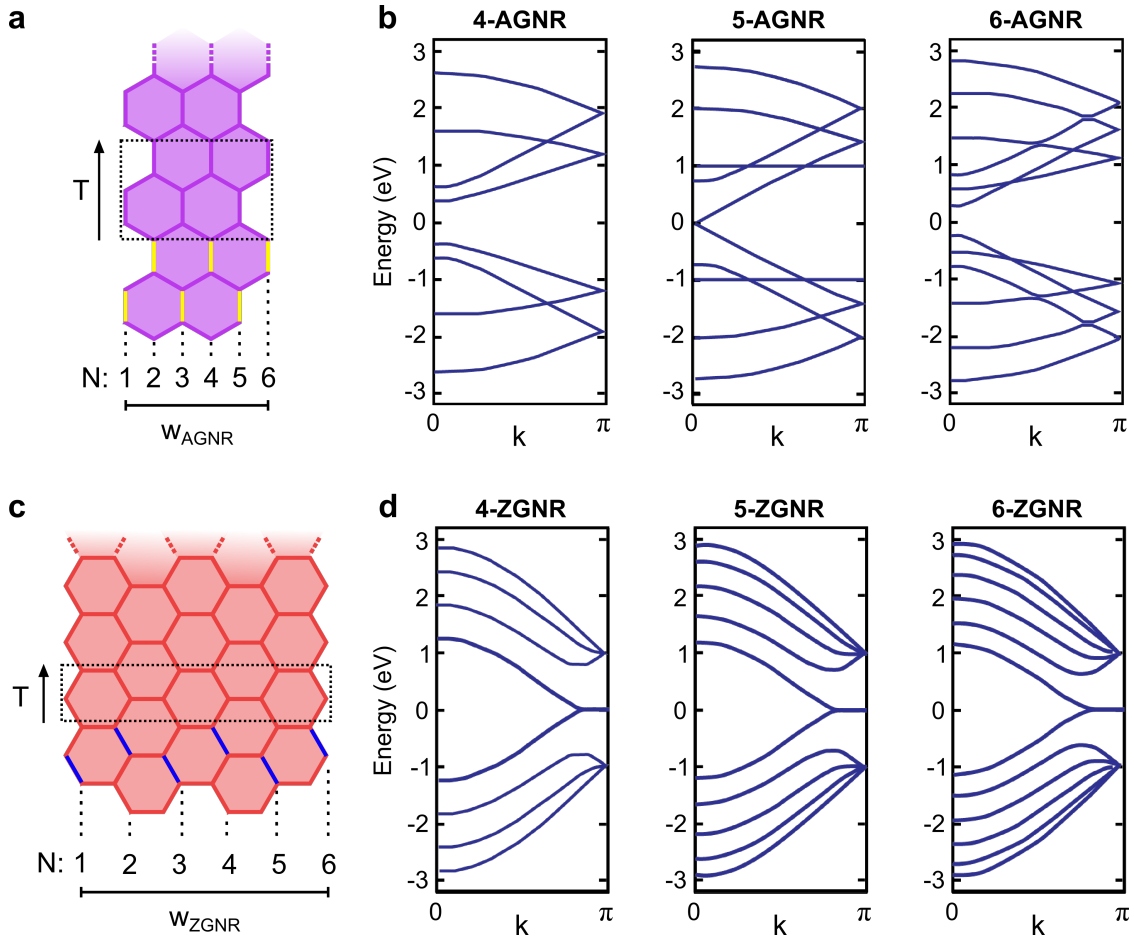


Figure 3.11: Unit cell and band structure of armchair and zigzag GNRs. **a)** Structure of a 6-AGNR with the unit cell (dotted box), translational vector $\mathbf{T}$ and the number of dimer lines (yellow) highlighted. **b)** Band structure of 4,5, and 6-AGNRs as calculated with a tight-binding model [58]. **c)** Representation of a 6-ZGNR including the unit cell, $\mathbf{T}$ and dimer lines (blue). **d)** Tight-binding modelled band structure of 4,5, and 6-ZGNR [58].

The width of N -AGNRs with odd N is equivalent to the chiral vector of a $(\frac{N-1}{2}, 0)$ zigzag CNT, whereas AGNRs with even N have no corresponding nanotubes [59].

The structure of ZGNR repeats itself within a distance of a along the ribbon axis. The length of the Brillouin zone in $k_{\parallel}$ direction is consequently equal to $2\pi/a$. The width of N -ZGNRs with odd N matches the circumference of a $(\frac{N-1}{2}, \frac{N-1}{2})$ armchair nanotube. For ZGNRs with even N , however, no corresponding CNTs exist. From these analogies, it is clear that the orientation of the allowed $\mathbf{k}$ lines in the Brillouin zone are the same for AGNR and zigzag CNTs and equally for ZGNR and armchair CNTs.

An approximate band structure of armchair and zigzag GNR can be retrieved with a single-orbital tight-binding model for the π electron network [58].

For AGNRs, the tight-binding model predicts valence and conduction band to overlap if $N = 3M + 2$, where M is an integer, and the existence of a band gap in all other cases ($N = 3M, 3M + 1$), see Fig. 3.11b. This agrees with the projection of the graphene band structure on the allowed AGNR subbands. However, DFT calculations on the same AGNRs demonstrated that all AGNRs possess non-zero band gaps, regardless of N . This discrepancy is attributed to the GNR structures being relaxed in these DFT calculations, causing the distances between carbon atoms to deviate from a perfect graphene lattice and thus distorting the hybridisation of carbon orbitals. The size of the band gap Δ differs between the three branches of AGNRs and generally follows $\Delta_{3M+1} > \Delta_{3M} > \Delta_{3M+2}$. Within each branch, Δ scales inversely with the ribbon width [60].

In the case of ZGNRs, the tight-binding modelled band structure in Fig. 3.11d resembles the projection of graphene bands onto the allowed $\mathbf{k}$ subbands known from armchair CNTs (see next section Fig. 3.13) and no band gap is present in all ZGNRs. However, instead of the valence and conduction band meeting at the K and K' points, there is a flat region close to the edge of the Brillouin zone at zero energy. This feature can not be derived from the graphene band structure. Instead, the zero-energy states at the zone boundary are highly-localised at the zigzag edges with their amplitudes decaying exponentially away from the edges [60, 61].

Cove-edged Nanoribbons

Cove-edged GNRs have a more complex edge structure than armchair and zigzag GNRs. As previously mentioned, they can be described as zigzag GNRs with only every third carbon hexagon present on the outermost layer, symmetrically on both sides. This results in a three times larger unit cell and in combination with the varying ribbon width means the electronic properties of cove-GNRs are not straightforward to calculate.

In addition, the cove-GNR sample studied in this work has bulky side groups attached to it (Fig. 3.12a), which have to be included in band structure calculations.

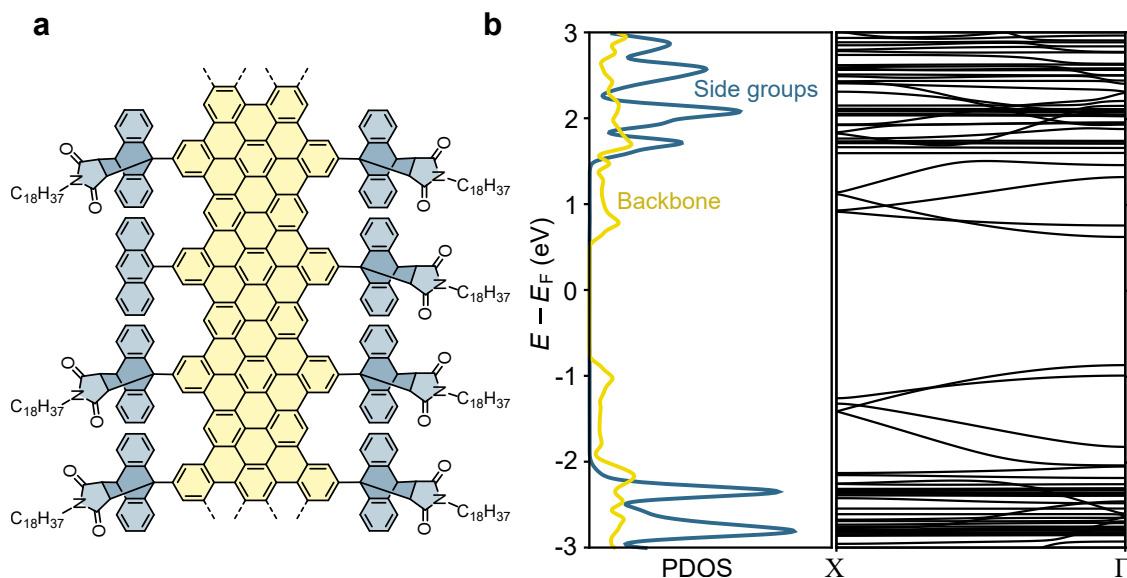


Figure 3.12: Molecular structure, projected density of states and band structure of cove-edged NOMI-GNRs. **a)** Molecular structure of NOMI-GNRs. The cove-edged GNR backbone (yellow) has *N-n*-octadecylmaleimide (NOMI) groups attached to 77% and anthracene groups on the remaining sites (both shown in blue). **b)** Projected density of states (PDOS) arising from the backbone (yellow) and side groups (blue). The right hand side shows the band structure of the sample. There are two low-energy bands relevant for optical transitions originating from the backbone. The bands cross and have their minima at the Γ point. Calculations were performed by collaborator F. Kong.

The side groups are *N-n*-octadecylmaleimide (NOMI) attached with a grafting ratio of 77% and anthracene groups on the remaining sites. Fanmiao Kong from Lapo Bogani's group at Oxford Materials has performed DFT calculations on these NOMI-GNRs and the projected density of states (PDOS) is shown together with the band structure in Fig. 3.12b. The PDOS demonstrates that all states close to the Fermi level arise from the GNR backbone. States related to the side groups are present at higher energies and thus irrelevant for the optical response of the sample. The band structure shows a multitude of bands related to the side groups at higher energies. The two highest valence and lowest conduction bands are in close proximity and arise from states on the GNR backbone. These two bands cross and have their minimum at the Γ point, which is distinctly different from the band structure of

CNTs or standard GNRs. We will rationalise these differences by directly comparing the band structure of graphene-related nanostructures in the following.

Starting off with graphene, we can derive the electronic properties of CNTs and GNRs from the quantum confinement and resulting effects on Brillouin zones. Graphene is a 2D material and the Brillouin zone is a hexagon, as we have described in Sec. 3.2.1. The 2D band structure of graphene can be described with a tight-binding model (Sec. 3.1.2) and has valence and conduction bands touching at the K and K' points of the Brillouin zone. The structure, Brillouin zone, and band structure of graphene are shown in Figs. 3.13a,e,i.

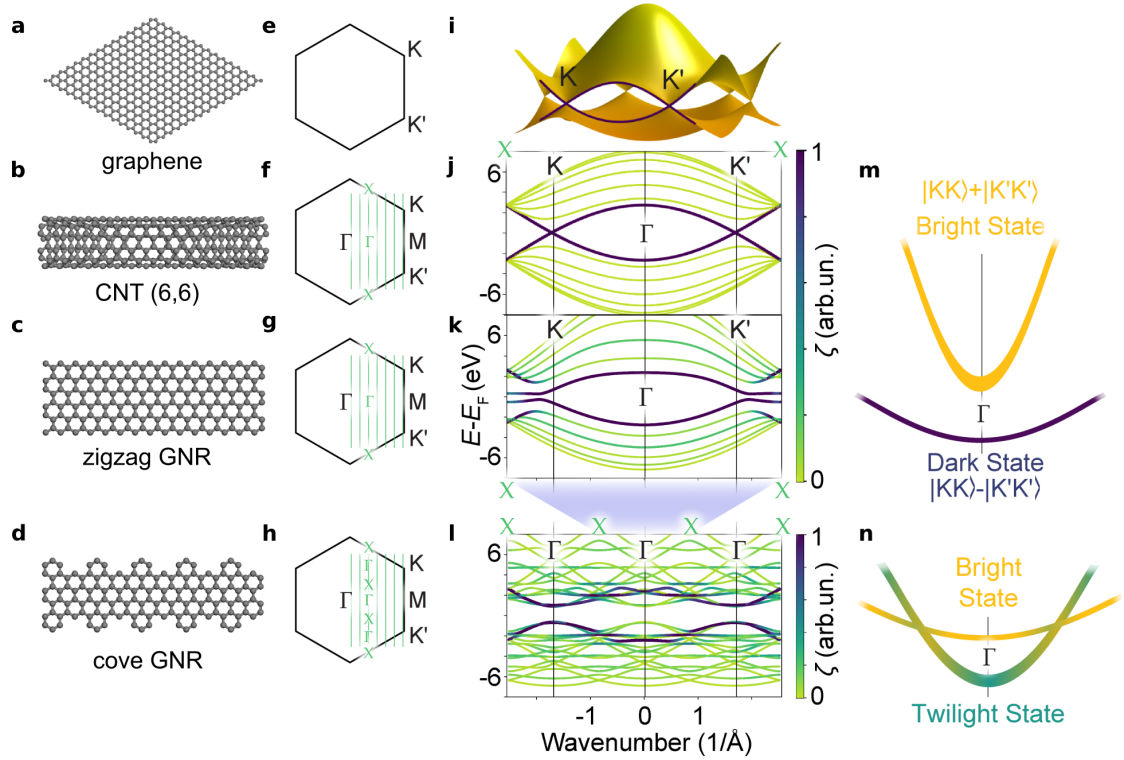


Figure 3.13: Origin of the twilight state. Comparison of graphene, a (6,6) carbon nanotube, a zigzag GNR and a cove-edged GNR via their **a-d)** real space lattices, **e-h)** reciprocal lattices with K , K' , M , Γ and X points indicated, together with the discretization produced by lateral confinement (green lines). **i-l)** The bands of each nanostructure are coloured based on their projection ζ of each point onto the graphene state, resulting in bright and dark states, from the linear combinations of valleys, or yielding the brighter twilight states for cove-edged GNRs. **m-n)** Arrangement of the first two subbands, giving rise to bright and dark states or bright and twilight states.

If we move on to CNTs, the necessity of rolling up a piece of graphene into a tube

adds lateral confinement, making CNTs effectively one-dimensional (Fig. 3.13b). This confinement results in the quantization of $k_{\perp}$, as described in Sec. 3.2.1, and the Brillouin zone consists of discrete lines in $k_{\parallel}$ direction at the allowed $k_{\perp}$ values (Fig. 3.13f). In Fig. 3.13j, the projection $\zeta = \left\| \langle \Psi_{n,k}^{gra} | \Psi_{n,k} \rangle \right\|$ of the wavefunction of a (6,6) CNT $\Psi_{n,k}$ onto the graphene wavefunction $\Psi_{n,k}^{gra}$ is displayed for the k line crossing the $K - M - K'$ points. To illustrate the meaning of the projection ζ , we show ζ for each wavevector k and band n of a (6,6) CNT in Fig. 3.14.

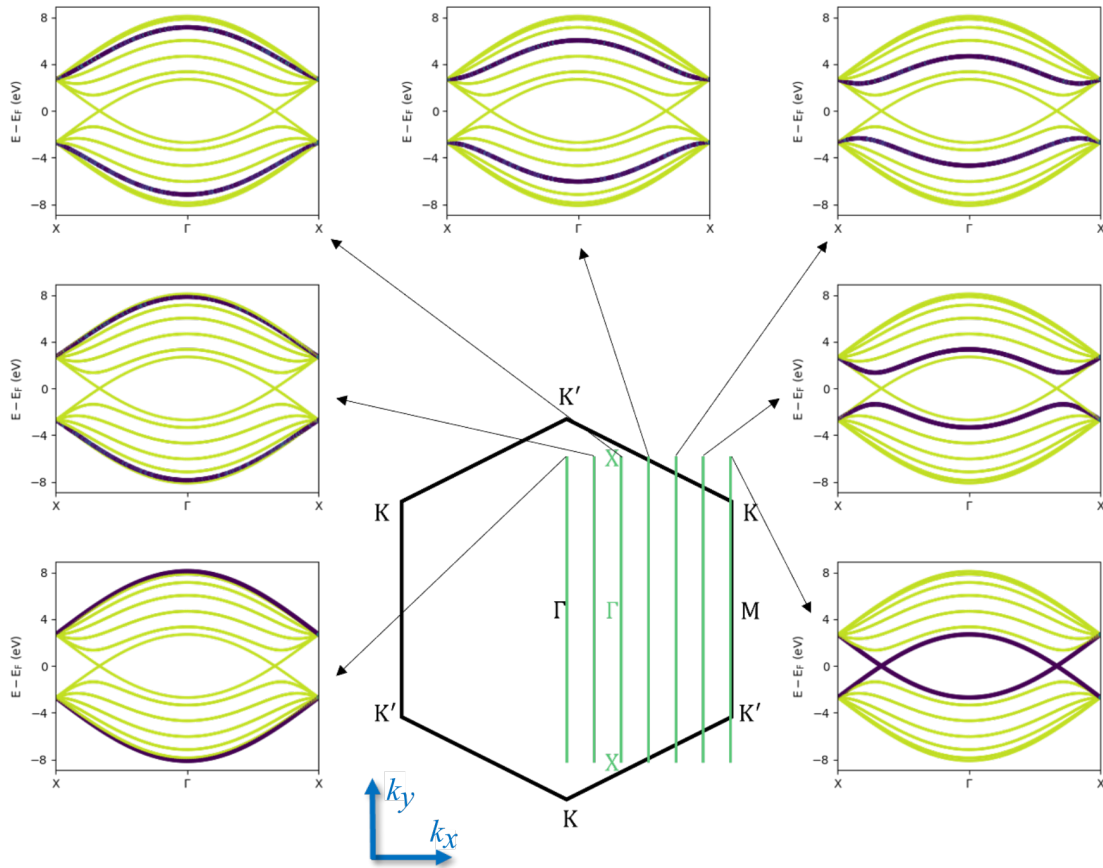


Figure 3.14: Projected band structure of a (6,6) SWCNT onto the bands of graphene. The green lines in the centre visualise the first Brillouin zone of a (6,6) CNT. Individual lines correspond to different transverse wavenumbers $k_{\perp}$. These discrete $k_{\perp}$ lines are projected onto the band structure of graphene to find the band structure of the (6,6) CNT in the zone-folding approximation. In the seven subfigures, the projection ζ of the (6,6) CNT bands onto graphene is shown.

Each of the discrete k lines in the Brillouin zone corresponds to one subband in the band structure. As expected, the k line crossing the $K - M - K'$ points produces the well-known two-valley structure. As we know from describing the zone-folding

approximation (Sec. 3.2.2), the subbands of CNTs project almost perfectly onto the states of graphene. Consequently, showing the projection ζ of CNT bands onto the bands of graphene basically reproduces the CNT bands.

Zigzag GNRs are equivalent to armchair CNTs but the presence of edges slightly modifies the band structure near the edge of the Brillouin zone, generating a band gap (Sec. 3.3.2). For a 6-ZGNR, the structure, Brillouin zone and projection ζ for the k line crossing $K - M - K'$ are shown in Figs. 3.13c,g,k. The projection shows that the 6-ZGNR bands are still similar to the bands of graphene and the graphene valleys at K and K' are present in GNRs as well.

Introducing the *cove* edge structure produces dramatic changes through the new three-fold symmetry of the edges (Fig. 3.13d). The Brillouin zone extends only one-third of the length in the $k_{\parallel}$ direction compared to 6-ZGNR (Fig. 3.13h). Remaining in a zone-folding picture, this threefold symmetry can be imagined as taking only the middle third of the 6-ZGNR Brillouin zone and repeating it three times, see Fig. 3.13l.

The projection ζ of the cove-GNR bands onto the bands of graphene is shown in Fig. 3.15 for the same k as before.

Due to the varying width of the cove-GNR, it is not obvious how many allowed k lines exist and $k_{\perp}$ is no longer a good quantum number. The figure shows that the band structure of cove-GNR can not be described by simply projecting the bands of graphene but rather shows strong signs of state mixing. In particular, the projection along the $K - M - K'$ line (bottom right of Fig. 3.15) highlights that the states that correspond to the K and K' cones in CNTs and GNRs have been zone-folded into the Γ point. This zone-folding directly affects the excitonic structure of cove-GNR.

Dark Excitons

In carbon nanomaterials such as CNTs and GNRs, the presence of dark excitons is a common issue, because conservation of momentum allows PL only from states that have zero net angular momentum. In semiconducting CNTs, the multiple K -points of the graphene Brillouin zone lead to the formation of a dark valley doublet state and two coupled singlets, only one of which is bright. The edges present in zigzag

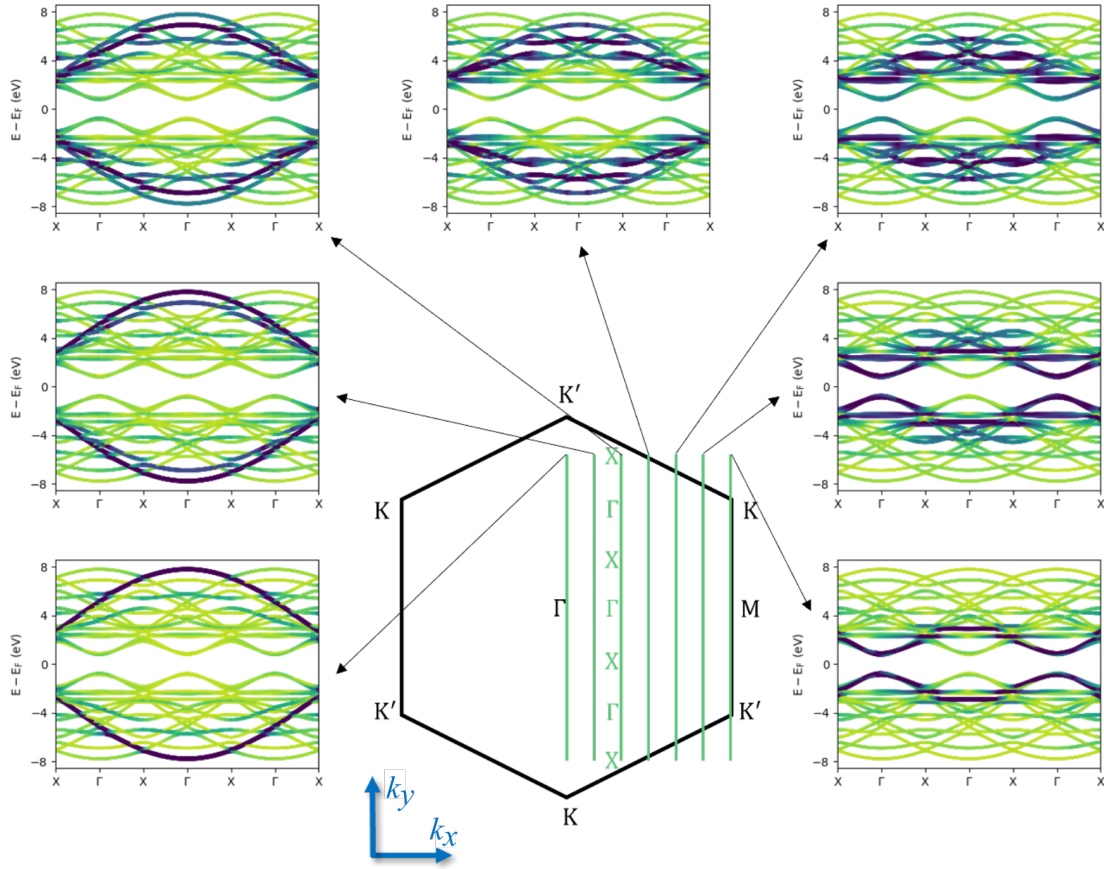


Figure 3.15: Projected band structure of cove-GNR on the bands of graphene. The green lines in the centre are identical to the lines in Fig. 3.14, however, in this case, they extend over three Brillouin zones of the cove-GNR. The seven subfigures show the projection of the cove-GNR band structure as calculated via DFT onto the band structure of graphene at the discrete $k_{\perp}$ lines previously used.

GNRs generate a band gap as the valleys cross and mix, allowing modest brightening of the otherwise dark states. The introduction of the *cove* edge structure produces zone-folding of the dark states into the Γ -point zone centre allowing all of the previously-dark excitons to mix and become much more emissive. We dub these previously-dark states *twilight* states, to distinguish them from conventional bright ones. The arrangement of the first two conduction bands for both scenarios is displayed in Figs. 3.13m,n. The valence bands are mirror images.

4

Materials, Methods and Characterisation Techniques

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4.1 Materials and Methods

4.1.1 Graphene Nanoribbons

Cove-edged graphene nanoribbons with dodecyl side chains (Dodecyl-GNR) were synthesised by Dr Xuelin Yao in the group of Prof Lapo Bogani at Oxford Materials according to the procedure reported by Narita *et al.* [62] (structure

shown in Fig. 5.1a). Cove-edged GNRs with identical backbones but the bulky *N*-*n*-octadecylmaleimide side chains (NOMI-GNR) were prepared by Wenhui Niu and Dr Ji Ma in the group of Prof Xinliang Feng at the Technical University of Dresden, Germany. The synthetic route is summarized in Fig. 4.1 and a detailed description is provided in reference [63].

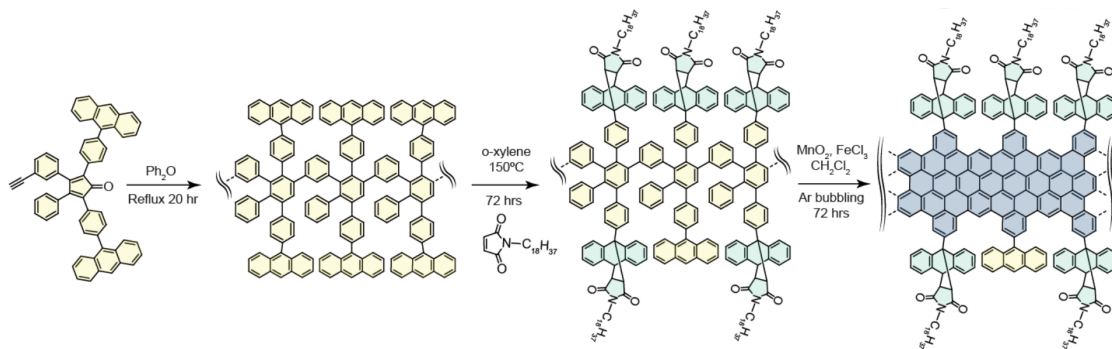


Figure 4.1: Synthetic design of NOMI-GNR. The synthetic route sees first the creation, via Knoevenagel condensation, of a diene and a dienophile, and then removal of the triisopropylsilyl protecting groups to afford the monomer. AB-type Diels–Alder polymerization leads to a polyphenylene precursor pendent with anthracene functional groups. Subsequently, Diels–Alder ‘click’ cycloaddition with *N*-octadecylmaleimide produces a polyphenylene with the desired bulky groups on the sides. Intramolecular oxidative cyclodehydrogenation eventually forms the aromatic backbone and yields the NOMI-GNRs. Schematic reproduced with permission from Springer Nature from reference [63].

The NOMI side chain was prepared following the reported synthetic route [64]. The resulting NOMI-GNRs have a width of $w = 1.13$ nm. The GNR length distribution of $l = 10 - 371$ nm was estimated from the molecular weight via gel permeation chromatography [63]. The bulky NOMI side group extends in three dimensions with a diameter of $\gtrsim 0.5$ nm, which importantly is larger than the interlayer distance in graphite (~ 0.3 nm). A space-filling model of the NOMI side group and a NOMI-GNR is provided in Fig. 4.2.

Both NOMI- and Dodecyl-GNR samples were dissolved in chloroform at a concentration of 0.05 mg/ml and dispersed via brief sonication.

For spectroscopic measurements at 4.2 – 295 K, polystyrene or EVA polymer was added to the GNR solution in a 50:1 polymer:GNR weight ratio. The solution was consequently deposited on a glass substrate that was heated to 50°C via drop-casting

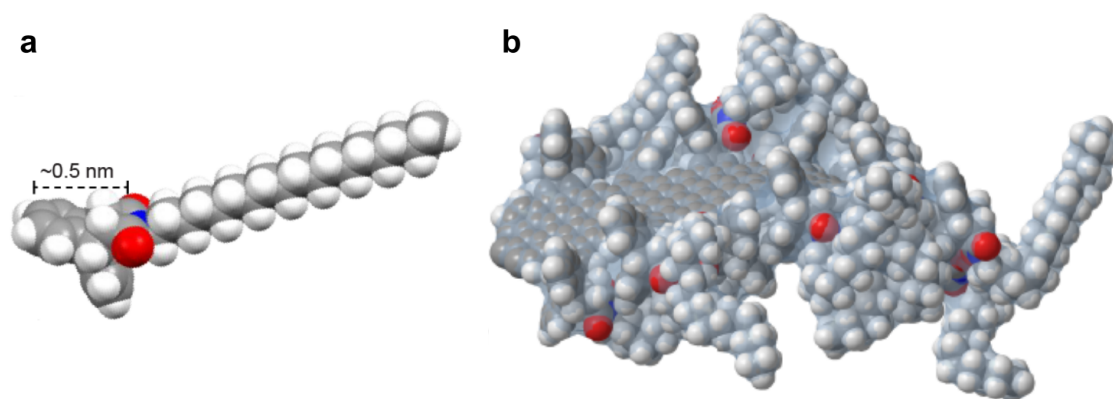


Figure 4.2: 3D Models of *N-n*-octadecylmaleimide (NOMI) and a section of NOMI-GNR. The models show oxygen atoms in red, carbon in grey, hydrogen in white and nitrogen in blue. The molecular structure of NOMI-GNRs is displayed in Fig. 5.1b. **a)** The NOMI side group consists of the bulky maleimide group ensuring inter-ribbon separation and an octadecyl alkyl chain providing excellent solubility in organic solvents. **b)** Space-filling model of a section of NOMI-GNR highlighting the Connolly solvent-excluded surface in light blue. Both figures are reproduced with permission from Springer Nature from reference [63].

to form a film of GNR in the polymer matrix. We used two different polymers to investigate the possible effects of the polymer matrix. When comparing room temperature spectra of GNR in solution and in polymer matrix we found no effect of the polymer for PL, Raman or absorbance measurements (not shown), see Fig. 4.3. The small differences in the Raman spectra in Fig. 4.3b are due to the different

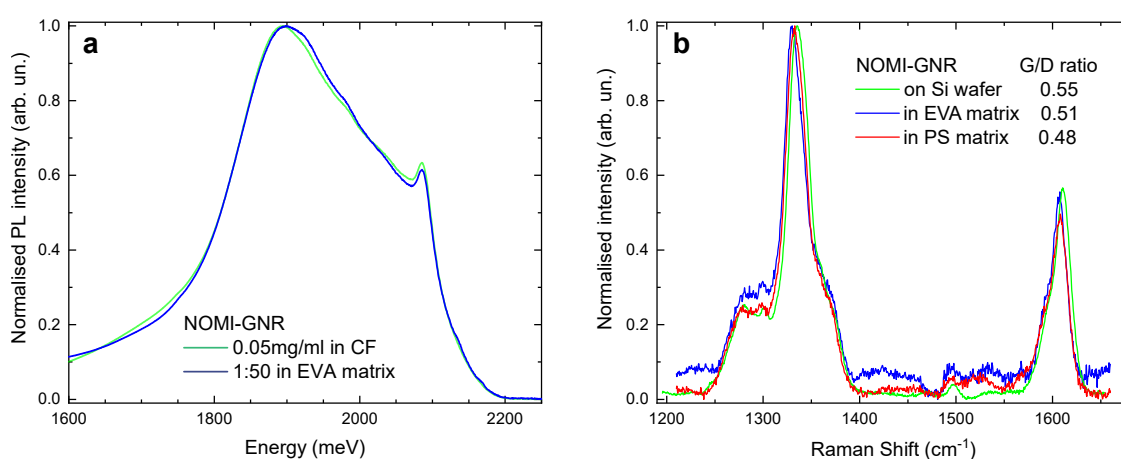


Figure 4.3: Comparison of NOMI-GNR films and solutions in PL and Raman data. **a)** Normalised PL spectra of NOMI-GNR in chloroform solution and EVA matrix. **b)** Normalised Raman spectra of NOMI-GNRs deposited either directly from chloroform solution on a Silicon wafer or in ethylene-vinyl acetate (EVA) or polystyrene (PS) matrices on glass. The D and G peaks are clearly visible around 1330 cm⁻¹ and 1600 cm⁻¹.

substrates. The GNR samples in polymer matrix were deposited on glass instead of crystalline silicon, which causes a higher scattering background. Overall, we observed a high consistency between data of different GNR samples of the same type, confirming the high solubility of NOMI-GNRs.

4.1.2 Carbon Nanotube Films

Synthesis of Carbon Nanotubes

There are several synthesis methods for CNTs. The first SWCNTs observed by S. Iijima and T. Ichihashi in 1993 were grown by arc-discharge evaporation [65]. This and other methods such as laser ablation have later been replaced by catalytic chemical vapour deposition (CCVD) methods for their lower cost, easier scalability and versatility of both carbon source input and CNT output [66]. In the CCVD synthesis process, a catalyst, commonly consisting of metal nanoparticles, is placed in a furnace and the furnace is heated to 500 – 1200 °C. Subsequently, a carbon-bearing gas is ducted into the furnace to cause carbon deposition as CNTs on the catalyst via catalytic decomposition [67]. This process has been studied extensively in the past decades, resulting in a drastic price reduction and an increasing level of control over the resulting carbon nanotubes. A promising approach towards the chirality-controlled synthesis of SWCNTs has recently been identified in the fabrication from unimolecular CNT seeds that allow to unambiguously predefine the SWCNT chirality [68]. However, until now fabrication of uniform chirality-pure SWCNT samples is not possible and post-synthesis purification via selective dispersion is required.

The CNTs used in this work were all synthesized by CCVD methods. Their properties are summarized in Tab. 4.1, and prices used are per gram or scaled from the minimum purchase amount. Among the three types of SWCNTs, HiPco and CVD tubes were chosen as they have been studied in detail before and Tuball tubes for their 5 – 50 times greater length and nearly 100-fold lower price [69–71]. Further, various types of MWCNT were investigated. They were obtained from Nanocyl, Cheaptubes or Nanotechlabs and differed in dimensions and purity [72–74].

Table 4.1: Properties of the CNT types compared in this work. Values were adopted from the provided data sheets [69–74].

CNT type	product name	Diameter (nm)	Length (μm)	Purity (wt%)	Price (€/g)
SWCNT	HiPco	0.85 ± 0.25	$0.1 - 1$	95	550
	CVD	0.9 ± 0.2	~ 1	95	1,300
	Tuball	1.6 ± 0.4	> 5	80	6
MWCNT	Nanocyl	~ 9.5	1.5	90	0.65
	Boron doped	~ 30	50	92	75
	Few walled	~ 7	> 10	92	150
	Cheaptubes 13-18	~ 15	~ 30	95	10

Carbon Nanotube Networks

Electronic Properties

While in individual SWCNTs ballistic charge transport with electrical conductivity of up to $2 \times 10^5 \text{ S/m}$ [75] and corresponding electron mobility of up to $1 \times 10^5 \text{ cm}^2/\text{Vs}$ [76, 77] can be observed, these properties typically decrease to values around 60 S/m [78] and $10 - 20 \text{ cm}^2/\text{Vs}$ [79, 80] in networks. This reduction of charge transport characteristics is due to large junction resistances R_{jx} occurring at nanotube-nanotube charge transitions [81–86]. These can be on the order of $100 \text{ k}\Omega - 20 \text{ M}\Omega$ [81, 82, 87–89] depending on the spatial overlap and distance between the crossing tubes. It is hence expected that larger diameter tubes possess lower junction resistances. In addition, Schottky barriers between semiconducting and metallic nanotubes increase the electrical resistance [81, 90], compare Sec. 2.2.4. The resistance of an individual nanotube of $1 \mu\text{m}$ length is approximately $1 - 10 \text{ k}\Omega$ [83, 87–89], consequently, the overall resistance of randomly oriented CNT networks is dominated by junction resistances.

Polymer Functionalisation

A major obstacle when working with CNT networks is their tendency to agglomerate into large bundles due to attractive van der Waals forces. This is unfavourable as only the outermost tubes in a bundle participate in charge transport [91]. Apart

from detrimental effects on optoelectronic performance, agglomeration also prevents the solubilisation of CNTs and thereby inhibits facile processing routes.

A common approach to overcome this challenge without affecting the electronic or optical properties of CNTs is non-covalent functionalisation [92–94]. In this process, a dispersion agent is used to wrap around individual carbon nanotubes that have been separated by vigorous mixing. The agent decreases the contact area of neighbouring CNTs, thereby screening the van der Waals forces and enhancing solubility.

Typically, this was done with expensive conjugated polymers, costing $> 100\$/\text{g}$, since $\pi - \pi$ -stacking interactions were thought to be the main driving mechanism for the wrapping process [95]. Among the most studied wrapping polymers is poly(3-hexylthiophene) (P3HT) [96–101], which is therefore used as reference wrapping agent throughout this work. However, a recent study by our group [102] has demonstrated the solubilisation of CNTs with the non-conjugated copolymer ethylene-vinyl acetate, details will follow below. This suggests that interactions between CH-groups or C=C bonds in polymers and the π -bonded sp^2 hybrid orbitals in carbon nanotubes can also drive the wrapping process [102]. A negative side effect of polymer wrapping is the reduction of CNT surface area available for CNT-CNT junctions. This likely increases junction resistances due to less spatial overlap and limits the number of junctions resulting in a higher total resistance of the composite network [103]. For this reason, the polymer content in CNT-polymer composite films should be kept as low as possible.

Ethylene-Vinyl Acetate

Ethylene-vinyl acetate (EVA) is a copolymer comprised of the monomers ethylene and vinyl acetate (VA). The chemical structure is depicted in Fig. 4.4. EVA is a widely used polymer with a global annual production volume in the range of $3 - 6 \times 10^6$ tonnes per year [104, 105]. EVA combines high mechanical resilience and hydrophobicity [106]. It is optically transparent in the visible range and has a low vapour transmission rate [107]. EVA is also electrically insulating and costs well below 1€/per kg. The precise properties of the copolymer can be tuned by

varying vinyl acetate:ethylene ratio, molecular weight, distribution of monomers and branching of chains, whereof the last two are of minor importance [108].

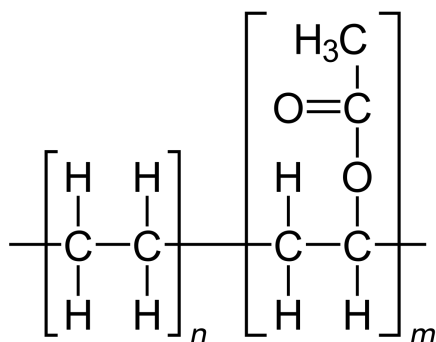


Figure 4.4: Molecular structure of the copolymer ethylene-vinyl acetate (EVA).

Table 4.2: Properties of EVA polymers. The vinyl acetate (VA) content and melt index (MI) which is inversely related to the molecular weight are listed as retrieved from product data sheets [109].

Resin name	VA wt%	MI
ELVAX 670	12	0.35
ELVAX 4355	25	5.7
ELVAX 4320	25	150
ELVAX 210W	28	400
ELVAX 150	32	43
ELVAX 40L-03	40	3
ELVAX 40W	40	52

The key factor to EVA properties is the VA content. As polyethylene is crystalline and VA amorphous, increasing the VA content decreases the degree of crystallinity in the copolymer. Decreasing crystallinity has a detrimental effect on mechanical properties, such as stiffness modulus and tensile strength, but also lowers chemical resistance and melting point. On the other hand, a lower degree of crystallinity means enhanced optical clarity and a higher stress crack resistance [108, 110]. The second effect of the VA content is caused by the polar nature of the acetoxy side chain. Hence more VA results in a higher polarity of the copolymer, increasing compatibility with polar resins, specific adhesion and printability [108].

The other major factor determining EVA's properties is the molecular weight, with longer chains resulting in higher viscosity, higher chemical resistance and improved mechanical properties, but a detrimental effect on solubility and processability [108]. It should be noted here that as usual in industrial plastics, instead of molecular weight the melt index (MI) is provided by the manufacturer. The MI can be measured by the international standard protocol ASTM D123 and is inversely related to molecular weight [108].

The described tuning factors give EVA a high versatility that is reflected in the wide range of applications. These typically include hot-melt adhesives, drug

delivery, shoe soles, and cable insulation [108, 110, 111]. More recently, a CNT-EVA composite has also been demonstrated as electrode for flexible supercapacitors [112].

The formulation mainly used in this work is the product Elvax 150 by DuPont which contains 32 wt.% vinyl acetate. It has first been proposed for use as encapsulation material in photovoltaic modules by Cuddihy *et al.* in 1983 [113] and is the industry standard for silicon solar cells to date. For comparison, six other types of EVA have been employed to solubilise carbon nanotubes, their VA content and melt index are displayed in Tab. 4.2b as retrieved from their data sheets [109]. For easier reference, the polymers are referred to with VA content and melt index in the following.

Preparation of Transparent Conductive Films

The preparation process used in this work was originally developed by S. Habisreutinger and G. Mazzotta [102] and is depicted in Fig. 4.5. Unless otherwise stated, the process consisted of the steps described below.

At first, 5mg of SWCNT, or alternatively 1mg of MWCNT, raw material is added to 10ml solution of EVA in chlorobenzene of a given concentration, typically 0.5 – 5 g/l. The mixture is tip ultrasonicated at 150 W power for 10 minutes causing debundling of the tubes and wrapping of individual CNTs with polymer chains. After sonication, the mixture is centrifuged at 10,000g for 8 minutes to precipitate the remaining CNT bundles. The supernatant, containing only individually-wrapped tubes in the polymer solution, is collected. To remove the remaining excess polymer, 20ml of toluene is added to the supernatant and the vial is kept on a hotplate at 80°C for at least 2 hours. Due to the lower solubility of CNTs in toluene, the polymer-wrapped nanotubes reaggregate while unattached EVA remains dissolved. Next, the suspension is centrifuged for 4 minutes at 16,000g. The higher rotational speed causes the CNT precipitate to form pellets that allow precise control over the transmittance and sheet resistance of the resulting films. The CNT pellets are re-dispersed in 50ml chloroform by tip sonicating for 1 minute. The resulting dispersion of individually wrapped nanotubes is stable for days up to months,

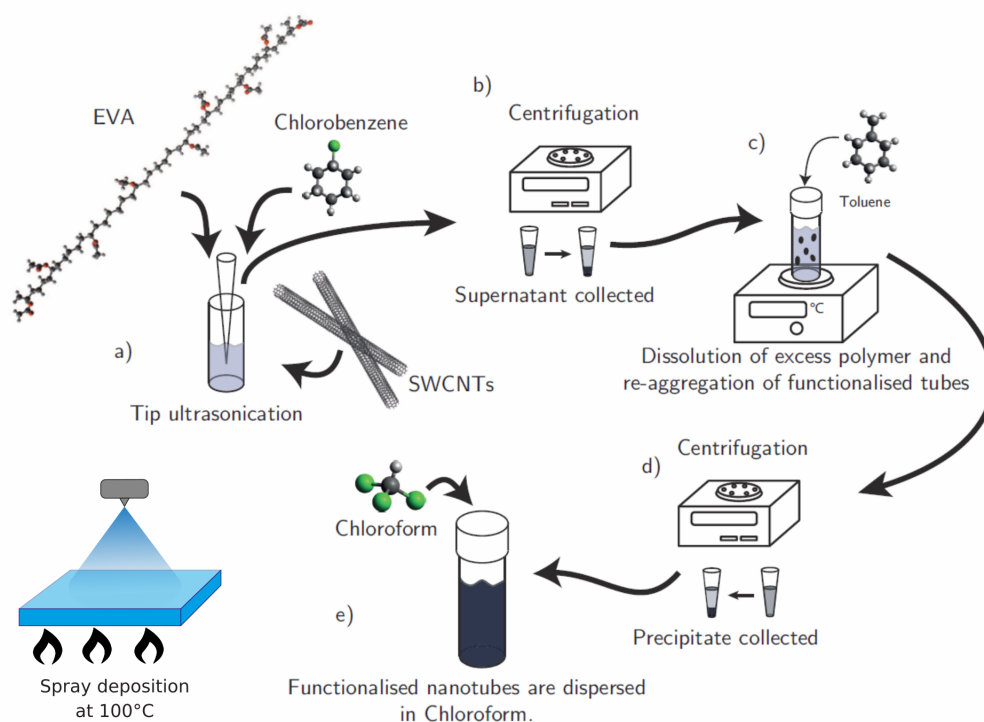


Figure 4.5: Solubilisation of CNTs with ethylene-vinyl acetate for thin film deposition. a) CNTs and EVA polymer is tip sonicated in chlorobenzene. b) The supernatant of the centrifuged dispersion is collected, precipitated CNT bundles are removed. c) Added toluene dissolves EVA but reaggregates EVA-wrapped CNTs. d) After another centrifugation step, the EVA-wrapped CNTs are contained in the precipitate. Excess EVA in the supernatant is discarded. e) Chloroform is added and the solution is redispersed via sonication. The solution is then deposited via spray coating at 100°C. Schematic reproduced and adapted with permission from the American Chemical Society from reference [114].

depending on concentration and CNT type, and ready for deposition. There are several deposition methods available, such as spin coating, drop casting and spray coating. As was shown by M. Dollmann [115], spray coating produces the most homogeneous and reproducible results and was consequently chosen for all films in this work. The spray coating setup was custom-built by Grey Christoforo [116]. The solution is sprayed at a flow rate of 4 ml/min with an air pressure of 3 bar through an atomizing nozzle onto the glass substrates. The substrates are heated to 100°C, well above chloroform's evaporation point at 61°C, to evaporate the solvent before getting in direct contact with the substrate. The spraying nozzle is located at a height of 45 mm above the substrates and moves across them at a

speed of 200 mm/s for a total of 600 passes. The number of passes can be adjusted to achieve a specific film thickness. The total area covered by the nozzle is 63 cm² and can be reduced for smaller substrates.

4.1.3 Transparent Conductive Film Performance

The two parameters of interest when comparing transparent conductive films (TCFs) are the sheet resistance R_s and the transmittance T . T is typically evaluated at 550 nm, where the luminosity curve of the human eye has its maximum. In order to relate the optical and electrical properties of CNT films, we express T in terms of the film thickness t as [117]

$$T = \left(1 + \frac{Z_0}{2} \sigma_{op} t\right)^{-2} \quad (4.1)$$

with the vacuum impedance $Z_0 = 1/\epsilon_0 c = 377 \Omega$ and the optical conductivity σ_{op} which has been shown to be equal to $\sigma_{op} = 1.7 \times 10^4 \text{ S/m}$ for carbon nanotube films [118, 119]. From this we can find a relation between T and R_s

$$T = \left(1 + \frac{Z_0 \sigma_{op}}{2 R_s \sigma_{dc}}\right)^{-2} \quad (4.2)$$

where σ_{dc} is the dc conductivity of the CNT film [120]. Here, the ratio σ_{dc}/σ_{op} serves as a figure of merit (FoM) for comparison of TCF performance, where large FoM values correspond to low R_s and/or high T . Minimum FoM requirements have been proposed for touch panels (FoM > 4.5), LCD screens (22), OLED displays (70) and photovoltaic electrodes (348), the last one is equivalent to $10 \Omega/\text{sq}$ at 90% transmittance [121]. This model works well for bulk-like materials, but as De *et al.* [122] pointed out, percolation effects need to be considered for nanostructured material classes such as flakes or nanotubes. These materials do not show bulk-like behaviour below a critical thickness t_{min} and the dc conductivity decreases with decreasing thickness for thinner films. This is due to the fact that with decreasing thickness more and more parts of the film are isolated and do not contribute to electrical conduction but still absorb light. The thickness at which only one percolating pathway is left is called the percolation limit and typically occurs at an average film thickness of 1 nm for nanotube networks [123].

As a consequence of the above, there are multiple aspects to consider when optimising the TCF performance of carbon nanotube-polymer networks.

The average nanotube length determines the number of junctions required to pass through a given macroscopic film. Therefore, longer tubes allow for higher conductivities, scaling like $\sigma \propto L^{1.46}$ [124]. The nanotube length is typically limited by the harsh mixing required during the dispersion process. Hence, there is a trade-off between longer CNTs and smaller CNT bundle size, as more extensive mixing allows for better individualisation of tubes but also results in shorter tubes [125, 126].

Another key aspect is CNT purity. Impurities, such as amorphous carbon, strongly reduce the conductivity. Further, the detrimental effects of Schottky barriers on the electrical conductivity can be reduced by a higher fraction of metallic nanotubes in the film and using SWCNT of similar radius to decrease electrical barrier heights [127, 128]. This can be achieved via better synthesis routes, improved purification processes and a better understanding of the selectivity of the wrapping process.

Finally, the electrical conductivity can be enhanced post-deposition via chemical doping. This has proven an effective way to enhance electrical conductivity by factors around 10 [129]. Common dopants include chlorinated metals or acids [127], a detailed discussion follows in the next section.

Chemical Doping

Chemical doping describes the process of intentionally implementing impurities into a semiconductor material to change its electronic properties. In contrast to inorganic semiconductors, where this is typically realised by lattice doping, dopant adsorption has proven more effective in carbon nanotubes.

This process describes charge transfer between dopant molecules and CNT, the resulting Coulomb attraction between positive and negative charge stabilises the dopant on the CNT sidewall [130, 131]. Due to the low electron affinity of CNTs, p-doping is commonly used rather than n-doping. Various dopants have been identified, the most promising being acids and halogenated metals [129, 132–134].

For chloroauric acid, the electrical conductivity of SWCNT films has been improved by factors of up to 13.5 [135]. In this work, nitric acid (HNO_3), chlorobromic acid (H AuBr_4), chloroauric acid (H AuCl_4), gold chloride (AuCl_3), copper chloride (CuCl_2), iron chloride (FeCl_3), nickel chloride (NiCl_2) and aluminium chloride (AlCl_3) were assessed for their suitability to dope SWCNT-EVA films.

To achieve optimal performance when doping CNT films, a homogeneous distribution of dopant molecules across the film has to be ensured. Therefore, different dopant deposition methods have been investigated as shown in Fig. 4.6. These experiments were performed with help of MPhys student Nicole Jacobus.

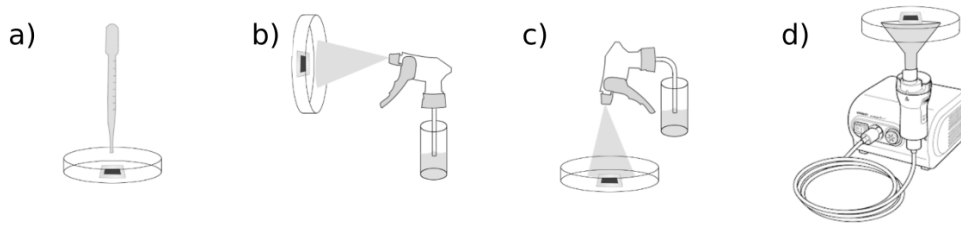


Figure 4.6: Dopant deposition techniques. The four different dopant deposition techniques investigated in this work are **a)** dripping, **b)** horizontal spraying, **c)** vertical spraying and **d)** nebulising.

For every method, the corresponding dopant was dissolved in ethanol at a concentration of 5mM. This solution was then deposited via either drip doping (Fig. 4.6a), horizontal spray doping (b), vertical spray doping (c) or nebuliser doping (d).

The spray doping was done with a standard polyethylene terephthalate spray bottle rather than the spray coater, as the acidic dopants would corrode its metal spray nozzle. The nebulising was done with an OMRON compressor nebuliser NE-C801.

While distributing dopant molecules homogenously is important, at the same time, dopant leakage to the outside of the film has to be avoided, for acids in particular. Leakage of dopants has been shown to damage adjacent layers when implemented in devices [127].

For this purpose, a layer-by-layer doping technique was employed to make use of the insulating nature of EVA and to encapsulate the dopant molecules inside the film. This was investigated by depositing CNT-EVA solution and dopant solution alternately, the process is depicted in Fig. 4.7.

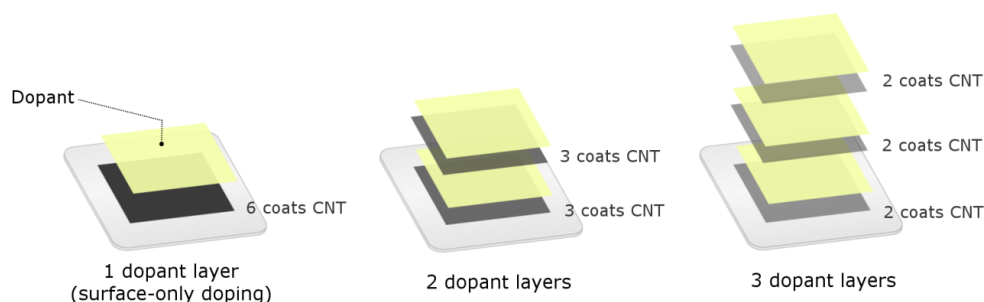


Figure 4.7: Distribution of chemical dopants within CNT-EVA thin films. Opposed to standard top-only doping (left), the layer-by-layer doping technique involves alternating deposition of CNT-EVA and dopant solution. The technique has been tested with two and three (middle, right) and up to five dopant layers.

4.1.4 Perovskite Solar Cells

In this section, the details of materials and fabrication procedures used for the perovskite solar cells reported in this work are laid out. Devices were prepared by Suer Zhou in the group of Prof Henry Snaith at Oxford Physics.

Solar Cell Materials.

Formamidinium iodide (FAI) (>99.99%) was purchased from Greatcell Solar Materials. PbI_2 (99.999%) and PbBr_2 (>98.0%) were purchased from TCI. Methylammonium bromide (MABr) was purchased from Xi'an Polymer Light Technology Corp. Methylammonium chloride (MACl), potassium chloride (KCl) and phenethylammonium iodide (PEAI) were purchased from Sigma-Aldrich. 2,2',7,7'-tetrakis(N,N'-di-p-methoxyphenylamine)-9,9'-spirobifluorene (spiro-OMeTAD) (>99.5%) was obtained from Luminescence Technology Group. Lithium bis-(trifluoromethanesulfonyl)imide (Li-TFSI, >99%), 4-tert-butylpyridine (tBP, 98%), Isopropanol (IPA, 99.5%), N, N-dimethylformamide (DMF, anhydrous 99.8%), dimethyl sulfoxide (anhydrous DMSO, >99.9%), anisole (anhydrous, 99.7%), chlorobenzene (CB, 99.8%), acetonitrile (ACN, anhydrous 99.8%) were purchased from Sigma-Aldrich. Chemicals were used as received without further purification. Gold pellets for evaporation were purchased from Kurt J. Lesker.

Solar Cell Fabrication.

Solar cells were prepared as described by Mazzotta *et al.* [102] with the following modifications. The FTO substrates (Pilkington Tec7) were cleaned by subsequently sonicating in Decon 90 solution (1% vol. in D.I. water), D.I. water, acetone, and isopropanol for 10 minutes each. Afterwards, the substrates were dried in a continuous stream of nitrogen gas and UV-ozone cleaned for 15 minutes before SnO₂ layer deposition. The SnO₂ chemical bath deposition was done following the same methods as described in reference [102]. KCl was used to passivate the SnO₂ layer. Briefly, 20 mM of KCl solution in D.I. water was made and spin-coated onto the substrates at 3000 rpm for 30 s. Then the substrates were dried on the hotplate at 100°C for 10 minutes. The substrates were UV-ozone cleaned for another 15 minutes before the perovskite film deposition. 1.6M FAPbI₃ 99% with 35% excess MAcl and 1% MAPbBr₃ additive was used as the absorber material. The chemicals were dissolved in 4:1 DMF:DMSO and stirred on the hotplate at room temperature for 1 hour. Then 100 μ L of precursor solution was drop-casted on the substrate and spun at 6000 rpm for 30 s (3000 rpm/s ramp speed). 300 μ L of anisole was dripped onto the substrate 10 s into the spinning program. The perovskite films were then annealed at 150°C for 15 minutes. After the perovskite layer deposition, a 5mM PEAi was dissolved in isopropanol and spin-coated onto the perovskite layer for passivation. The PEAi solution was drop-casted onto the substrate dynamically spinning at 3000 rpm for 30 s. The substrates were then either spray-coated with CNT-EVA on top or left as they were for the control devices. For the control devices with doped spiro-OMeTAD, 85mg of spiro-OMeTAD was dissolved in 1 mL chlorobenzene. Then 33 μ L of tert-butyl pyridine (tBP) and 20 μ L of Li-TFSI (520 mg/mL in acetonitrile) were added to the spiro-OMeTAD solution. For the devices with undoped spiro-OMeTAD, 85mg of spiro-OMeTAD was dissolved in 1mL chlorobenzene. Then only 33 μ L of tBP was added to the spiro-OMeTAD solution. After depositing the CNT-EVA layers (or perovskite control), 60 μ L of doped or undoped spiro-OMeTAD solution was dropped onto the

substrates spinning at 2000 rpm for 30 s. Afterwards, 80 nm gold electrodes were evaporated onto the samples under a vacuum of $< 9 \times 10^{-9}$ bar.

4.1.5 Perovskite Single Crystals

FAPbI₃ single crystals were grown by Elisabeth Duijnste and Benjamin Gallant in the group of Prof Henry Snaith. All single crystals were fabricated in N₂ from a seed crystal by following the inverse temperature crystallization method [136, 137].

The control FAPbI₃ single crystals were prepared by dissolving equimolar FAI and PbI₂ in γ -butyrolactone (GBL). The solution is then stirred at 60°C for four hours. Next, the solution is filtered with a 25 mm diameter 0.45 μ m GMF filter. 4 ml of the filtrate is placed in a vial that contains a seed FAPbI₃ crystal, and the vial is kept in an oil bath undisturbed at 95°C for 12 hours. The resulting α -FAPbI₃ single crystals measured between 2 – 4 mm in size.

For the FAPbI₃-M and FAPbI₃-H single crystals, alongside equimolar FAI and PbI₂ either 3.8 mol% MDACl₂ or 0.63 mol% HMTA (with respect to the Pb content) is added. For crystals where HMTA and NH₄Cl were added, the concentrations were 0.63 mol% and 5 mol%, respectively.

The same procedure as for the reference FAPbI₃ crystals was then followed. Note that in contrast to Min *et al.* [138] no MACl was added to any of the precursor solutions, aiming to isolate and investigate the effect of MDACl₂ on FAPbI₃ phase stability.

After growth, single crystals were heated in a vacuum oven at 180°C for 30 min to remove residual solvent from the crystal surface and ensure the crystals are in the α -phase. Single crystal X-ray diffraction (SCXRD) was used to confirm the 3D perovskite phase in each case prior to further usage of the crystal batch. The crystal structure was found to be in the Pm $\bar{3}$ m cubic space group, as previously reported [139].

4.2 Characterisation Techniques

Details of the experimental techniques used to acquire the results reported in this work are described here.

4.2.1 Surface and Structural Characterisation

The high aspect ratios of carbon nanotubes make it inherently difficult to produce homogeneous CNT films of low surface roughness. The tools to analyse film morphology are listed here.

DekTak and Atomic Force Microscope (AFM)

DekTak and atomic force microscope (AFM) are standard instruments to measure thin film thickness and surface morphology. In AFMs a cantilever is moved across a sample in x, y-direction, obtaining the forces acting on the cantilever in z-direction via deflection of the laser beam that is focused on it, see Fig. 4.8a. The forces between the sample and cantilever tip can be of attractive or repulsive nature, typically van der Waals and Coulomb forces dominate the instrument response that keeps the detected forces on the cantilever in set boundaries by adjusting the piezoelectric stage. AFM data in this work were taken with an *Oxford Instruments MFP-3D AFM* in dynamic tapping mode in ambient conditions either on glass or silicon substrates. The *Bruker DekTak profilometer* can be viewed as a simplified AFM, mapping the surface only in one dimension. For film thickness measurements, a thin stripe of CNTs was removed from the substrate with a razor blade and the profilometer scanned across.

Scanning Electron Microscope (SEM)

The scanning electron microscope (SEM) generates signals by directing a beam of high-energy electrons onto the sample surface in a vacuum. Magnetic lenses and apertures focus the electron beam and allow it to be scanned across the specimen, a schematic is shown in Fig. 4.8b. In principle, the resolution is limited by the *de Broglie* wavelength $\lambda_{dB} = h/p$ with electron momentum p and the Planck

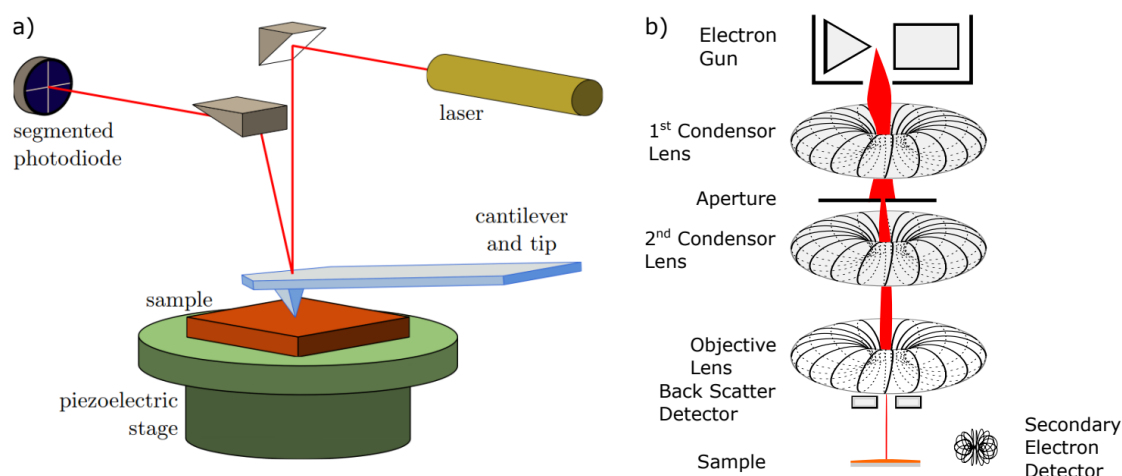


Figure 4.8: Working principles of atomic force microscope (AFM) and scanning electron microscope (SEM). a) Basic components of an atomic force microscope. b) Working principle of a scanning electron microscope with magnetic condenser lenses, electron beam (red) and two different detectors. Figures adapted from [115].

constant h . However, at high electron energies charging of the specimen blurs images and eventually leads to sample damage, limiting the resolution to several nanometers. Multiple types of signals can be detected upon the deceleration of incident electrons at the sample surface. Standard SEM images rely on secondary electrons, but detection of back-scattered electrons or photons are also viable modes of operation. For this work, a *Hitachi S-4300* SEM was used with acceleration voltages between 15 and 20 kV.

Small-Angle Neutron Scattering (SANS)

Small-Angle Neutron Scattering (SANS) was performed by Andreas Lauritzen, Oxford Physics, at the Larmor beamline at the *ISIS Neutron and Muon Source*. Samples were measured using neutrons with $dQ/Q = 8\%$ and a wavelength range of $0.9 - 13.5 \text{ \AA}$ with an unpolarised square beam of dimensions $6.6 \text{ mm} \times 6.6 \text{ mm}$ to avoid uneven film edges. The collected Q ($Q = 4\pi/\lambda \cdot \sin(\theta/2)$) range was 0.0052 to $0.67 \text{ \AA}^{-1}$, but only data from $5.5 \times 10^{-3} \text{ \AA}^{-1}$ to $6 \times 10^{-2} \text{ \AA}^{-1}$ was considered structurally relevant. Sample illumination time was approximately 4 hours to ensure sufficient counts were recorded. Samples were measured in aluminium containers with 0.5 mm thick quartz entry and exit windows (Quartz type “WHQ” from *Knight*

Optical) which is chosen due to its low contribution to coherent scattering. Film coating was done as described in Sec. 4.1.2. The measured sample configurations consisted of 10 quartz substrates (same type as used for the container windows) coated with about 150 nm of CNT-EVA composite each as well as 6 spacer substrates to fit the geometry of the container all stacked on top of each other. This was done to increase the scattering sample volume due to the low thickness of the films. Sample scattering was normalised by subtraction of scattering from 16 uncoated substrates in a container as well as the empty beam.

4.2.2 Conductivity Measurements

The electrical conductivity of CNT thin films was measured with four-point probes in two geometries. Since conductivity and resistance depend on sample dimensions, a quantity invariable under scaling, the sheet resistance R_s , is used instead. It is connected to the bulk resistivity ρ via $R_s = \rho/t$ with the film thickness t . If the film thickness is known, bulk resistivity and conductivity $\sigma = 1/\rho$ can be calculated.

By default, the sheet resistance of pristine films was measured with an in-line four-point tungsten carbide probe from *Jandel Engineering* at 0.635 mm spacing and a *Keithley 2450* source meter. A current is forced through the outer probes and the voltage drop across the inner probes is measured in a sweep scan of 20 points. The slope of the current-voltage line multiplied by the correction factor $\pi/\ln(2)$ for the in-line probe configuration can be used to calculate the sheet resistance. Typically, five measurements were taken across every sample and the results were averaged.

To prevent damaging the probes, doped films were measured with a *van der Pauw* geometry. For this purpose, small silver contacts were applied to the four corners of every sample with a paint brush and silver conductive ink. Current-voltage curves were taken as before but in two different directions. The sheet resistance is calculated according to

$$R_s = \frac{\pi}{\ln 2} \frac{R_0 + R_{90}}{2} f \quad (4.3)$$

with the slopes of the I-V curves R_0, R_{90} and the correction factor f , which is a function of their ratio [140]. Errors associated with the size of the contacts

scale with $(r/D)^2$ with contact diameter r and contact separation D [140] and are expected to be around 1% for the samples in this work. Unlike the in-line four-point probe, the van der Pauw setup is not a local but a global measurement of the sample. Results can therefore slightly deviate between the two geometries due to inhomogeneities within samples. Both setups were calibrated with a *NIST* $12\ \Omega/\square$ ITO sample prior to each measurement.

4.2.3 Solar Cell Characterisation

J-V measurements were performed by Suer Zhou in Prof Henry Snaith's group at Oxford Physics. The following details are reproduced from reference [141]. The photovoltaic devices were characterised in ambient conditions with the room temperature around $20 - 24^\circ\text{C}$ and 45% relative humidity under AM1.5G simulated sunlight generated by a class AAA *WaveLabs Sinus-220* solar simulator, using a *Keithley 2400* source meter. The intensity of the solar simulator was set to produce $100\ \text{mW}/\text{cm}^2$ equivalent irradiance using a certified KG3-filtered silicon reference photodiode (*Fraunhofer ISE*). The voltage was swept at a rate of $0.61\ \text{V}/\text{s}$ first from forward bias to reverse bias (forward sweep) followed by a reverse sweep in the opposite scan direction. The minimum voltage was $-0.1\ \text{V}$ and the maximum voltage was $1.2\ \text{V}$. On each substrate, there were 3 devices with an area of $0.25\ \text{cm}^2$ and 1 larger device with an area of $1.00\ \text{cm}^2$. The areas were defined using black anodised aluminium shadow masks in direct contact with the glass side of the substrates within enclosed sample holders. The equivalent solar irradiance used for power conversion efficiency calculations was estimated before each solar cell measurement run based on the integrated spectrum of the solar simulator's internal spectrometer compared to the integrated value measured at the same time as its intensity was set using the certified reference photodiode. The equivalent irradiance was found to be in the range of $0.985 - 1.004$ suns, which has been applied to calculate power conversion efficiencies as described in Sec. 2.3 eq. 2.10.

4.2.4 Nuclear Magnetic Resonance (NMR)

To characterise FAPbI₃, nuclear magnetic resonance (NMR) measurements were performed on a two-channel *Bruker Avance III HD Nanobay 400 MHz* instrument running *TOPSPIN 3* equipped with a 5 mm z-gradient broadband/fluorine observation probe. The signal from residual non-deuterated DMSO solvent was used for reference. These measurements were performed by collaborators Benjamin Gallant, Silvia Collavini and Dominik Kubicki.

4.2.5 Optical Characterisation

The following section provides an overview of the optical characterisation techniques involved in this work.

Absorption and Transmittance Measurements

Room temperature absorption and transmittance data were obtained with a *Perkin-Elmer Lambda 1050 UV-vis-IR* Spectrophotometer using 1 nm steps in the visible region and 2 nm steps in the infrared region. The instrument was used with a 2 mm beam diameter. To account for reflectivity, blank reference substrates or cuvettes were measured and used for calibration. Low-temperature transmittance measurements were performed as described in the next section.

Photoluminescence and Reflectance Spectroscopy

Temperature-dependent steady-state photoluminescence (PL), reflectivity and transmittance measurements were performed in a custom-built setup. For PL measurements, the sample was excited with a *LaserQuantum Ventus532* 532 nm laser or a custom-built 405 nm laser diode. Laser power was adjusted with neutral density filters. To prevent side modes or higher order modes from affecting the spectra, laser emission was passed through narrow bandpass filters before being coupled into a 500 μm optical fibre. Transmission and reflectivity measurements were conducted with a *Ocean Optics HL-2000-FHSA* halogen white light source that was coupled to the fibre directly with an SMA connector.

The optical fibre led to the sample holder inside a liquid helium cryostat controlling the temperature in the range of 4.2 – 450 K. A *Lake Shore Cernox CX1050SD-HT* resistance temperature sensor was attached to the sample holder with GE-varnish to measure the temperature close to the sample during experiments. The sensor was operated by four-terminal sensing and calibrated with known temperatures such as the boiling points of helium, nitrogen or water and by comparison with a calibrated temperature sensor, results are given in Fig. 4.10a. The accuracy of the temperature measurements is limited by the calibration and can be assumed to be below 5 K in the entire 4.2 K to 450 K temperature range.

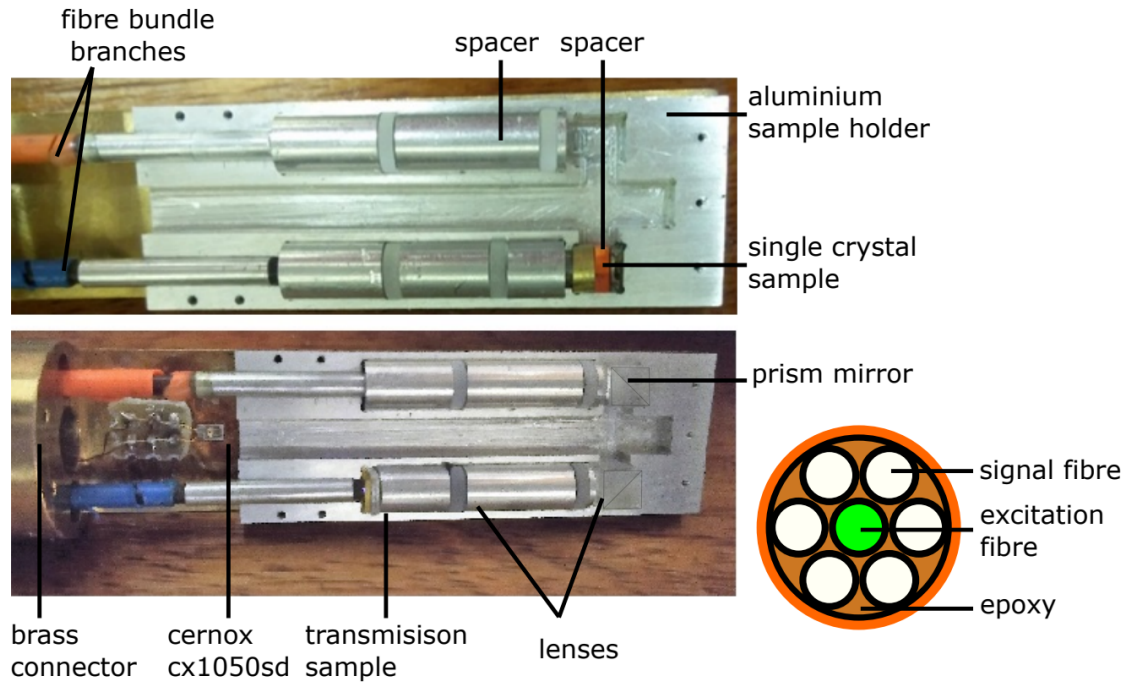


Figure 4.9: Sample holder for PL and reflectivity measurements. The fibre optics setup is shown in PL/reflectivity (top) and PL/transmission (bottom) configuration. Optical fibre bundles consist of multiple fibres with the central fibre carrying excitation light and the outer fibres returning the signal, as shown on the bottom right.

In the brass sample holder, depicted in Fig. 4.9, the beam irradiates the sample orthogonally and was focused to a $< 1 \text{ mm}^2$ spot. The sample holder can be adapted for different types of measurements. In the PL/reflectivity geometry, two lenses focus the excitation light onto the sample surface. The same lenses allow for efficient coupling of emitted or reflected photons back into the fibre bundle.

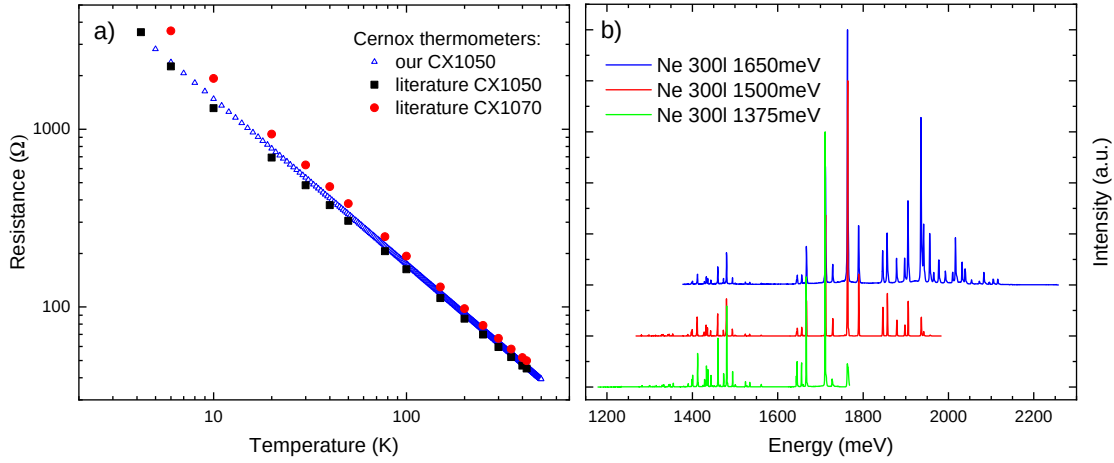


Figure 4.10: PL spectrometer and temperature sensor calibration. a) Temperature calibration of the Cernox temperature sensor with tabulated values of the resistive thermometer. b) Spectrum of the Neon (Ne) lamp used for energy calibration of the 300-line grating of the spectrometer. Energy values in the legend give the centre position of the spectrometer.

In this geometry, only one fibre bundle is active, with the central fibre carrying excitation light and the outer fibres returning the optical signal to the spectrometer. In the PL/transmission configuration, prism mirrors guide the photons through the sample holder into the orange fibre bundle (Fig. 4.9). Again, lenses refocus the diverging beams for better coupling to the optical fibre. This geometry allows measurements of thin film transmission in addition to PL.

For both sample holder configurations, the sample response was collected by a bundle of fibres passing it to a 0.3 m *Princeton Applied Research Model 1235* triple grating 300, 1200, and 2400 line spectrograph coupled to an *Andor iDus 416A-LDC-DD* back-illuminated silicon CCD equipped with appropriate optical filters. The camera was cooled to 240 K for all measurements to ensure a good signal-to-noise ratio. The centre wavelength position of the spectrograph can be tuned by changing the alignment of the central grating. A *Newport 6032* pen-style Neon calibration lamp was used to calibrate the wavelength axis before each set of measurements, an exemplary spectrum is provided in Fig. 4.10b. The calibration lamp allows an absolute accuracy of the wavelength axis down to about 1 nm. However, as long as the central grating position is kept the same, relative changes in peak positions

much smaller than that can be detected with the 2000 pixel CCD. The spectra were typically captured using 200 accumulations at an exposure time of 30 ms.

For all measurements, background spectra were acquired under identical conditions without a sample present and subtracted from the data to remove internal reflections and other noise. Similarly, to account for the spectral response curve of the spectrometer, the sample data was divided by a spectrum of the *Ocean Optics HL-2000-FHSA* halogen white light source, which has an almost constant emission intensity in the wavelength region of interest. Background subtraction was performed on the white light spectrum as well.

Photoluminescence Excitation (PLE) Spectroscopy

Photoluminescence excitation (PLE) spectroscopy was carried out on a custom-built setup depicted in Fig. 4.11.

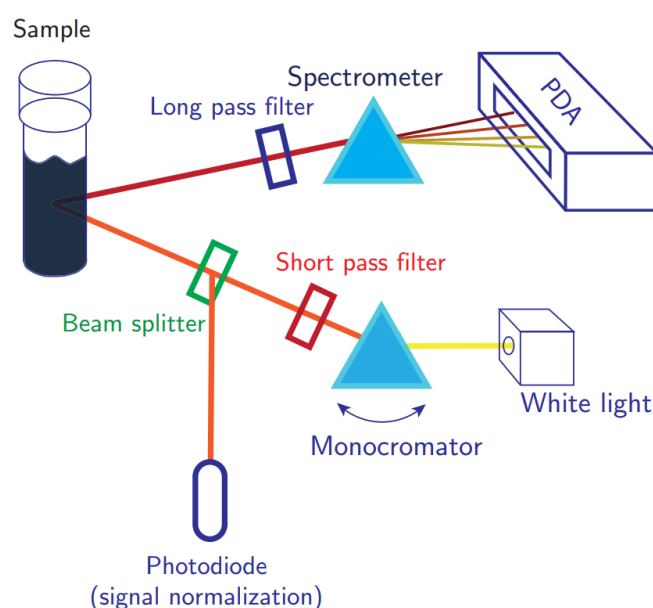


Figure 4.11: The photoluminescence excitation (PLE) setup. The emission of the white light source is filtered by a monochromator and short-pass filter. A small fraction of the beam is used for intensity normalisation, the remainder excites the sample. Photoluminescence emission of the sample passes a long-pass filter and spectrometer to be collected by an InGaAs photodiode array (PDA).

The excitation light source is a 75 W *Photon Technologies International Inc.* Xenon lamp that is filtered by a 0.3 m monochromator grating. A short pass filter

removes unwanted higher-order modes from the excitation light. To account for the energy-dependent spectral output of the Xenon lamp, a quartz beam splitter reflects a small part of the light onto a silicon photodiode measuring the intensity. This intensity is subsequently used to scale the individual PL spectra accordingly. The main part of the beam is focused on the sample by a combination of lenses. The photoluminescence emission of the sample is collected by a second system of lenses and filtered through a long pass filter, removing residual excitation light. Finally, a triple grating 0.3 m spectrometer passes the light to a *Princeton Instruments OMA V* liquid nitrogen cooled InGaAs photodiode array (PDA). The system is calibrated with the Neon lamp described in the previous section.

Photoluminescence Quantum Efficiency (PLQE) Measurements

Photoluminescence quantum efficiency (PLQE) was measured in an integrating sphere as detailed in reference [142]. The PLQE η can be calculated as

$$\eta = \frac{E_i - (1 - A) \cdot E_o}{E_e \cdot A} \quad (4.4)$$

with the area under the emission profile with the sample in the laser line E_i , the fraction of laser light absorbed upon one pass through the sample A , the area under the emission profile with the sample out of the laser line E_o and the area under the laser excitation curve with empty integrating sphere E_e .

Samples were excited with a *Roithner MLL-III-405nm-200mW* laser or a *Roithner laser RTLMLL-532nm-1.5-3W* 532 nm laser and the intensity controlled with ND filters. The luminescence was detected with a calibrated *QEPro OceanInsight* grating spectrometer.

Raman Spectroscopy

Raman spectra were acquired with a *Jobin Yvon T64000* triple spectrometer and an *Andor DU420A-OE* CCD. The spectrometer was calibrated with the 520.7 cm^{-1} line of a Silicon wafer. Samples were excited with a *Ventus solo* Nd:YAG 532 nm laser or a *Melles griot* He:Ne 633 nm laser.

5

Revealing Brightly Fluorescent States in Molecular Graphene Nanoribbons

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A manuscript based on the data presented in this chapter was submitted to *Nature* on 24 March 2023 by BERND K. STURDZA, FANMIAO KONG, XUELIN YAO, WENHUI NIU, JI MA, XINLIANG FENG, MORITZ K. RIEDE, LAPO BOGANI, ROBIN J. NICHOLAS

Since the isolation of graphene was first reported by Geim and Novoselov in 2007 [143], an extensive field of research has emerged around the promising electronic and mechanical properties of this new material [144–146]. However, the absence of an energy band gap severely limits the number of applications for graphene.

This issue can be overcome by reducing the size of graphene sheets to quasi-one-dimensional strips called graphene nanoribbons (GNRs). This introduces additional quantum confinement of charge carriers which can result in the opening of a band gap, analogously to CNTs [58].

Like most semiconducting carbon nanostructures, GNRs have direct band gaps and are expected to yield high photoluminescence quantum efficiencies from excitons with large binding energies [147, 148]. They offer tremendous potential for applications in bio-imaging, solar energy conversion, optoelectronics and in display devices, as well as in quantum technologies for single-photon sources, up-conversion, and sensing [149–155].

Alas, non-radiative dark states, disorder, and interactions among the carbon nanostructures all lead to substantial PL quenching [156]. The most appealing systems, i.e. those with large exciton-diffusion coherence lengths, such as CNTs, are actually those affected most adversely. CNTs need surfactants to prevent $\pi - \pi$ -stacking interactions and bundling, but this introduces disorder, severely limiting the fluorescence yields. While individual CNTs can reach PLQE yields as high as 7% [157], bundles are quite dark, and dispersions in solvents typically produce yields around 1-2% [158–160], with higher yields obtained only via Flavin-mononucleotide analogues in aromatic solvents [161].

Molecular graphene nanoribbons, a novel form of carbon nanostructures with large exciton-diffusion lengths, hold the promise to solve these issues. Their emission energy can be chosen depending on their morphology, easily reaching the visible spectrum, and they display long coherence times [162] and electronic states with nontrivial magnetic and topological properties [163] that should be optically accessible. They are thus a superb platform, once issues with inter-ribbon exciton transfers, which typically broaden optical spectra and degrade the PLQE yields dramatically both on surfaces and in bundles [164], are solved.

Nonetheless, GNRs offer a path forward. In CNTs, covalent functionalisation breaks the π -conjugation, and non-covalent surfactants are randomly arranged around the CNT surface; both mechanisms severely disrupt electronic properties [93,

94]. By contrast, in GNRs the solubilising groups can be placed regularly at the nanoribbon edges without impeding the π -conjugation [62].

Recently, GNRs with bulky side groups achieved PL quantum yields up to 9.1% and high solubility in organic solvents [165]. However, the photoluminescence spectra of those samples remain broadened and without features, an indication of exciton delocalisation over multiple monomers.

In this chapter, the issue of GNR solubility and inter-ribbon exciton transfer will be addressed by comparing two nanoribbon samples with identical cove-edged graphene backbones but different-sized side chains. Optical characterisation reveals brightly fluorescent states that provide insights into the electron-phonon coupling and connected internal processes in graphene nanoribbons. Electron-phonon coupling is a key parameter in determining the suitability of GNRs for both optical and electronic applications as it defines heat conductivity, Raman scattering and many transport properties of a given material [166].

N-*n*-octadecylmaleimide-GNR samples investigated in this chapter were synthesised by Wenhui Niu and Dr Ji Ma, Dodecyl-GNR samples were prepared by Dr Xuelin Yao, and DFT and vibronic calculations were performed by Fanmiao Kong.

5.1 Solubility of Molecular Graphene Nanoribbons

Conventionally, alkyl chains are attached covalently to GNR edges to make them dispersible in organic solvents [167, 168]. More recently, novel synthesis routes opened the door to maleimide-based side groups that combine alkyl chains with a bulkier compound and thus have the potential to screen $\pi - \pi$ -stacking interactions between GNRs, see Sec. 4.1.1.

Here, two samples with identical cove-edged graphene nanoribbon backbones but different-sized side groups, one alkyl and one maleimide based, are compared. This allows us to study the impact of the side groups on the optical properties of the GNR directly. The sample with alkyl side groups has dodecyl chains ($\text{C}_{12}\text{H}_{25}$) attached to every prominent carbon ring as shown in Fig. 5.1a. The second sample

has bulky *N-n*-octadecylmaleimide (NOMI) side groups attached with a grafting ratio of 77% and anthracene groups on the remaining sites (Fig. 5.1b) [63].

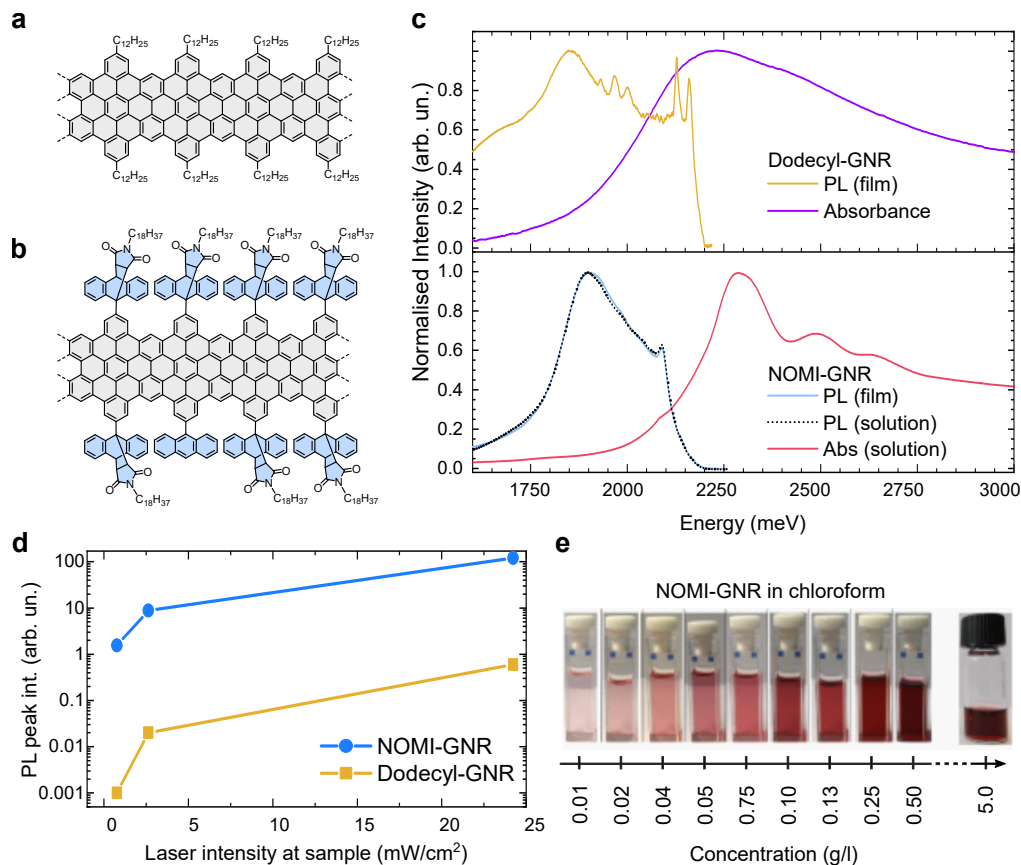


Figure 5.1: Photoluminescence and absorption of Dodecyl-GNR and NOMI-GNR. **a)** Molecular structure of graphene nanoribbon functionalised with dodecyl side chains (Dodecyl-GNR). **b)** Structure of GNR functionalised with *N-n*-octadecylmaleimide (grafting ratio 77%) and anthracene side groups (NOMI-GNR). **c)** Photoluminescence and absorption spectra of the two GNR samples, normalised at the 1.9 and 2.3 eV peaks, respectively. No PL was observed for the Dodecyl-GNR sample in solution. Photoluminescence spectra were taken with 2.33 eV laser excitation. **d)** Comparison of PL peak intensities of the 1850 and 1900 meV peaks for Dodecyl-GNR and NOMI-GNR, respectively, for different laser intensities. **e)** NOMI-GNR dissolved in chloroform at different concentrations.

Absorption and photoluminescence spectra of the two GNR samples in chloroform solution (Fig. 5.1c) highlight the differences in solubility. Spectra were normalised and PL spectra were taken with 2.33 eV laser excitation. The absorbance of Dodecyl-GNRs shows a singular wide peak centred at 2.23 eV. In contrast, NOMI-GNRs display three resolved peaks at 2.29 eV, 2.49 eV and 2.63 eV plus a narrow feature at 2.09 eV. A similar trend is present in the photoluminescence response.

On the one hand, NOMI-GNRs display an identical PL response in chloroform solution (0.05mg/ml) and in an EVA polymer matrix (see Sec. 4.1.1), consisting of a single narrow feature at 2.09 eV and a wider peak at 1.90 eV. On the other hand, Dodecyl-GNRs show no detectable photoluminescence at all in chloroform solution. Only when immobilised in a transparent polymer matrix, Dodecyl-GNRs give a weak PL response comprising five narrow peaks and a wider peak at 1.85 eV. However, the narrow lines can be clearly identified as D and G Raman lines which implies the wide 1.85 eV peak is the sole PL response of the sample not caused by scattering. This wide peak is again red-shifted compared to its counterpart in NOMI-GNRs and thus assigned to excimer emission from GNR bundles in accordance with previous results [164]. In contrast, the narrow 2.09 eV peak in NOMI-GNRs cannot be assigned to a Raman mode due to its position. This is confirmed when considering the PL peak intensity; NOMI-GNRs show a PL response 2-3 orders of magnitude stronger than Dodecyl-GNR, see Fig. 5.1d, suggesting that all Raman scattering peaks are hidden within the strong PL emission in NOMI-GNR, while Raman peaks dominate the PL spectrum of Dodecyl-GNR due to the absence of an appreciable PL response. A detailed analysis of GNR Raman spectra will follow in the next section. The nature of the optical response of NOMI-GNR will be discussed in detail in Sec. 5.3.

Since the PL intensity of NOMI-GNR is increased by orders of magnitude compared to Dodecyl-GNR, we performed PLQE measurements on this sample. The PLQE for the de-bundled GNRs reaches a value of $6.4 \pm 0.2\%$ at room temperature (Fig. 5.2) and appears to be independent of concentration in the range of 0.002 to 0.2 mg/ml, see Tab. 5.1. We assign the slight increase in PLQE with concentration to the presence of a constant scattering loss that is less important at higher PL intensities. Uncertainties in the efficiency values were determined experimentally and are of the order of $\pm 0.5\%$. Upon cooling, the total PL intensity increases by 20% (Fig. 5.6) leading to a remarkably high overall 7.7% PLQE.

In summary, the broadened absorption and quenched PL response of Dodecyl-GNRs suggest a much lower solubility of these nanoribbons compared to NOMI-

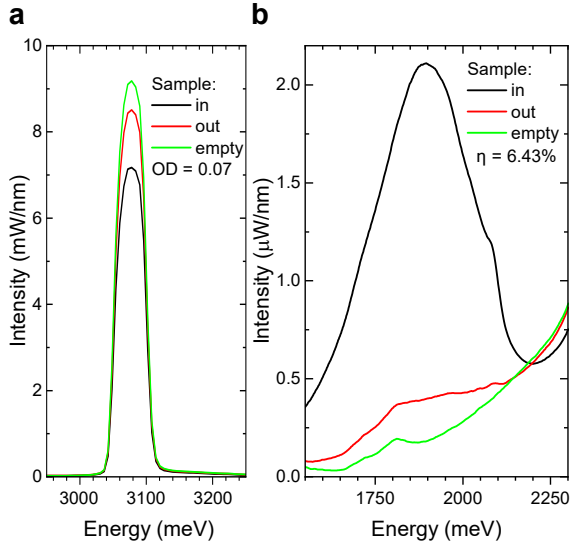


Figure 5.2: PLQE of NOMI-GNRs. Spectra of **a)** 3.06 eV laser excitation, **b)** GNR emission with sample cuvette in (out) beamline or empty integrating sphere.

Table 5.1: PLQE of NOMI-GNRs in chloroform solution at different concentrations. Data was acquired with 3.06 eV laser excitation in cuvettes with different path lengths.

Conc. (mg/ml)	cuvette (mm)	OD	PLQE (%)
0.002	10	0.01	6.13
0.066	1	0.03	6.25
0.066	10	0.26	6.32
0.20	1	0.07	6.43

GNRs which causes Dodecyl-GNRs to agglomerate to bundles. This can be confirmed qualitatively in chloroform solutions of the two samples. While NOMI-GNRs dissolve well in chloroform at concentrations up to 5 mg/ml (Fig. 5.1e), dispersions of Dodecyl-GNR precipitate within hours even at concentrations below 0.05 mg/ml. By contrast, our first NOMI-GNR sample shows no signs of aggregation after 16 months of cabinet storage at a concentration of 0.2 mg/ml. This highlights the exceptionally high solubility of NOMI-GNRs and clearly demonstrates the important role of the bulky maleimide group in enhancing GNR solubility. On a microscopic level, this can be explained by the dimensions of the maleimide side groups ($r \approx 0.5$ nm) that are larger than the inter-layer spacing of graphite and thus effectively prevent $\pi - \pi$ -stacking interactions between GNRs and consequently the formation of GNR bundles. Alkyl chains on the other hand appear to be too small to suppress the attractive interactions between individual GNRs fully.

5.2 Vibrational Properties

To understand electron-phonon interactions, an essential first step is knowing what vibrational modes (phonons) are present in a material. Phonon modes

play a key role in heat or charge conduction and often determine the structure of optical spectra. Phonon modes with even symmetry upon inversion can be detected via Raman spectroscopy.

The Raman spectrum of Dodecyl-GNRs (Fig. 5.3a) is dominated by the D and G modes of graphitic carbon, depicted in Fig. 5.3b, and their second order overtones 2D, D+G and 2G [169]. The peak positions are provided in units of cm^{-1} and meV in the inset and agree with each other down to 1 meV, demonstrating high accuracy for our Raman measurements. The five modes are easily identified as the same modes present in the PL spectrum (Fig. 5.1e) confirming our previous assignment.

The Raman spectrum of NOMI-GNRs (Fig. 5.3c) presents the same D and G mode peaks, while higher-order D and G modes are hidden within the strong PL response for NOMI-GNRs. In both samples, we observe a multi-peak structure of D and G modes, which results from the lifting of the two graphene sub-lattice degeneracy produced by lateral confinement [170, 171]. Edge functionalisation also relaxes the planar symmetry of the GNRs, resulting in a multitude of smaller Raman peaks caused by the mixing of longitudinal, transverse, and normal modes [170, 171]. This effect might be enhanced further in NOMI-GNRs by the presence of two different side groups and the resulting variations in the local microscopic environment along the ribbons. The small differences in D and G mode energies between Dodecyl-GNRs and NOMI-GNR are attributed to the different weights of the side groups [171].

In addition to the above modes, the Raman spectrum of NOMI-GNRs reveals several low-energy peaks. The radial breathing-like mode (RBLM) is the first overtone of the fundamental transverse acoustic (TA) mode and is the dominant feature alongside a weaker second overtone visible at twice the energy.

These modes can be visualised by simulating the phonon modes of cove-edged GNRs (provided by Fanmiao Kong) in Fig. 5.3d. The two modes on the left and the right display RBLM and 2RBLM vibrations without side groups. The RBLM mode with anthracene side groups is displayed in the centre. NOMI side groups are replaced by anthracene side groups for the sake of clarity. The green arrows indicate the movement of atoms.

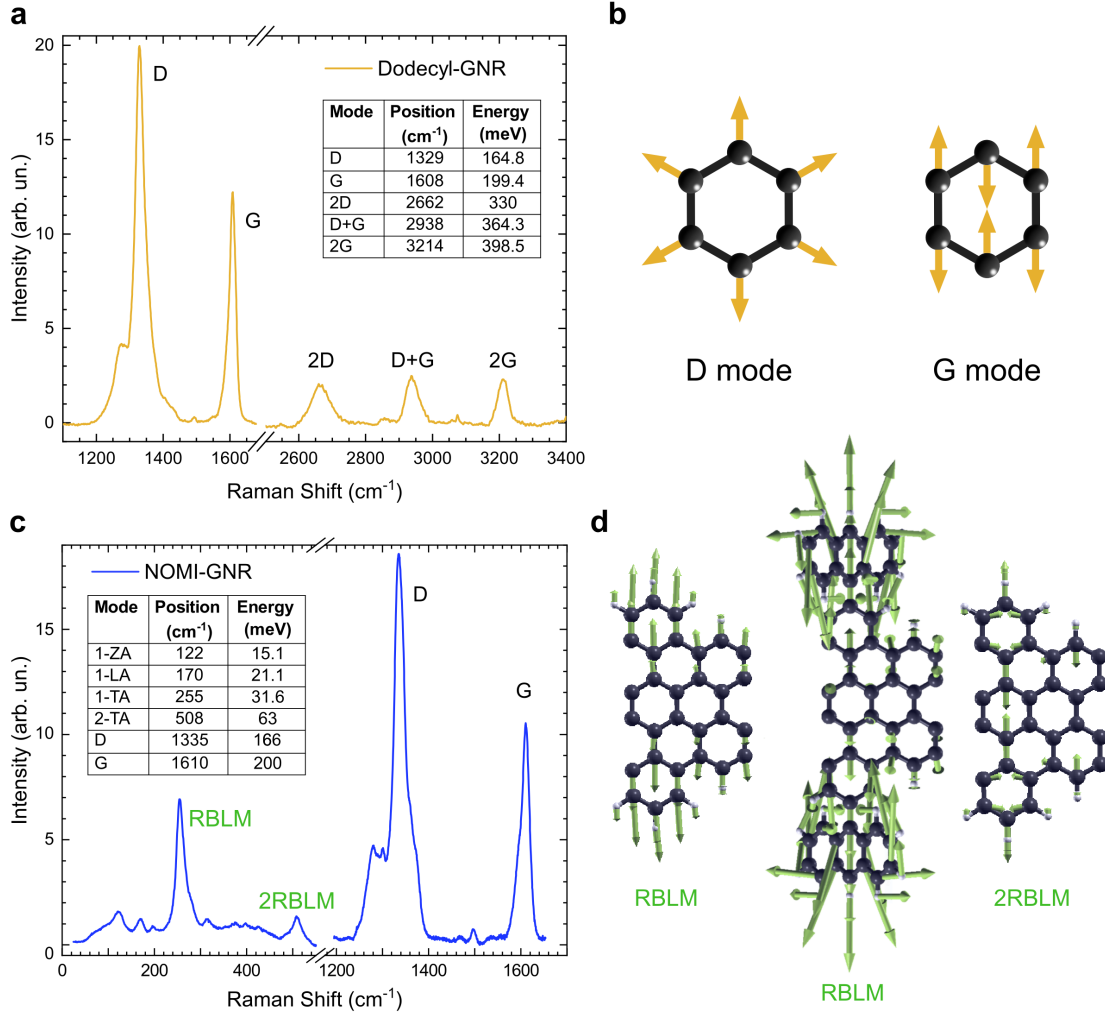


Figure 5.3: Raman spectra and phonon modes of Dodecyl-GNRs and NOMI-GNRs. Spectra were acquired with 2.33 eV excitation in thin films. **a)** Raman spectrum of Dodecyl-GNRs with D mode, G mode and corresponding two phonon modes present. The inset table reports peak positions. **b)** Visualisation of D and G mode vibrations in graphitic carbon structures. **c)** Raman spectrum of NOMI-GNRs. The D, G, and radial-breathing-like modes (RBLM) are labelled. Longitudinal acoustic (LA) and out-of-plane acoustic (ZA) modes were also identified. **d)** Symmetries of the calculated RBLM (1-TA) and 2RBLM (2-TA) modes for a cove-edged GNR. The RBLM mode is shown with and without side groups. The bulky NOMI side groups are replaced by anthracene for clarity. Calculations were performed by Fanmiao Kong.

The two weaker peaks at 122 cm⁻¹ and 170 cm⁻¹ match the calculated positions of the first overtones of out-of-plane acoustic (1-ZA) and longitudinal acoustic (1-LA) modes of a 6-ZGNR [59, 172]. Since our cove-edged GNRs have the same width and orientation of the graphene lattice as 6-ZGNR, we assign these two modes to (1-ZA) and (1-LA).

The positions of the acoustic modes depend strongly on the ribbon width and shift upwards in wavenumber for thinner backbones [59, 172]. The additional small peaks in the $200 - 400 \text{ cm}^{-1}$ region could thus originate from acoustic modes of the narrower part of the ribbon backbone, or, as observed for D and G modes, from the relaxation of the planar symmetry due to edge functionalisation.

Following a zone-folding model, the RBLM frequency is linked to the ribbon width via $\omega_{RBLM} = \frac{3222 \text{ Åcm}^{-1}}{w_{GNR}}$ independent of the ribbon edge structure [172]. Similarly to previous studies [170, 173] this model holds well and the observed frequency of 255 cm^{-1} (31.6 meV) corresponds to a width of 12.6 Å coinciding exactly with the expected width of our GNRs up to the centre of the bonds to the side chains for an assumed C-C bond length of 1.4 Å. The observed energy of the RBLM mode matches our calculations and the calculated mode is shown in the centre of Fig. 5.3d.

In accordance with theory, our Raman data identified RBLM, D and G modes as the three dominant phonon modes in GNR, while the presence of additional small peaks suggests the presence of some symmetry breaking.

5.3 Optical Properties

5.3.1 Electronic Transitions and Phonon Side Bands

With knowledge of the dominant phonon modes in our GNR sample, we can now track features in the optical spectra at different temperatures to investigate their origin. Since Dodecyl-GNRs provide no features worth further analysis in their optical spectra, we move on to focus entirely on NOMI-GNRs for the following sections.

The calculated projected density of states and band structure as discussed in Sec. 3.3.2 demonstrate that the optical response of NOMI-GNRs is driven by states of the graphene backbone rather than the side chains. Further, the DFT results predict the first and second interband transitions E_{11} and E_{22} to be close in energy, with a separation of $\Delta E = E_{22} - E_{11} = 0.28 \text{ eV}$.

However, a recent theoretical study on identical cove-edged GNRs by Villegas *et al.* found that these first two direct interband transitions are forbidden [174],

shown as dashed purple transitions in Fig. 5.4a. Instead, the first observed transition is predicted between the first valence band and the second conduction band at $E_{21} = 2.09$ eV. The second allowed transition E_{12} , accordingly, is predicted between the second valence band and the first conduction band. Both E_{21} and E_{12} are labelled following the largest contribution, but, according to Villegas *et al.*, originate from combinations of transitions between the first two valence and conduction bands, including the originally forbidden direct transitions.

The electronic interband transitions can be assigned to features present in optical spectra upon measuring at low temperatures, shown in Fig. 5.4b. The absorption spectrum of NOMI-GNRs at 77K still consists of three wide peaks at 2.29 eV, 2.49 eV and 2.63 eV, but with a more pronounced narrow feature at 2.09 eV. The PL spectrum shows this feature even more clearly, it is decreasing in intensity for lower temperatures and by 4.2 K it is dominant. This indicates that the 2.09 eV feature is the zero-phonon line (ZPL) of the interband transition E_{21} , corresponding to the semiconducting energy gap Δ_G . The fact this can be resolved for a GNR for the first time demonstrates its high degree of morphological definition at the molecular level and the consequent cleanliness of the optical response in de-bundled samples. In addition, the PL spectrum at 4.2 K presents a series of narrow features with a periodicity of about 30 meV.

The main features of the optical response at 77 K can be reproduced by a Franck–Condon (FC) like model that includes both the G and RBLM phonons, plus a low-energy excimer peak at 1860 meV (identified from bundled GNRs) and a wide Gaussian contribution for the high-energy absorbance (Fig. 5.4c). The modelling is described in detail in Appendix A.1.

The green and golden graphs in Fig. 5.4c represent the Franck–Condon progressions of RBLM and G phonons. This shows clearly that the main peaks in both the photoluminescence and the absorption spectra are the 0-1 G phonon replica of the zero-phonon line. The absorption spectrum also contains a 0-2 G side band, which is not present in the PL response. The narrow features in the low-temperature PL data can be reproduced well with an RBLM phonon sideband.

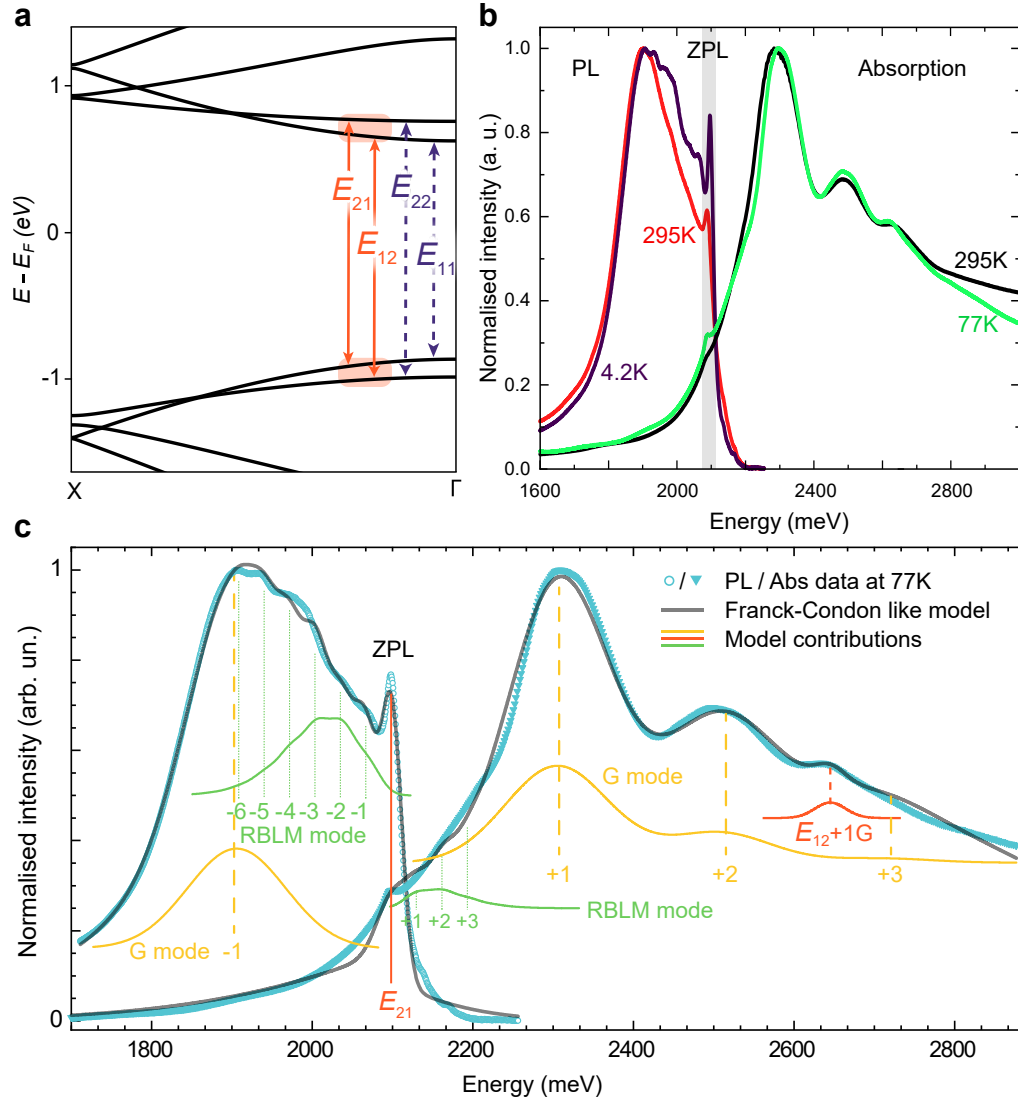


Figure 5.4: Interband transitions and phonon sidebands in optical spectra of NOMI-GNRs **a)** Band structure of NOMI-GNRs as calculated by Fanmiao Kong. Direct transitions between the first (E_{11}) and second (E_{22}) conduction and valence bands are forbidden (purple dashed arrows), such that the first two allowed transitions are E_{21} and E_{12} (orange arrows). **b)** Photoluminescence ($E_{exc} = 2.33$ eV) and absorption spectra of NOMI-GNRs at room and low temperatures. **c)** NOMI-GNR photoluminescence and absorption spectra at 77K shown with a Franck–Condon like model and G (golden) and RBLM (green) phonon contributions. The first and second allowed interband transitions E_{21} and E_{12} are shown in orange in accordance with a).

The modelling suggests the presence of a similar but much weaker RBLM side band in the 2.2 eV shoulder of the absorbance.

The 2.63 eV peak in the absorbance can not be reproduced by RBLM, G or even D mode phonon replica and we thus conclude that it originates from the second

allowed interband transition E_{12} . However, since the linewidth of the peak is too large for a zero-phonon line and the 1-G overtones are so dominant for the first allowed transition, we hypothesize that this peak is the 1-G sideband of the E_{12} interband transition. With this, we find a separation between the first two allowed interband transitions of $\Delta E = E_{12} - E_{21} = 330$ meV, which is in close proximity to the DFT results discussed above (280 meV).

The data presented in Fig. 5.4c show obvious differences in the phonon progressions between PL and absorption. For a purely Franck–Condon coupled electron-phonon interaction, however, PL and absorption data taken at the same temperature should be mirror images of one another. This strongly suggests the presence of a second type of electron-phonon coupling, which we will investigate in the following section.

5.3.2 Temperature-evolution of the PL and Electron-Phonon Coupling

The temperature evolution of the photoluminescence is presented in Fig. 5.5 for 2.33 eV and 3.06 eV laser excitation. Spectra recorded at different temperatures show a gradual evolution of the optical response.

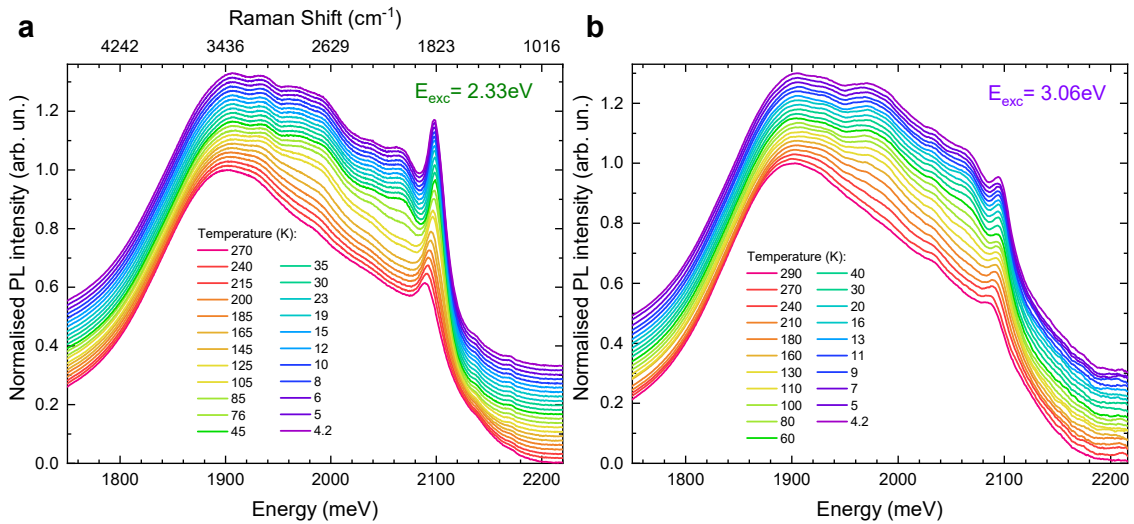


Figure 5.5: Temperature evolution of PL spectra of NOMI-GNR thin films. Spectra were normalised and vertically shifted for clarity. **a)** PL spectra acquired with 2.33 eV and **b)** 3.06 eV laser excitation.

Upon cooling, the narrow peaks originating from RBLM phonons can be resolved at both excitation energies. The zero-phonon line at 2.09 eV is present in all spectra but more pronounced for the lower excitation energy data, as expected. The D and G Raman peaks discussed in the previous section are resolved from the high energy tail of the 2.33 eV PL response at low temperatures. The spectra were analysed by considering the Debye–Waller factor $\alpha = \frac{J}{J+\Phi}$, which determines the probability of zero-phonon transitions [175] by comparing the integrated intensities of the ZPL $J(\omega)$ and of the phonon wing $\Phi(\omega)$. The type of electron-phonon coupling present is then revealed by the T -dependence of α (Fig. 5.6a). In purely Franck–Condon (FC) coupled systems, α is strongly T -dependent [176], while for Herzberg–Teller (HT) coupling α is T -independent [177]. In the presence of both FC and HT couplings, we expect different values of α for absorption and fluorescence bands [177]. Our measurements give $\alpha = 0.010 \pm 0.003$ for absorbance vs. $\alpha = 0.06 \pm 0.01$ for PL at 77 K, showing that both types of coupling are actually present. The observed temperature dependence suggests that FC coupling is dominant. This confirms our interpretation of the modelling results presented in the previous section that the electron-phonon coupling in our GNR is not purely Franck–Condon based.

Herzberg–Teller coupling can be understood as a first-order correction to the Franck–Condon approximation when one of the assumptions made, typically fixed nuclear coordinates or adiabatic electronic transitions, breaks down. This is commonly observed in aromatic molecules due to nonadiabatic state mixing, meaning that more than two states are involved in electronic transitions. This agrees with the results from Villegas *et al.* discussed above, confirming that excitonic transitions in cove-shaped GNR involve combinations of transitions between the first two conduction and valence bands [174].

One of the recurring issues of carbon nanomaterials is the presence of dark excitons, which successfully quench the PL. The ZPL peak intensity shows a maximum around 75 K (Fig. 5.6b), indicating the presence of a lower dark excitonic state separated by a small energy Δ from the lowest bright exciton, in agreement

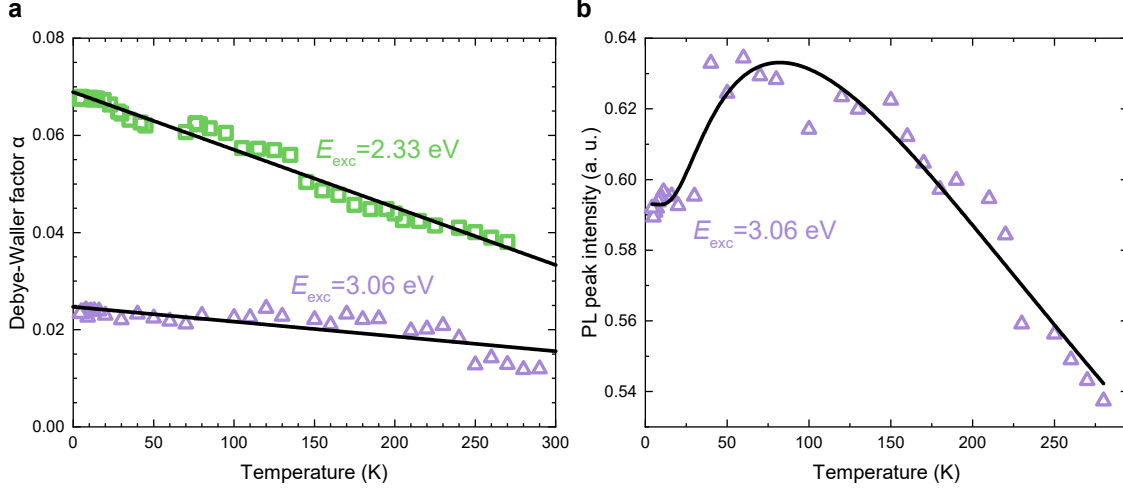


Figure 5.6: T-dependence of the Debye-Waller factor and the ZPL peak intensity of NOMI-GNR thin films. a) Debye-Waller factor α for PL data acquired with 2.33 eV and 3.06 eV laser excitation. **b)** Zero-phonon line peak intensity at different temperatures together with a dark-exciton fit after eq. 5.1.

with theoretical predictions [174, 178, 179]. Assuming exciton thermalisation between bright and dark states, the PL intensity I can be described as [180]

$$I \propto \frac{1}{(T^2 + T_0^2)^{1/4}} \cdot \frac{m + e^{-\Delta/kT}}{1 + e^{-\Delta/kT}}, \quad (5.1)$$

where the power-law dependence is characteristic of one-dimensional excitons, m describes the spectral weight of the dark vs. bright states [181, 182] and T_0 is a T -independent Lorentzian broadening term. The model describes the data exceptionally well, providing $T_0 = 19.7 \pm 1.5$ meV, which is close to the inhomogeneous contribution to the ZPL linewidth (see next section, Tab. 5.3), and $\Delta = 6 \pm 1$ meV, which agrees well with values for CNTs [183], highlighting the presence of similar excitonic structures consisting of bright singlet and dark triplet states. By contrast, the spectral weight of the dark triplet state $m = 0.68 \pm 0.04$, is ≈ 4 times greater than in CNTs [180].

This can be explained when considering the selection rules of K and K' valleys in CNTs and our GNRs. While in CNTs only one out of four valley combinations in the exciton is optically active, the nanoribbons have a direct band gap and the selection rules are circumvented by symmetry breaking (see Sec. 3.3.2), so we would expect them to be four times brighter, exactly as we find. CNT dispersions

reach PLQE yields of 1 – 2% [158–160], we observe 6.4% in our GNRs at room temperature in the absence of any optimisation.

Thus, while dark excitonic states are still present, the GNRs are much less affected by their existence than CNTs, leading to a much higher PLQE. In the following, we will thus label these brightened dark states as *twilight states*. Further support for this picture comes from the low- T decrease in PL energy (Fig. 5.10) due to the significant contribution from the previously-dark states which occurs at the same temperature as the intensity drop.

5.3.3 Time Resolved Photoluminescence

To study the internal processes and decay mechanisms in the nanoribbons further, we performed time-resolved Photoluminescence (TRPL) measurements on both GNR thin films and chloroform solutions. Both samples show similar behaviour and the PL decay at the two main features, ZPL (2.1 eV) and 1G (1.9 eV), is given for a thin film with 3.06 eV and a solution with 2.46 eV excitation in Fig. 5.7a and b.

Bi-exponential fits to the PL decays reveal the presence of a rapid and a slower decay mechanism in all data sets. The rapid decay $\tau_1 = 0.44 \pm 0.1$ ns is similar for all measurements and seems to be independent of excitation and emission energy. By contrast, the slower mechanism possesses longer lifetimes in chloroform solution than in thin film samples and we observe the same trend for the lower excitation energy (2.46 eV) compared to the higher one (3.06 eV), see insets in Fig. 5.7. More importantly, slow decay emission at the zero-phonon line returns about 50% longer lifetimes than 1G emission in both data sets.

To investigate this further, we measured TRPL intensities at 90 different emission energies under otherwise identical conditions. The results are plotted as a vertically normalised false colour map in Fig. 5.7c and as vertically shifted normalised PL spectra in Fig. 5.7d. The temporal evolution of the PL spectra shows the presence of a rapid shift that sees initial emission from the RBLM and G modes (1.7 – 1.9 eV), while at longer times (> 5 ns) emission is mainly from D and ZPL energies.

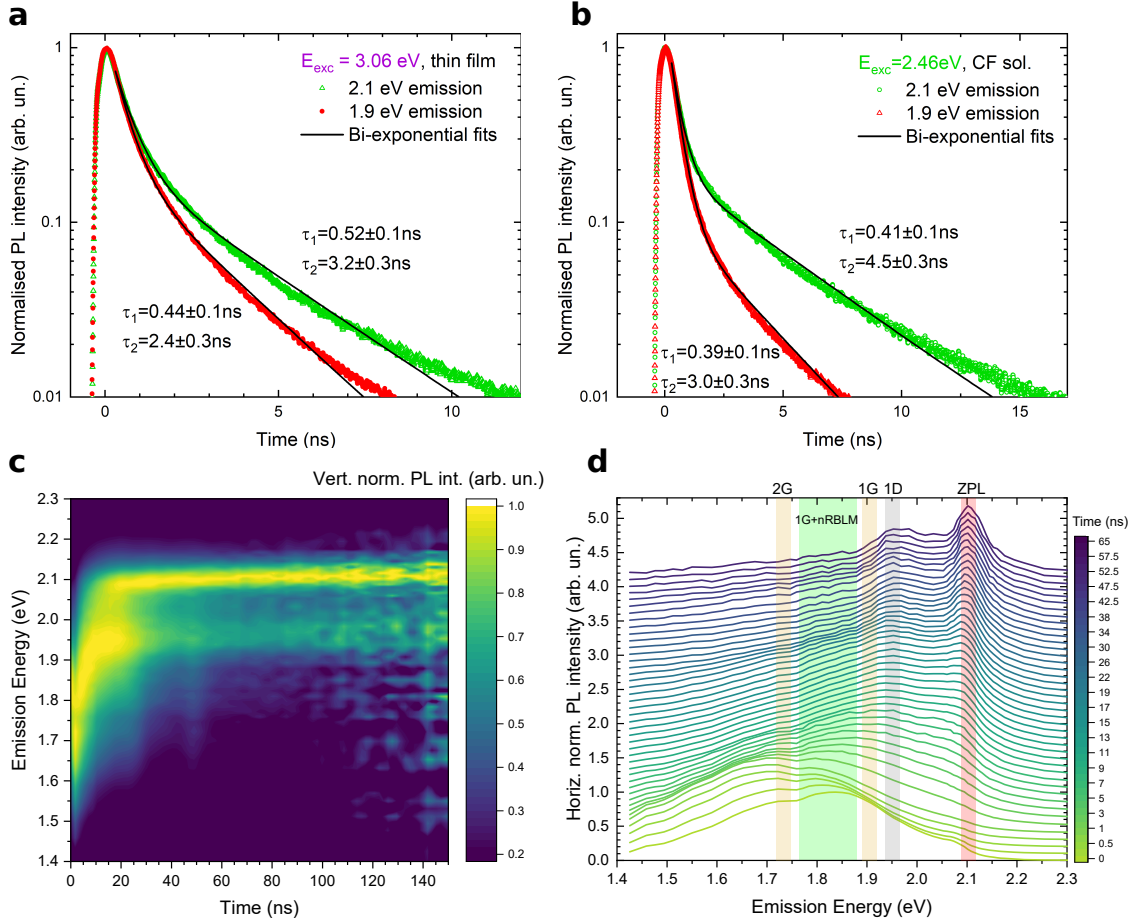


Figure 5.7: Time resolved Photoluminescence of NOMI-GNR. Decay of the PL intensity over time at 2.1 eV and 1.9 eV emission for laser excitation with **a)** 3.06 eV on a GNR-EVA thin film and **b)** 2.46 eV on a GNR chloroform solution. **c)** Vertically normalised PL intensities taken at 90 different emission energies for different time steps on a GNR-EVA thin film with 3.06 eV laser excitation. Emission from the ZPL (2.1 eV) and 1D phonon (1.94 eV) are the dominant mechanisms at $t > 20 \text{ ns}$. **d)** Normalised PL spectra of the same data as **c)**, vertically shifted to indicate the different time steps after excitation.

Interestingly, emission from the D mode has not been detected in any of the continuous wave measurements we previously discussed, indicating that coupling to the D mode is much weaker than our Raman data in Fig. 5.3c suggests. The fact that the ZPL emission can still be identified as the main emission line for times up to 140 ns in Fig. 5.7c highlights the strong emission and molecular purity of our GNR sample.

In combination with our previous results on electron-phonon coupling types and bright and dark excitonic states, the TRPL data suggest that the PL decay

consists of an initial, very bright, cascade from the bright, Franck–Condon coupled states followed by emission from the twilight, Herzberg–Teller coupled states at longer timescales.

The internal processes in our GNR sample can thus be summarised as depicted in Fig. 5.8. The state lifetimes shown in the figure were extracted from the bi-exponential fitting of thin film TRPL data excited with a 2.46 eV laser as this is the sample-excitation combination used most throughout this work.

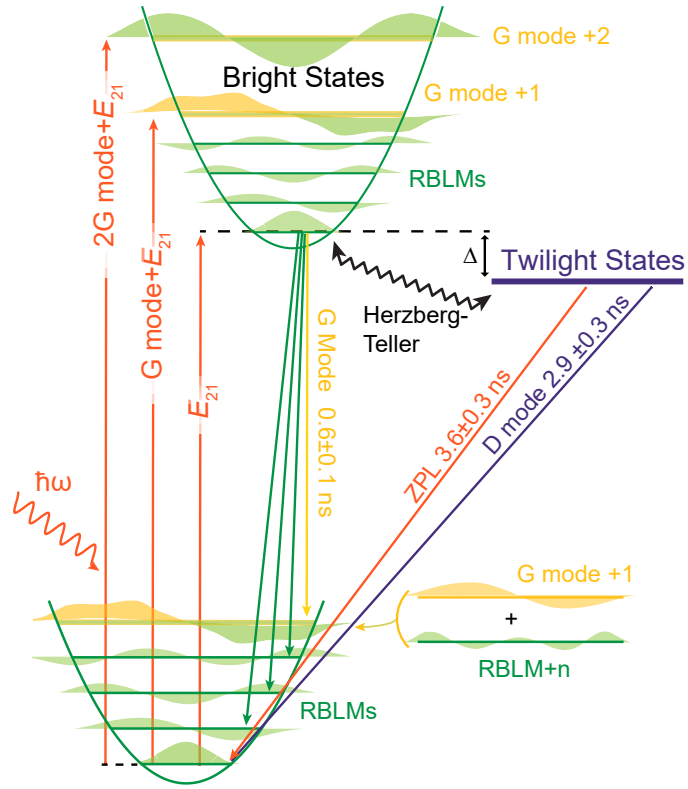


Figure 5.8: Schematic of electron-phonon processes in NOMI-GNR. Franck–Condon coupling between bright excitonic states and phonon modes produces the features in optical spectra of GNR, while Herzberg–Teller coupling to brightened dark (labelled twilight) states is responsible for populating these twilight states and modifies the observed intensity of the phonon modes. The colouring of the interband transitions as well as RBLM and G-modes is kept consistent with Fig. 5.4c.

Franck–Condon coupling between bright excitonic states and RBLM and G phonon modes produces the features in the GNR optical spectra we have now thoroughly discussed. On the other hand, the nonadiabatic mixing of electronic states caused by Herzberg–Teller coupling is responsible for populating dark states. Since these dark states are significantly brightened in our GNRs due to the presence

of a direct band gap and symmetry breaking, we label them *twilight* states instead. The presence of these lower-energy twilight states affects the probability of the phonon-assisted transitions in absorption and emission. This results in the reduction of higher order G mode replica in the PL and causes the observed differences between absorption and PL spectra.

5.3.4 Photoluminescence Excitation Spectroscopy

Photoluminescence excitation spectroscopy (PLE, Fig. 5.9) reveals the internal processes of excited carriers and will allow us to validate our previous conclusions. Fig. 5.9a shows the PLE data as a false colour map with the 1G phonon peak as the strongest emitting peak. Both the 2G phonon and $E_{12} + 1G$ peaks can be resolved but are easier to identify in a normalised line plot (Fig. 5.9b). This figure shows vertical line cuts of Fig. 5.9a at 1900 and 2090 meV, at ZPL-1G and ZPL energies, respectively, in comparison to the absorption spectrum. The onset and peak position of the 1G peak around 2.2 – 2.3 eV excitation are slightly shifted in the PLE data due to the long pass filter used in the experiment. The positions of the two remaining peaks match the absorption data well, confirming the assignment described above for the PL response.

However, the peak intensities of the 2G and $E_{12} + 1G$ peaks vary between the three spectra and we, therefore, plot a colour map of vertically normalised PLE slices in Fig. 5.9c. This figure clearly highlights the variations in peak intensities of the 2G and $E_{12} + 1G$ peaks relative to the 1G peak. Interestingly, the intensity of the $E_{12} + 1G$ peak at $E_{exc} = 2.60$ eV is much stronger in the PLE compared to the absorbance data and further increases in intensity with increasing emission energy towards E_{ZPL} , confirming our assignment to a second interband transition. The strengthening of the peak for higher energy emission further suggests that internal relaxation to the lowest band at low- k values is more likely than a multi-phonon-assisted transition.

The 2G excitation peak is strongest for emission energies around 1800 – 1900 meV (Fig. 5.9c), suggesting that if two G phonons are created upon absorption, the emission processes involving the annihilation of G phonons are enhanced.

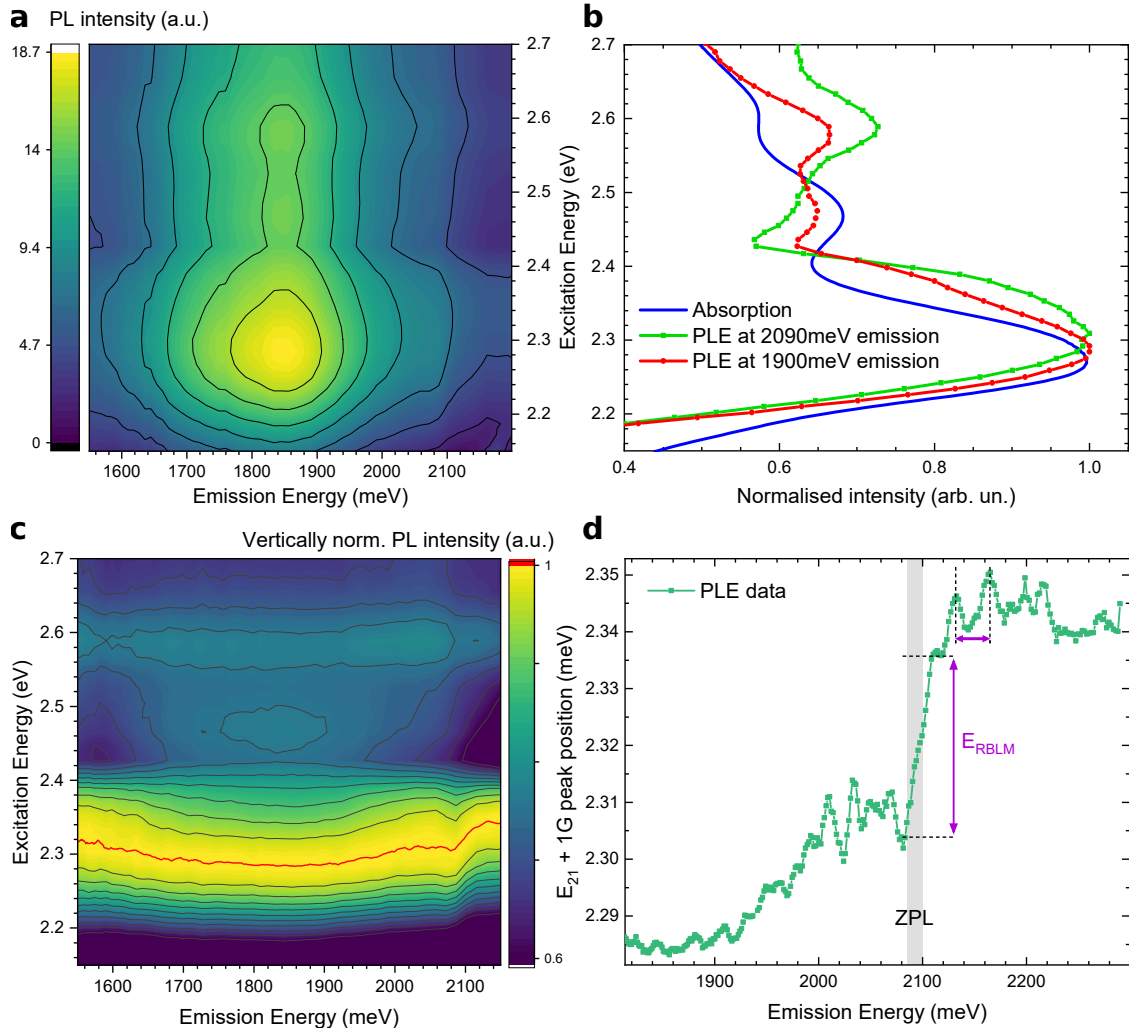


Figure 5.9: Photoluminescence excitation measurements. a) PLE map of GNRs in chloroform solution, excited with a white light source through a monochromator. b) Line plots of the PLE map at 1900 and 2090 meV emission in comparison to the absorption spectrum. c) Colour map of vertically normalised PLE slices with the red line indicating the maximum of the emission. d) Excitation position of the $E_{21} + 1G$ peak for different emission energies.

Furthermore, the red line in Fig. 5.9c indicates the position of the 1G peak at different emission energies. The same data are plotted in Fig. 5.9d at a higher resolution. This reveals a very interesting phenomenon: The ZPL+1G peak shifts by the energy of one RBLM phonon ($E_{RBLM} = 31.6$ meV) when the emission energy is increased across the zero-phonon line. In other words, the excitation energy that yields the highest PL intensity shifts from $E_{exc} = 2.30$ eV (ZPL+1G) at emission energies below 2.08 eV to $E_{exc} = 2.34$ eV (ZPL+1G+1RBLM) for

emission energies above 2.10 eV.

This implies that, at emission energies below the ZPL, the creation of one G phonon is the dominant mechanism in both absorption and consecutive PL emission, whereas the creation of both an RBLM and G phonon upon absorption leads to the strongest ZPL emission. This observation can be rationalised with the following thought: For emission above the ZPL energy, phonons need to be annihilated to provide the excess energy. We know that the dominant phonon modes are RBLM, D and G phonons, but the energies of D and G phonons are above 150 meV and thus irrelevant here. Therefore, a large population of RBLM phonons is required for efficient PL emission at $E > E_{ZPL}$. The simplest way to create more RBLM phonons is to increase the excitation energy by E_{RBLM} which is exactly what we observe.

In addition to this trend, Fig. 5.9d appears to show a modulation of the peak position just above the ZPL emission energy with a periodicity of the RBLM energy. Possibly, a similar feature is present at emission energies just below the ZPL, but cannot be distinguished from noise sufficiently. The periodicity of E_{RBLM} in direction of emission energy means that at the next peak, an additional RBLM phonon is required for the emission process. However, the amplitude of the excitation energy modulation is only 5 – 10 meV, which is insufficient to provide that energy. We speculate that this modulation might be related to a low energy phonon mode that is Raman inactive [63] or a phonon scattering process, but further experiments are required for a more detailed discussion of this feature.

5.3.5 Direct Implications of Phonons on the Zero-phonon Line

As the relevant electron-phonon processes in NOMI-GNRs are now established, in this final section we will study their implications on the position and linewidth of the zero-phonon line at different temperatures. The T -evolution of the GNR band gap can be extracted directly from the ZPL position in the PL spectra (Fig. 5.5) and is provided in Fig. 5.10.

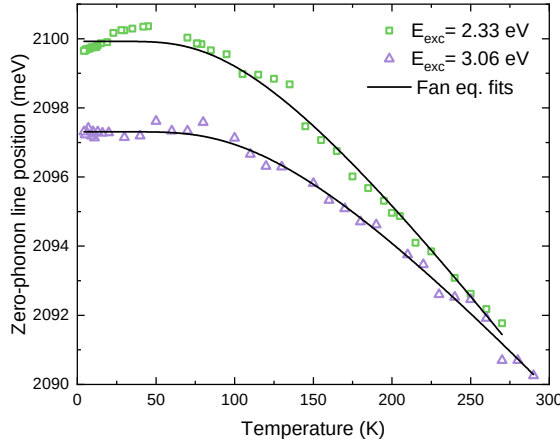


Figure 5.10: T -evolution of the zero-phonon line (ZPL) position. ZPL positions for different T as retrieved via peak fitting from Fig. 5.5 shown with fits of eq. 5.2.

Table 5.2: Fit parameters for the GNR ZPL position. Data were fitted with eq. 5.2 with their uncertainties as provided by the fits.

Parameter	excitation energy	
	2.33 eV	3.06 eV
A (meV)	22 ± 2	22 ± 2
$E_g(0)$ (meV)	2099.9 ± 0.1	2097.3 ± 0.1
E_{ph} (meV)	30 ± 2	35 ± 2

The ZPL peak position shows a 2 meV difference in PL data taken with 2.33 eV and 3.06 eV excitation, which is attributable to photoluminescence from hotter charge carriers when exciting at 3.06 eV. After excitation, excitons recombine before being fully thermalised via electron-phonon coupling, resulting in emission from carriers with a temperature higher than the macroscopic temperature of the sample. The low- T non-monotonic behaviour resembles what was observed in semiconducting CNTs [184], and the slight peak position decrease in the 2.33 eV data at $T < 50$ K is attributable to increased emission from the lower-energetic twilight states rather than the bright exciton.

It is important to notice that, as in other carbon-based nanomaterials [184], the total shift of the band gap is around 10 meV, much larger than the 1 meV effect produced by thermal expansion. By contrast, the behaviour shows good agreement with the Fan equation, as expected for semiconductors [185, 186]:

$$E_g(T) = E_g(0) - \frac{A}{e^{E_{ph}/k_B T} - 1} \quad (5.2)$$

where k_B is the Boltzmann constant, A is the Fan parameter of the material, and the Bose-Einstein statistical factor contains the characteristic phonon energy E_{ph} driving the thermal shift of the band gap energy [187, 188].

We obtain $E_{ph}=30\pm 2$ meV and 35 ± 2 meV for the two excitation wavelengths (see Tab. 5.2), in close proximity to the RBLM energy, suggesting that phonon coupling to the RBLM mode is the key mechanism modulating the semiconducting band gap. Intuitively, this is expected, as the RBLM is the mode altering the GNR width, responsible for the electronic confinement.

The full width at half maximum (FWHM) of the zero-phonon line at different temperatures can be retrieved via peak fitting (Fig. 5.11). The T -dependence of the line-broadening parameter $\Gamma(T)$ for ZPL follows [189]:

$$\Gamma(T) = \Gamma_0 + \Gamma_{ph} = \Gamma_0 + \frac{\gamma}{e^{E_{ph}/k_B T} - 1} \quad (5.3)$$

where Γ_0 is a T -independent inhomogeneous broadening term arising from scattering on defects or terminations [190] and Γ_{ph} a homogeneous broadening term produced by phonon scattering [191, 192] with electron-phonon coupling strength γ .

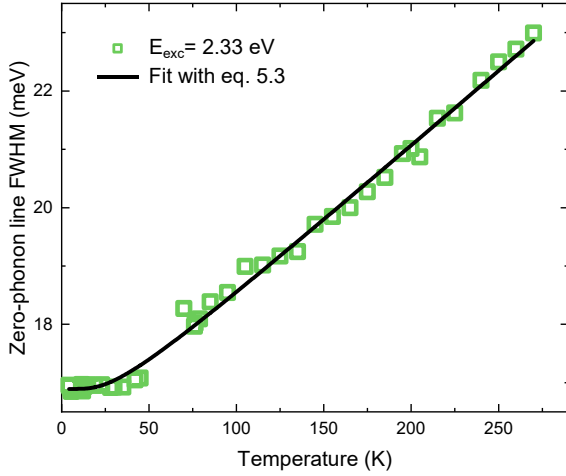


Figure 5.11: Full width at half maximum of the zero-phonon line at different temperatures. Data acquired with 2.33 eV laser excitation and fitted with eq. 5.3.

Table 5.3: Fit parameters for the GNR zero-phonon line linewidth. Results of the fit curve shown to the left after eq. 5.3 with uncertainties as provided by the fit.

Parameter	fit result
Γ_0 (meV)	16.89 ± 0.03
γ (meV)	2.1 ± 0.3
E_{ph} (meV)	7.1 ± 0.7

The fit results are provided in Tab. 5.3. It is worth noting that the phonon energy provided by the fit matches the energy of the transverse bending mode, detected in transport measurements on the same GNRs [63]. This result shows that defects and finite-size effects are the main limiting factor for the lifetime of the electronic states, whereas phonons only start playing an appreciable role above 50 K.

5.4 Summary

In this chapter, the electron-phonon interactions in cove-edged graphene nanoribbons were studied via optical spectra at a higher resolution than previously achieved. In the first section, we demonstrated that *N-n*-octadecylmaleimide side groups provide GNRs with superior solubility compared to dodecyl chains, which was attributed to their bulky size that prevents $\pi - \pi$ -stacking interactions and bundling of GNRs. These NOMI-GNRs possess outstanding solubility in organic solvents and emit with a photoluminescence quantum efficiency of 6.4% in chloroform solution at room temperature.

In the second section, the RBLM, D and G phonon modes are identified as dominant vibrational modes via Raman spectroscopy. Additionally, weaker out-of-plane and longitudinal acoustic modes were detected in line with theory.

The third section presents a detailed analysis of GNR optical spectra. We determine the first and second allowed interband transitions of the NOMI-GNR $E_{21} = 2090$ meV and $E_{12} = 2381$ meV while E_{11} and E_{22} transitions are forbidden. The NOMI-GNRs demonstrate strong Franck–Condon coupling to radial breathing-like and G-mode phonons and a weaker, temperature-independent, Herzberg–Teller coupling. Absorption and PL emission of the sample can be modelled successfully with these two phonons with low Huang-Rhys factors and dominant 0-1 transitions in both cases. We detect a dark excitonic state 6 meV lower in energy than the bright E_{21} exciton. The dark exciton carries about four times as much spectral weight as similar dark excitons in carbon nanotubes which leads to a four-fold brightening of the PLQE. We assign this effect to the selection rules of K and K' valleys of CNTs being circumvented by symmetry breaking in cove-edged GNRs and label the brightened dark states *twilight states*.

For the first time, the zero-phonon line is resolved in GNRs. By analysing the zero-phonon line, we show that the variation of the band gap energy with temperature is driven by internal coupling to the RBLM phonon rather than thermal expansion and that exciton lifetimes are limited by defects and finite-size effects rather than phonon scattering.

PLE data confirm our PL and absorbance results and suggest that internal relaxation processes are typically assisted by 1G or 1G+1RBLM phonons. PLE maps show a stronger contribution from a higher energy E_{12} transition which may contribute to symmetry-breaking states.

Overall, these findings present molecular graphene nanoribbons as a promising versatile new class of materials for a variety of applications including bio-imaging, optoelectronics and quantum technologies.

6

Flexible Transparent Conductive Films made from Carbon Nanotubes and Ethylene-Vinyl Acetate

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6.1 Introduction

In the past two decades, carbon nanotubes (CNTs) have drawn large scientific and industrial interest due to their outstanding optical, electronic and mechanical properties [193]. These make CNTs a promising candidate for a variety of applications,

such as touch panels, light emitting diodes and photovoltaics [194]. In particular, their long-term stability and flexibility have driven efforts to replace costly and brittle indium tin oxide (ITO) in transparent conductive films (TCFs) [20], as due to the crystalline structure of metal oxides their performance is inherently poor in the emerging field of flexible and stretchable optoelectronic devices [195, 196]. During the past decade, various other candidate materials including graphene, silver nanowires, conducting polymers and metal mesh have been investigated for TCF applications [194, 195, 197–200]. However, like ITO these materials struggle with poor cost-performance ratios and meeting the requirements of modern optoelectronic devices [121, 201], whereas CNTs benefit from the ability to produce more stable flexible films with higher mechanical strength than competitor materials [202].

Transparent conductive films are a fundamental part of most optoelectronic devices. Commonly, their performance is described by a figure of merit (FoM) that is given by the ratio of the optical and dc conductivities σ_{dc}/σ_{op} [122]. This ratio can be derived from the relation between transmittance (T) and sheet resistance (R_s), see eq. 4.2 in Sec. 4.1.3.

Recent advances in synthesis and doping have propelled CNTs back to the forefront of research by achieving FoMs of above 80 that approach the 350 achieved with ITO [135, 203]. Even though CNTs can be synthesised from cheap abundant sources of carbon, the consequent processing cannot be scaled up easily. Typically, for high-performance films, CNTs are collected on cellulose filters right after growth and then deposited on substrates via dry transfer [204]. For large-scale applications, solution processing is required instead. A large amount of effort has been put into overcoming the inherent tendency of CNTs to agglomerate into large bundles that make them practically useless. Non-covalent functionalisation via polymer wrapping has emerged as the most promising approach to stabilise individual nanotubes in solution. The attractive van der Waals forces between single nanotubes can be suppressed by the side chains of the polymers wrapping the CNTs. Typically, this is done with conjugated polymers like poly(3-hexylthiophene) (P3HT), where

the binding interaction between polymer and CNTs is expected to be driven by $\pi - \pi$ or π -CH stacking [205].

In a previous study, we showed that the insulating non-conjugated co-polymer ethylene-vinyl acetate (EVA) allows the dispersion of individual CNTs in organic solvents and consequent deposition of CNT-EVA thin films [102]. EVA offers a range of beneficial properties, such as its low cost, high mechanical and chemical resilience and low water vapour transmission rate [107]. EVA is widely used in industry and is the standard encapsulant for silicon solar cell modules.

This chapter will attempt to bridge the gap between high performance and cheap large-scale availability of CNT TCFs. By process optimisation and changing the dispersion technique we dramatically decrease the material cost of CNT-EVA films to around 2 €/m^2 (excluding solvents) and develop a fully scalable preparation routine that allows deposition on arbitrary substrates at 100°C . We investigate the effect of the preparation route on resulting CNT-EVA thin films via Raman spectroscopy, scanning electron microscopy (SEM) and small-angle neutron scattering (SANS). The cost of our films is extremely low compared to e.g. CNT:P3HT based films ($\sim 900 \text{ €/m}^2$) [206]. We further demonstrate successful chemical doping of the CNT-EVA films that, in combination with optimised processing, results in TCF performance with an FoM of $\sigma_{dc}/\sigma_{op} = 15$ which is 100 times higher than previously reported for this material system and comparable to PEDOT:PSS [102]. We explore the impact of EVA monomer ratio and molecular weight on the selectivity of CNT wrapping, TCF performance and film resilience upon bending.

6.2 Initial Considerations

At the start of this project, the best performing CNT-EVA films to date were based on Nanocyl multi-walled carbon nanotubes (MWCNTs) achieving $\sigma_{dc}/\sigma_{op} = 0.13$ and fabricated as described by Mazzotta *et al.* [102]. To render these films useful for transparent conductive film applications, the figure of merit had to be improved dramatically, see Fig. 7.1a for FoM requirements of different applications.

Since using EVA as a wrapping agent with CNTs was a completely new approach, many possible routes towards optimised performance existed. In particular, the combination of a large number of processing parameters and the absence of evaluation methods at intermediate processing steps, which is due to the nanometer size of CNTs, complicate this task.

In this work, we investigate the effects of raw material and solvent choices, as well as details of dispersion, centrifugation, heating and deposition techniques. In early experiments, we established that replacing the solvents originally used by Mazzotta *et al.* [102] (chlorobenzene, toluene and chloroform) did not provide any promising results and thus proceeded with the same solvents as proposed. Changing the EVA polymer did not affect the FoM significantly, but provided candidates to replace the initially used *Elvax 150* polymer, as will be discussed in Sec. 6.5.

By contrast, the carbon nanotube raw material and the details of the preparation process have a strong impact on film performance. We thus adopted the approach to first find the most promising CNT raw material and then optimise the preparation process in detail for these CNTs.

There is a large number of CNTs commercially available at a wide range of purities and prices. In general, MWCNTs cost less than SWCNTs and are expected to perform worse in TCF applications due to the larger amount of carbon and consequently absorption of light per unit length of nanotube. However, MWCNTs do not possess an electronic band gap and thus do not suffer from high intertube resistances due to Schottky barriers. To identify which of these two effects dominates in our system, we compared both multiple MWCNT and SWCNT raw materials, listed in Tab. 4.1.

Further CNT raw materials were investigated but did not provide sufficient yield in the preparation process to produce relevant CNT-EVA thin films. For all of the CNT types listed, multiple batches of CNT-EVA solution were prepared following the description by Mazzotta *et al.* and thin films were deposited. The processing parameters varied slightly between batches but were kept consistent for all CNT types.

The two metrics considered for the resulting films are the TCF figure of merit σ_{dc}/σ_{op} and the film thickness achieved. The film thickness is important to quantify the processing efficiency of different CNTs with EVA. We found large differences in this yield, that can be linked to the dimensions of the CNTs. EVA does not wrap tubes with diameters above 30 nm well and for CNTs longer than 50 μm the separation of wrapped tubes from bundles via centrifugation fails.

The results of CNTs with sufficient yield are given as box plots in Fig. 6.1.

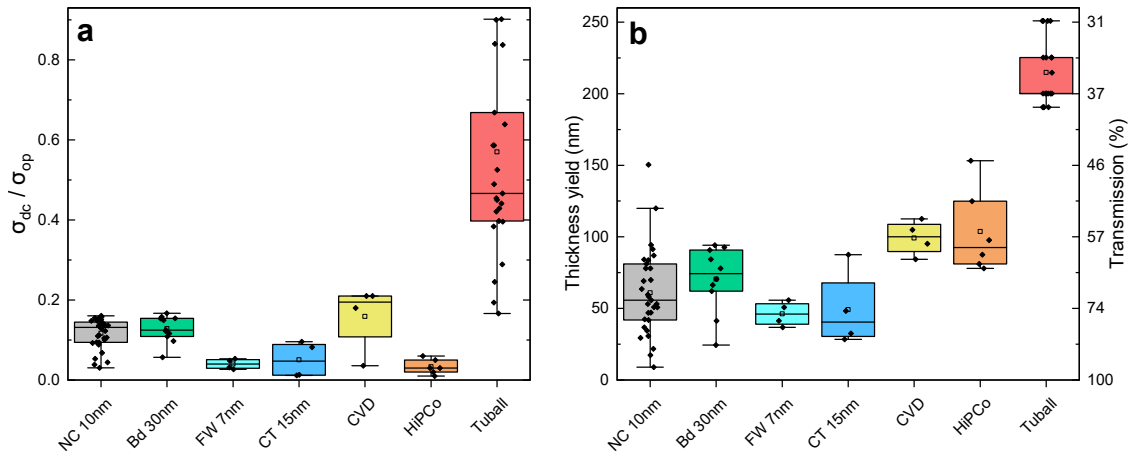


Figure 6.1: Thin film performance for different CNT types. The labels on the x-axis of the box plots indicate the different CNT types. Nanocyl (*NC 10nm*), Boron doped (*Bd 30nm*), Few walled (*FW 7nm*) and Cheaptubes (*CT 15nm*) are all multi-walled CNTs, whereas CVD, HiPCo and Tuball are single-walled carbon nanotubes. Detailed CNT properties are given in Tab. 4.1. **a)** TCF figure of merit for the different CNTs. **b)** Thin film thickness yield with standardised processing for the different CNT types. The film thickness was calculated via eq. 4.1 from the transmittance.

In the box plots, the coloured boxes indicate the 25th to 75th percentile, the horizontal line within the box is the median, the square in the centre of the box is the mean and the whiskers range an additional 1.5 interquartile ranges from the 25th and 75th percentile, respectively. The thickness yield given in Fig. 6.1b was derived from the transmittance at 550 nm via eq. 4.1. This was confirmed for a number of films with Dektak measurements of the film thickness.

The different number of data points for different CNTs in Fig. 6.1 are based on additional batches prepared for the more promising CNT candidates. The results clearly show that Tuball SWCNTs perform best in both FoM and thickness yield. It is worth noting that the large spread of σ_{dc}/σ_{op} in Tuball films is a

consequence of the high yield, resulting in higher CNT concentrations during the purification steps of the process, which impairs film performance. At reduced CNT concentrations, the performance of Tuball SWCNTs improved significantly and we consequently chose these large-diameter SWCNTs for the following optimisation of the preparation process.

6.3 Process Optimisation

Charge transport within CNT networks is limited by large inter-tube junction resistances that dominate over the resistance along the tube axis [81, 82], see Sec. 4.1.2. To achieve high transmittance at low sheet resistances it is, therefore, preferable to increase tube length while avoiding bundling of tubes [207, 208]. Standard dispersion protocols for carbon nanotubes typically involve ultrasonication, which is limited to small volumes and has been shown to shorten CNTs [160]. In contrast, shear force mixing is a process that can readily be scaled up to industrial volumes [160]. We thus adapted our preparation routine to employ shear force mixing and increase the batch volume from 10 to 100 mL CNT-EVA solution, corresponding to 0.3 m^2 of film at 85% T .

To investigate the effect of our processing on the carbon nanotubes we perform Raman spectroscopy. Two of the CNT typical modes are the disorder (D) and graphitic (G) modes at 1340 cm^{-1} and 1590 cm^{-1} , respectively. The disorder mode represents a second-order scattering process that is enhanced by defects in the nanotube structure. The graphitic band is a tangential C-C stretching vibration and is a first-order scattering peak unaffected by defects [209]. Therefore, the G/D peak intensity ratios in Fig. 6.2 can be used as an indicator of structural CNT quality.

We find that the G/D ratio decreases from a value of 131 ± 8 for the Tuball SWCNT raw material down to 123 ± 6 for 48h shear-force mixed and 81 ± 5 for 10min tip sonicated samples. This indicates that shear force mixing produces CNT-EVA dispersions with lower defect densities than tip sonication, which is in agreement with literature [160]. Further, the G-band position is blue-shifted to 1595 cm^{-1} in EVA-wrapped CNTs compared to the CNT raw material (1593 cm^{-1}).

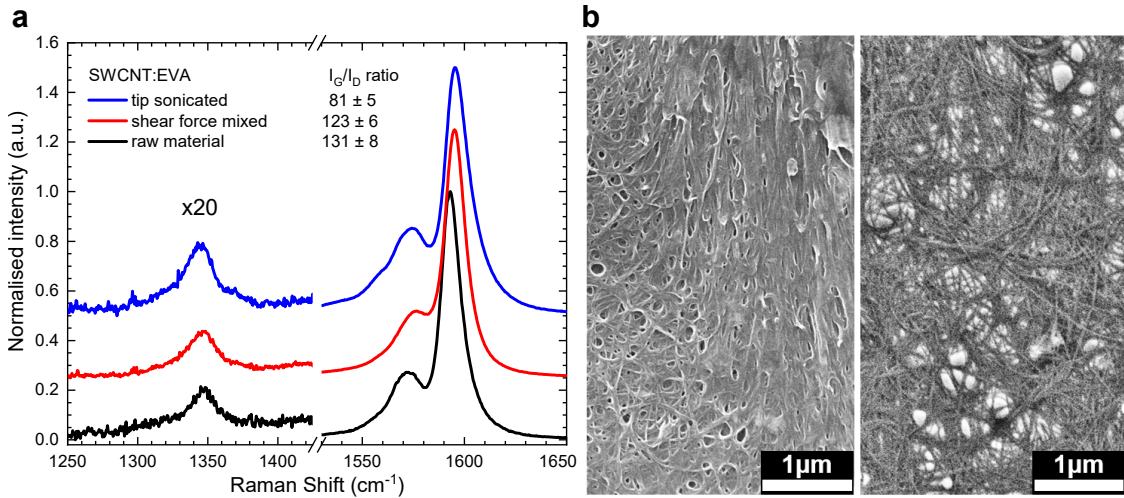


Figure 6.2: Process optimisation of SWCNT-EVA films a) Raman spectra displaying the disorder (1340 cm^{-1}) and graphitic (1590 cm^{-1}) modes of Tuball SWCNTs before and after processing with EVA polymer. b) Scanning electron microscope images of SWCNT-EVA films prepared before (left) and after (right) process optimisation.

We speculate that the non-covalent attachment of EVA to CNTs causes an increase in the elastic constant of the harmonic oscillator of the polymer-wrapped CNTs [125, 210]. A similar shift can be observed in the second peak of the G band, the G^- mode, shifting from 1572 cm^{-1} to 1574 cm^{-1} upon polymer wrapping. The position of this mode correlates with CNT diameter, suggesting the dominant SWCNT species are about $1.7 \pm 0.2 \text{ nm}$ in diameter [211]. A detailed analysis of the SWCNT species present via the radial breathing mode will follow in the next section, see Fig. 6.5. Overall, our Raman data shows that both preparation routes produce SWCNT-EVA films with high structural CNT quality.

The centrifugation step following dispersion, see Sec. 4.1.2, is designed to separate solubilised tubes from bundles, but has been shown to precipitate other impurities, like metal catalysts, contained in the CNT raw material as well. We found that in a CNT raw material purity range of 80 – 95 wt% the purity had no effect on the quality of our films. This self-purifying nature of our processing demonstrates robustness against impurities and the low purity required significantly lowers the cost of CNT raw material. Combined with the negligible cost of EVA, the material cost of our films is thus reduced to 2 €/m^2 . The cost of solvents is excluded as it strongly

depends on the chosen concentration and any solvent-recycling scheme used. For the current protocol without any recycling, the cost of solvents is about 20 €/m².

Due to the insulating nature of EVA, removing as much of it as possible while preserving CNT solubility is crucial for TCF performance. Hence, we adapted the excess polymer removal step developed by Schuettfort *et al.*, and Mazzotta *et al.*, [99, 102] as described in Sec. 4.1.2 and repeated it once more. The effect of successful polymer removal can be observed in the scanning electron microscopy images in Fig. 6.2b. The optimised processing yields films with a lower EVA content and smaller CNT bundles (right) than the original process (left).

While SEM images allow the visualisation of film morphology, they represent only a small fraction of the film with limited statistical information. Therefore, we performed small-angle neutron scattering (SANS), which provides insights into sample structure averaged over large volumes of the bulk sample. SANS is able to probe the internal structure of CNT-polymer composites due to the natural scattering length density contrast between the hydrogen-rich polymer and the hydrogen-deficient CNTs [212]. The SANS in this work covers length scales between approximately 10 and 100 nm in the substrate plane. Accessing this information requires the fitting of scattering data, a detailed description of which is given in Appendix A.2. SANS experiments and data analysis were performed by Andreas Lauritzen.

Porod plot analysis of ($\log(I)$ vs $\log(Q)$), where I is the integrated neutron scattering intensity and Q is reciprocal length, shows linear regions that can be described well by either one or two power law fits and point to hierarchical fractal systems. Linear scattering regimes with Porod exponents between 2 and 3 correspond to mass fractals and are typical of the branched multi-level clusters formed by CNT-polymer composites. We find this to be in good agreement with the branched networks visible in the SEM images in Fig. 6.2b (right). Higher Porod exponents between 3 and 4 represent surface fractals with exponents close to 3 corresponding to a rough surface and exponents close to 4 to a smooth surface. A more densely packed system will generally result in a higher exponent [213, 214].

SANS data of thin film samples prepared via either tip sonication or shear force mixing and subjected to a given number of excess polymer removal steps are shown in a Porod plot ($\log(I)$ vs $\log(Q)$) in Fig. 6.3a.

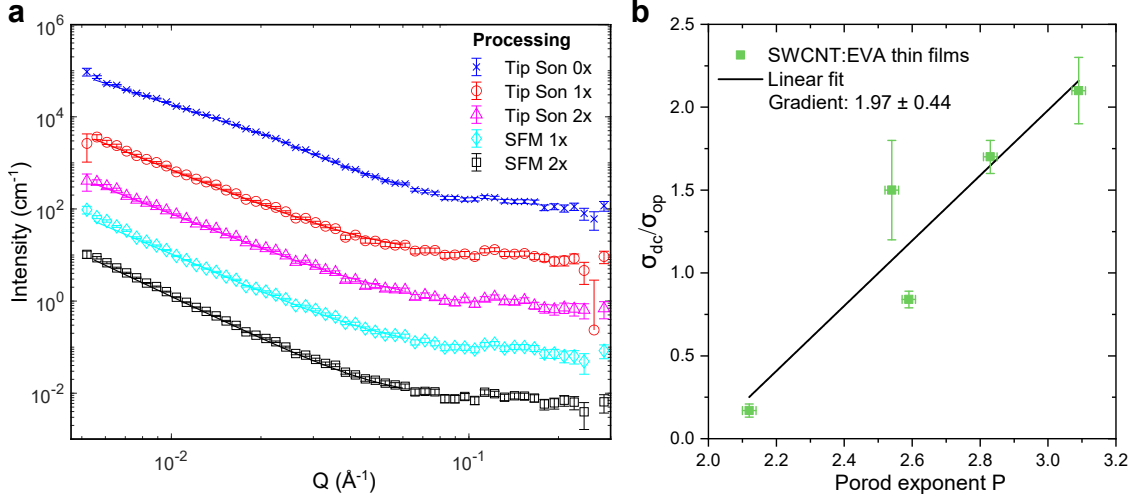


Figure 6.3: Small-Angle Neutron Scattering data analysis. **a)** Porod plot ($\log(Q)$ vs $\log(I)$) of SWCNT-EVA SANS data. The different processing history of the samples is indicated in the legend and data are shown together with power law fits. Data sets have been shifted vertically for the sake of clarity. **b)** Linear correlation between TCF figure of merit σ_{dc}/σ_{op} and the Porod exponent P shown with a linear fit.

We find that the 0x tip sonicated sample appears as having two linear regimes with Porod exponents P and P_{highQ} , representing larger and smaller length scales, respectively. Having two distinct linear regimes could indicate that the composite structure is non-identical at different length scales as observed in prior studies of CNT-polymer composites [214]. The two regimes could also be due to scattering contributions from the excess matter that is removed in the purification process since the samples where the polymer has been removed can be represented by a single Porod exponent P . The derived Porod exponents and corresponding TCF film performance in σ_{dc}/σ_{op} together with uncertainties in the last digit are presented in Table 6.1.

The tip sonicated sample without polymer removal has a low Q exponent of $P = 2.12$ (2) and a high Q exponent of $P_{highQ} = 2.84$ (5) possibly suggesting that the smallest components of the branching network are relatively denser. We hypothesize the higher scattering and background intensities can be attributed to

Table 6.1: Porod exponents of power law fits for CNT-EVA films. Samples were prepared via tip sonication (tip son.) and shear force mixing (SFM) with different numbers of polymer removal steps. Parameter uncertainties of the last digit are given in brackets.

Dispersion technique	Polymer removal steps	P	P_{highQ}	FoM σ_{dc}/σ_{op}
tip son.	0	2.12 (2)	2.84 (5)	0.17 (2)
tip son.	1	2.59 (2)		0.84 (5)
tip son.	2	2.54 (2)		1.5 (3)
SFM	1	2.76 (2)		1.7 (1)
SFM	2	3.06 (2)		2.1 (2)

the presence of larger quantities of hydrogen-containing polymer in the sample. This results in a larger background at high Q values due to the increased incoherent scattering of neutrons.

When the excess polymer is removed from the samples, only a single structural level is seen. The Porod exponent for both 1x and 2x polymer removal tip sonicated samples is close to 2.5, the expected value of a randomly branched object [215]. We note that this exponent differs from both regimes of the tip-sonicated sample without polymer removal, indicating that this step not only removes matter but also changes the average structure of the scattering film. The small difference between 1x and 2x polymer-removed samples further suggests that subsequent polymer removal steps affect the structure of tip-sonicated samples to a relatively small degree. The structural change induced by polymer removal is accompanied by a better TCF performance, improving the FoM from $\sigma_{dc}/\sigma_{op} = 0.17 \pm 0.02$ by a factor of 5 after one and by a factor of 9 after two polymer removal steps in the tip sonicated samples.

For the SFM samples, we found Porod exponents of 2.76 (2) and 3.06 (2) for 1x and 2x polymer removal. The higher P values of the SFM samples show that the packing is more structurally dense and the films have a more tightly packed mesh than the tip sonicated samples.

Unlike the tip sonicated films, removing EVA for the 2nd time seems to change the structure of the SFM samples. The Porod exponent increases from 2.76 (2) to 3.06 (2), indicating the packing has become so dense that the scattering arises

from a rough surface fractal interface, although we note that the fitted values are close to the boundary region between mass and surface fractals [216].

Overall, a tighter packing, expressed in a higher P value, appears to be connected to better TCF performance. This trend can be approximated by a linear relation between σ_{dc}/σ_{op} and P , see Fig. 6.3b. We suspect that denser packing has a positive effect on the number of CNT-CNT junctions and could lower their resistance, thereby increasing the electrical conductivity of the CNT-EVA network.

In summary, we have replaced the dispersion technique and optimised the centrifugation and excess polymer removal steps. The improved processing reported here led to a champion FoM of $\sigma_{dc}/\sigma_{op} = 3.6 \pm 0.1$ for CNT-EVA thin films, a factor of 28 higher than previously reported [102].

6.4 Percolation Effects

Carbon nanotube thin films can be interpreted as networks of randomly oriented rods. Upon lowering the network density, areas of the network become isolated and stop contributing to charge transport. This effect is called percolation and is a common issue among nanostructured transparent conductors. If the film thickness falls below a certain value called t_{min} , transport properties start to decay from the bulk behaviour and the dc conductivity decreases with decreasing thickness.

We compare the transmission and sheet resistance of the previously established Nanocyl MWCNT-EVA films with the optimised Tuball SWCNT-EVA films described in the last section in Fig. 6.4a.

The black lines are fits to the data after eq. 4.2 following the bulk conduction model. Apart from the obvious difference in TCF performance, the fits highlight the deviation from bulk behaviour at high transmission for MWCNT-EVA films. This trend becomes more obvious in Fig. 6.4b, where the film thickness calculated via eq. 4.1 is plotted against the sheet resistance. While for the optimised Tuball-EVA films all samples follow the same linear trend indicating bulk-like behaviour, there are two linear regimes present for MWCNT-EVA data. At film thicknesses below $t_{min} = 20 \pm 4$ nm the sheet resistance starts to increase much faster with

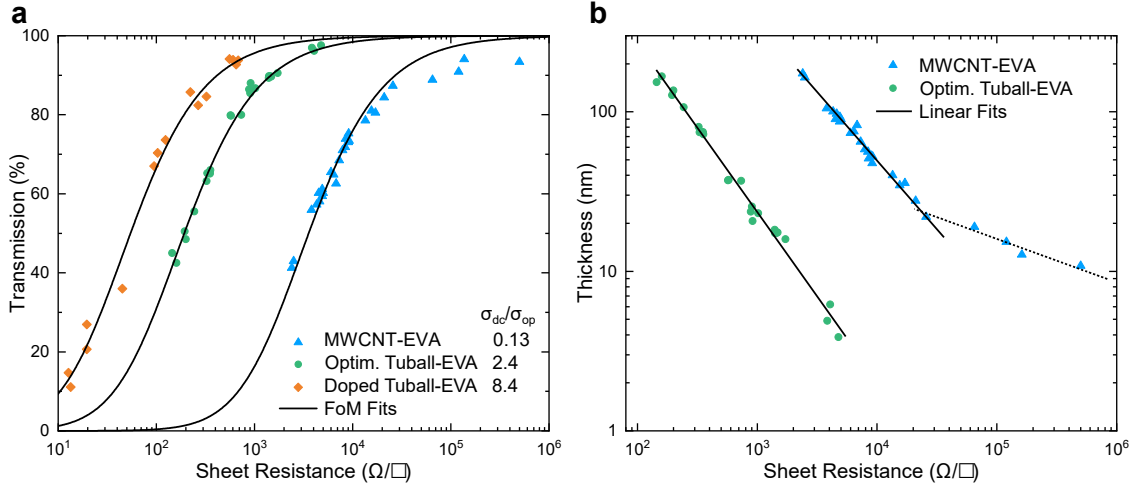


Figure 6.4: Percolation analysis of CNT-EVA thin films **a)** Transmission and sheet resistance for previously established Nanocyl MWCNT-EVA and optimised Tuball SWCNT-EVA films shown together with bulk model FoM fits. **b)** Log-log plot of the same data with the transmission converted to film thickness via eq. 4.1. While all optimised films follow the bulk model, MWCNT films are affected by percolation at thicknesses below 20 nm. The percolation regime is indicated by the dotted line.

decreasing thickness due to percolation effects. In a recent study, t_{min} has been linked to the smallest dimension D of the nanostructure via $t_{min} = 2.33D$ [122], which predicts $t_{min} = 2.33 \cdot 9.5 \text{ nm} = 22 \text{ nm}$ for Nanocyl MWCNTs and is in good agreement with our data.

In contrast, the smaller diameter Tuball tubes ($d = 1.6 \text{ nm}$) are expected to have a much smaller $t_{min} = 3.7 \text{ nm}$ and our films show no sign of percolation effects down to thicknesses of 5 nm, making them eligible for high-transmittance applications with up to $T = 95\%$. Further, this confirms our observation from SEM images (Fig. 6.2b) that the optimised CNT-EVA films consist of individually wrapped tubes rather than bundles since bundles would fall into the percolation regime at these low film thicknesses.

6.5 Versatility and Durability

Optoelectronic devices have application-specific requirements on TCF performance, but just as well on flexibility, durability and adaptability that many transparent electrode materials struggle to meet [196, 201]. A key aspect in this regard, and

in TCF preparation in general, is the deposition method. For solution-processed materials, which are preferred by industry, several deposition techniques have been demonstrated, such as aerosol jet [217], hydrographic printing [218] and spray coating [219]. We have chosen spray coating as it is an inexpensive, high-throughput and scalable technique that is compatible with low-temperature deposition on arbitrary substrates [220].

The most common issue with spray coating is the coffee ring effect and there is a range of parameters to consider in order to prevent it [221]. We find that with our custom-made open science hardware spray coater [116] and the parameters described in Sec. 4.1.2, we achieve highly uniform deposition with standard deviations of the sheet resistance typically below 5% across films. When depositing on different substrates with our system, we find that the spray conditions for ideal film performance can be optimised by changing a single parameter, the nozzle height. This allows deposition of films with performances of up to $\sigma_{dc}/\sigma_{op} = 3.6 \pm 0.1$ on glass and PET substrates, but CNT-EVA films can be sprayed on virtually any substrate like plastics, tape, or paper. Resulting sheet resistances depend on individual surface properties, but even on rough surfaces like weighing paper R_s increased only by a factor of two. Our films perform well above the $\sigma_{dc}/\sigma_{op} = 0.6 \pm 0.1$ that has been demonstrated for spray-coated graphene-PEDOT:PSS films on 3D substrates recently [221]. However, our current setup does not allow deposition on 3D surfaces yet.

As a co-polymer, EVA consists of chains of monomers ethylene and vinyl acetate (VA) as displayed in Fig. 4.4. The properties of EVA can be tuned by changing the monomer weight ratio and the polymer chain length. A higher wt% of VA will decrease the crystallinity and result in a lower tensile strength, stiffness modulus and chemical resistance, but at the same time enhance optical clarity and stress crack resistance [108, 110]. Due to the polar nature of the acetoxy side chain, a higher VA content will increase the polarity of the copolymer and as a consequence enhance compatibility with polar resins, specific adhesion and printability [108]. In industrial plastics such as EVA, the polymer chain length is described by the melt

index (MI) which is inversely related to the molecular weight. Longer chains, or lower MI values, result in higher viscosity, higher chemical resistance and improved mechanical properties, but detrimental effects on solubility and processability [108]. These tuning factors give EVA a high versatility that is reflected in its typical applications, ranging from shoe soles, cable insulation or drug delivery to electrodes for flexible supercapacitors in CNT-EVA composites [108, 110, 112].

To investigate the range of VA content and polymer chain length that can be used for making CNT-EVA thin films, we have prepared samples with six different types of EVA with 25 – 40%wt VA content and melt indices from 3-400, for details see Tab. 4.2. At lower VA percentages, EVA becomes insoluble in chlorobenzene and incompatible with our processing. The six EVA polymers used did not have any significant effect on the TCF performance of the resulting thin films, as is to be expected from the insulating nature of EVA.

In addition, we compare the different polymers in their ability to wrap and solubilise carbon nanotubes of different diameters via Raman spectroscopy measurements of the radial breathing modes (RBMs). The position of the RBMs is inversely proportional to the CNT diameter and RBM peak intensity is strongly enhanced when the excitation energy is close to interband transitions of the corresponding CNTs. Following the description by Maultzsch *et al.*, we assign individual chiralities to the most prominent peaks, see Fig. 6.5 [222].

Since there are 80 possible chiralities in the observed RBM frequency range and we are limited to two laser energies, the denoted chiralities represent the CNTs we can observe best rather than the absolute ratio of tubes present [223]. Therefore, we focus on the relative comparison between the spectra of raw and EVA-wrapped SWCNTs.

The full 1.1 – 2.0 nm range of CNT diameters contained in the Tuball SWCNT raw material can be observed with all five EVA batches. For 633nm excitation, mainly metallic tubes are in resonance, while for 532nm excitation most of the displayed chiralities are semiconducting. We find no wrapping preference for the electronic nature of the CNTs. However, the reduced peak intensity at 160 cm^{-1} at both excitation energies indicates that EVA wraps SWCNTs in the diameter

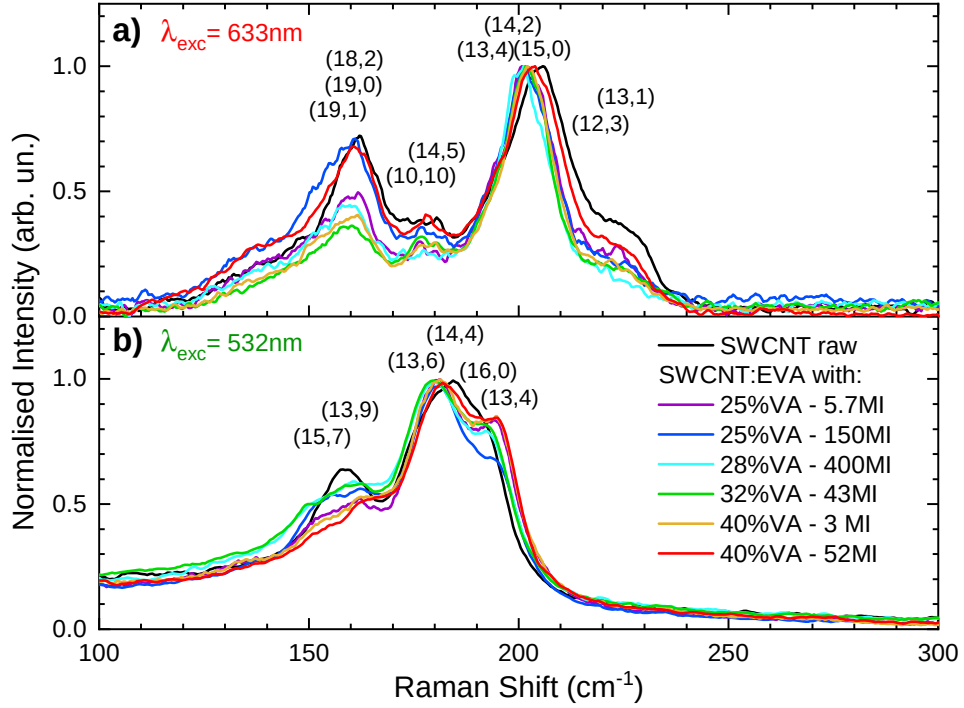


Figure 6.5: SWCNT wrapping selectivity of different EVA batches. The radial breathing modes identified via Raman spectroscopy reveal which CNT chiralities (provided in the figure) are still present post-processing. **a)** Raman spectra acquired with 633 nm laser excitation. **b)** Raman spectra taken with 532 nm excitation.

range around 1.5 nm less effectively than near the overall peak at 180 cm^{-1} (1.3 nm) and 205 cm^{-1} (1.1 nm), respectively. Similarly, Elvax 4320 (25%VA - 150MI), the batch with the lowest VA content and very short chain lengths seems to wrap SWCNTs with diameters close to 1.25 nm about 10-15% less effectively than the other batches. Overall, this demonstrates the versatility of EVA wrapping and that EVA polymers with 25 – 40%wt VA content and melt indices between 3 – 400 are suitable for making CNT-EVA thin films.

In order to test the durability of our films in flexible applications, we performed 2000 bending or folding cycles on CNT-EVA films made with three different EVA batches and deposited on PET substrates, see Fig. 6.6.

The bending radius was 5 mm for bending cycles and 2 mm for folding cycles. Sheet resistance measurements were taken in the relaxed state locally along the line of the highest bending strain after a given number of cycles. As outlined above, EVA

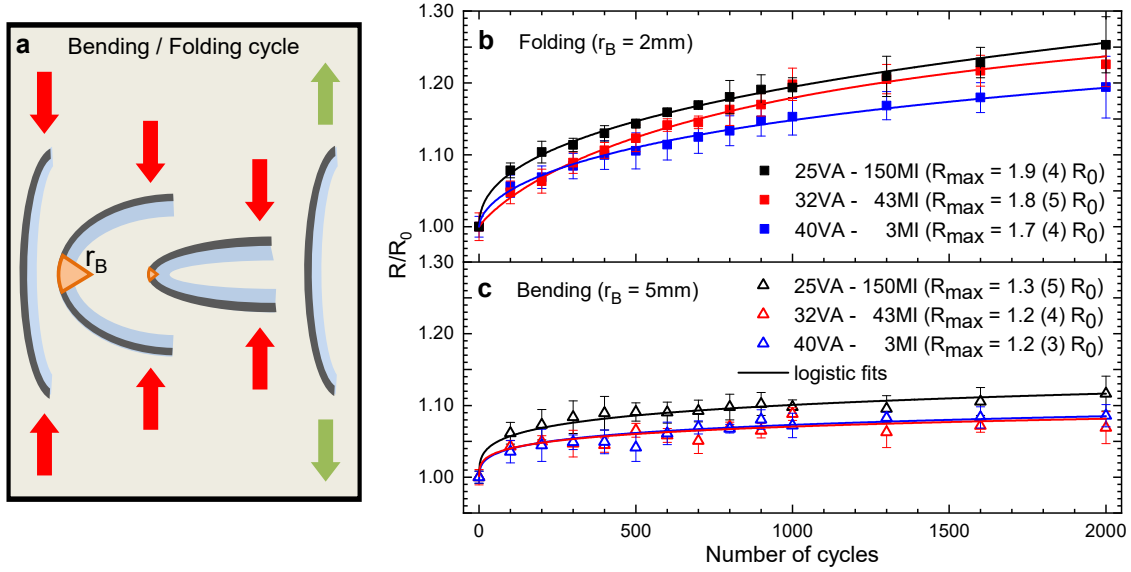


Figure 6.6: Bending and folding flexible SWCNT-EVA films. a) Diagram of one bending or folding cycle, the difference being the smallest achieved bending radius r_B of the film. Films are depicted in dark grey on a substrate (light blue). b)-c) Change of sheet resistance compared to initial sheet resistance R_0 for up to 2000 folding (bending) cycles of SWCNT-EVA films with different EVA polymers on PET. The data follows a logistic function with upper bound R_{max} .

polymers with higher VA content and lower MI values are expected to perform better in flexible applications. Therefore, we compare three EVA batches that represent the full range of these two parameters. We find that all samples perform well under folding. After an initial increase, the resistance changes less with more cycles, following a logistic function. We find that films with higher VA content and lower melt index perform better and use global fitting to estimate the upper bound of the sheet resistance R_{max} , which is below 2 times the initial value for all three samples.

EVA has proven to be a versatile dispersant of CNTs, whose properties can be tuned according to the desired application. Resulting CNT-EVA films can be deposited on a wide range of substrates via scalable spray-coating and perform well in flexible applications.

6.6 Chemical Doping

Doping is a standard technique to increase the charge carrier density in semiconductors. In contrast to inorganic semiconductors, where this is typically realised by

lattice doping, dopant adsorption has proven more effective in carbon nanotubes. This process describes charge transfer between dopant molecules and CNTs, the resulting Coulomb attraction between positive and negative charge stabilises the dopant on the CNT sidewall [130, 131]. In CNT networks doping has the beneficial effect of removing Schottky barriers between semiconducting and metallic tubes by making more of the semiconducting tubes metallic and thereby reducing effective inter-tube junction resistances. Due to their low electron affinity, CNTs are typically p-doped. Various dopants have been identified, the most promising being acids and halogenated metals [132, 133]. Nitric acid (HNO_3) has been widely used and shown to improve the electrical conductivity of CNT films by a factor of 10 [224], chloroauric acid (HAuCl_4) by factors of up to 13.5 [135]. Zhou *et al.* have used copper halides to achieve improvements up to a factor of 10 as well and argue that the dopants have the additional benefit of adding interconnections between CNTs in the film, further lowering the sheet resistance [134].

In our experiments, we chose a range of different halogenated metals and two acids and applied them to Tuball SWCNT-EVA films via 3x horizontal spray deposition. CNT-EVA films from the same batch were used and the dopants were all dissolved in ethanol at a concentration of 5 mM. Nitric acid proved incompatible with CNT-EVA films, as it decomposed EVA and detached thin films from the substrate. The remaining halogenated metals were employed successfully as dopants of SWCNT-EVA films, results are given as box plots in Fig. 6.7 with identical settings to the box plots in Sec. 6.2.

All halogenated metals improve the conductivity of our SWCNT-EVA films, see Fig. 6.7a. However, the two gold chloride-based dopants outperform the other dopants clearly, with HAuCl_4 providing the most promising results, reducing the sheet resistance of our films by factors of 7.6 ± 1 .

To investigate the long-term stability of doped films, which is an essential criterion for applications, we stored the doped films in ambient conditions for 450 days and repeated the measurements, see Fig. 6.7b. While the conductivity of FeCl_3 and CuCl_2 doped films improved slightly, for AlCl_3 , NiCl_2 and HAuBr_4 doped films

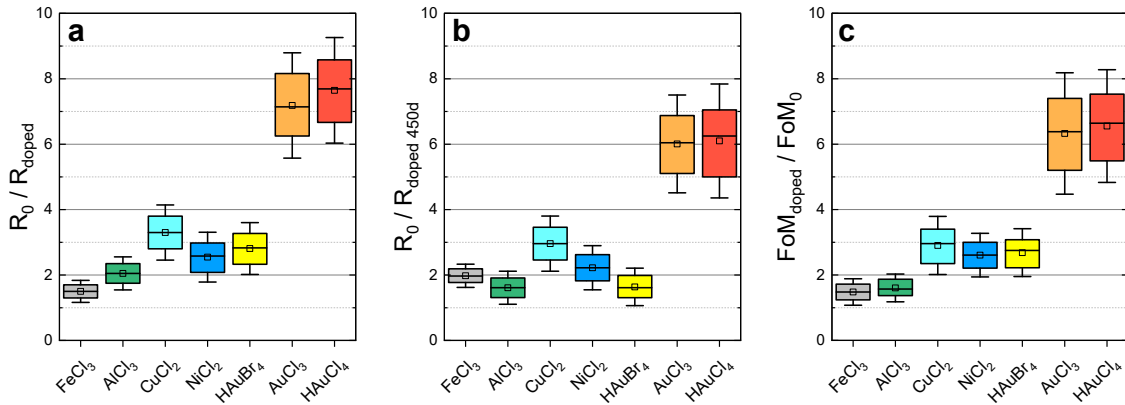


Figure 6.7: Dopants and their effect on SWCNT-EVA performance. Box plots show the relative change of the doped compared to the undoped film. For all dopants, Tuball SWCNT-EVA films from the same batch were used. Dopants were all applied from a 5 mM solution via spray application. **a)** Factorial improvement of the sheet resistance upon dopant exposure. **b)** Ratio of the sheet resistances of pristine films and doped films after 450 days. **c)** Change in TCF figure of merit in the same samples. The differences between a) and c) are caused by reduced transmittance of the doped films.

the conductivity showed a small decrease. Most adversely affected by ageing were the two gold chloride-based dopants, with a 20% decrease in conductivity.

For a perfectly transparent dopant, the change in electrical conductivity would be equal to the change in the TCF figure of merit. However, we found that all dopants either absorb light in the visible range or react to compounds that do, which means the increase in electrical conductivity is accompanied by a decrease in transmittance. To reflect both of these changes, we compare the TCF FoM σ_{dc}/σ_{op} in Fig. 6.7c. While the FoM improvements are only about 10% less than the conductivity improvements in Fig. 6.7a, this still suggests that the amount of dopant applied needs to be chosen carefully to limit the reduction of transmittance.

The reason why gold chloride-based dopants outperform the other halogenated metals can be found in the underlying chemical reactions of the doping process [131]. These are based on the transfer of electrons from the CNTs to the dopant molecules. To prevent the strongly electronegative halogen from drawing electrons from the metal instead of the CNTs upon disproportionation of the dopant, large electron affinities are required for the metal as well. The electron affinities of the elements

present in our dopants are given in Tab. 6.2. We hypothesize that the low performance of HAuBr_4 compared to HAuCl_4 might be linked to the lower electron affinity of Bromine compared to Chlorine. For the chlorinated metals, the metal electron affinity is plotted against the conductivity improvement in Fig. 6.8. The dopant performance increases with the electron affinity of the dopant metal. A linear fit is shown, but the data set is insufficient to distinguish a linear from a higher-order dependence.

Table 6.2: Electron affinities of the elements present in the dopants. Tabulated values adapted from [225–230].

Element		Electron Affinity (eV)
Iron	(Fe)	0.153
Aluminium	(Al)	0.443
Nickel	(Ni)	1.157
Copper	(Cu)	1.236
Gold	(Au)	2.309
Bromine	(Br)	3.364
Chlorine	(Cl)	3.613

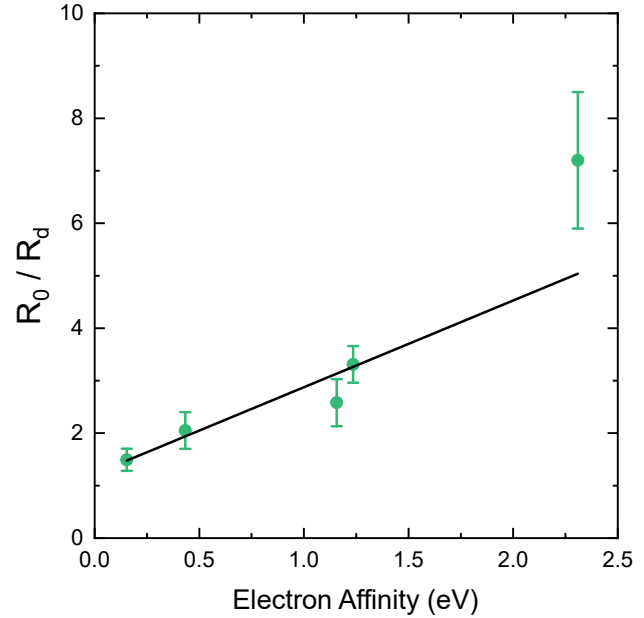


Figure 6.8: Metal electron affinity and dopant performance. The conductivity improvement, defined as the sheet resistance ratio of pristine (R_0) and doped (R_d) films, of SWCNT-EVA films doped with different chlorinated metals (Tab. 6.2) is plotted against the electron affinity of the metal. A linear fit is shown.

To investigate the doping mechanism further, we performed absorbance measurements in the range of 500 – 2500 meV of doped SWCNT-EVA films for different dopants, plotted in Fig. 6.9a relative to the absorbance of the pristine films. As expected, we find that the absorbance of doped films is slightly increased near the peak sensitivity of the human eye at 2.25 eV (550 nm), which is the wavelength used for calculating FoM.

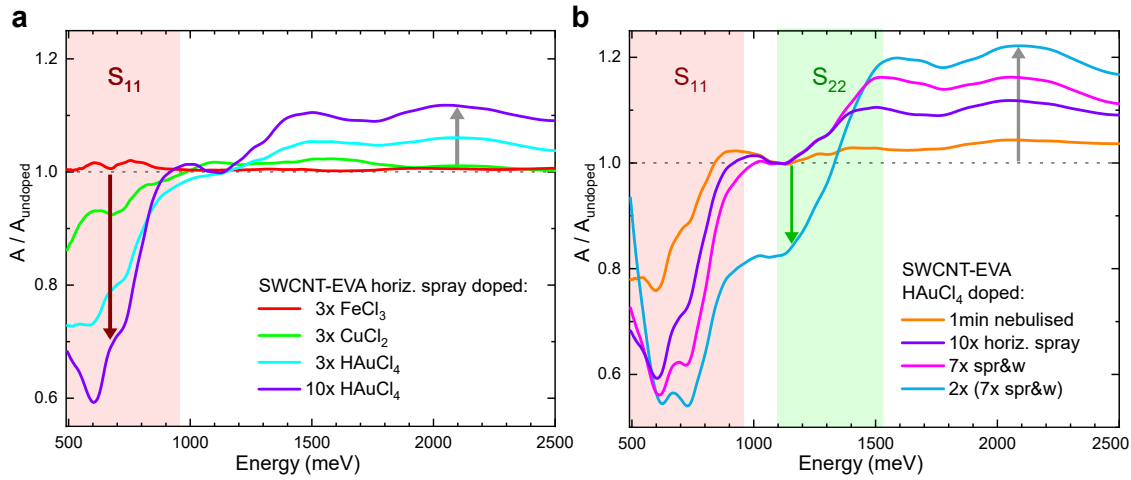


Figure 6.9: Absorption of doped SWCNT-EVA films relative to the pristine samples. The first (S_{11}) and second (S_{22}) semiconducting interband transitions are emphasised in red and green. Reduced S_{11} and S_{22} absorption is due to a p-doping-induced Fermi level shift into the valence band, and increased absorption in the visible region due to absorption by dopants. **a)** Relative absorption spectra of SWCNT-EVA films doped with different dopants. **b)** Effect of HAuCl_4 dopant applied with different deposition techniques on the absorption spectra of SWCNT-EVA films.

The expected energy range of the first interband transition (S_{11}) of the semiconducting SWCNTs is shaded in red. Chemical p-doping of CNTs shifts the Fermi level down into the first valence band and consequently quenches the absorption of the first interband transition as there are fewer occupied states in the valence band. We find that this effect correlates with the increase in the electrical conductivity of our films. For FeCl_3 , achieving conductivity improvements of x1.5, there is no appreciable change in the S_{11} absorption, whereas for CuCl_2 (conductivity x3.3) the S_{11} absorption is reduced by 5-10%. For HAuCl_4 (conductivity x7.6) we observe a 30% reduction in S_{11} absorption. This suggests that FeCl_3 does not induce a transfer of electrons from the CNT, but CuCl_2 and HAuCl_4 do, which agrees with our previous hypothesis about the importance of the electron affinity of the dopant metal. We conclude that the positive effect of FeCl_3 on the electrical conductivity of our SWCNT-EVA films is caused by adding interconnections between CNTs in the film rather than chemical p-doping [134].

The purple graph in Fig. 6.9a depicts a 10x HAuCl_4 spray-doped sample. Compared to the 3x spray-doped film, the effect on S_{11} intensifies from a 30%

to a 40% reduction of absorbance, but the absorption in the visible region is increased substantially as well. If even more HAuCl_4 solution is applied (blue graph in Fig. 6.9b), we find that the second interband transition S_{22} (green area) is partially quenched as well, suggesting that sufficient electrons have been removed from the CNTs to push the Fermi level down into the second valence band. This allows us to estimate the concentration of induced electron holes in the CNTs via eq. 3.31 to $p = 0.20 \pm 0.05 \text{ nm}^{-1}$ suggesting there is an induced electron hole for every 5 nm of SWCNT. This result demonstrates that SWCNT-EVA films can be heavily p-doped despite the presence of the insulating EVA polymer in the films.

However, high doping concentrations are only desirable if a high transmittance can be maintained. In consideration of this, we compared four different deposition methods, details in Sec. 4.1.3, for the best-performing dopant HAuCl_4 . We found that the deposition method plays a key role for dopant-induced absorbance in the visible region, see Fig. 6.9b. This is connected to the formation of dopant clusters when the solvent evaporates. These clusters are detrimental to performance as they do not contribute to electrical conduction but absorb light. For simple drop-casting of the dopant (not shown), there is a visible coffee ring effect upon solvent evaporation. For the dopant solution applied with a spray nozzle, the droplet size is still too large to prevent dopant cluster formation.

We, therefore, adapted the nebuliser doping technique reported by Tsapenko *et al.* [135] to minimise dopant droplet size and additionally heated our substrates to 50°C . This accelerates solvent evaporation and reduces optical absorption of the dopant layer at 550 nm from 8% for simple drop-casting to 2% for the optimised nebuliser technique at identical dopant concentrations.

In summary, we demonstrated the chemical p-doping of SWCNT-EVA films for a range of halogenated metals. A large electron affinity of the metal appears to be a critical factor for successful p-doping, which we confirmed both in electrical and optical measurements. While the best-performing dopant was the established HAuCl_4 , we found CuCl_2 is a promising low-cost alternative to the expensive gold-based dopants. Finally, the deposition method of the dopant solution holds the

key to reducing the effect of doping on the optical transmittance which is linked to the formation of dopant clusters upon solvent evaporation.

6.7 Summary

This chapter presents a detailed study of the connection between processing and optoelectronic properties of carbon nanotube–ethylene-vinyl acetate thin films. After Tuball SWCNTs had been identified as the most promising CNT raw material, we optimised the preparation process of these CNT-EVA thin films in detail, revealing the dispersion technique and polymer removal steps as the crucial parts for improving TCF performance. The optimised films suffer less from percolation effects at low thicknesses and allow deposition of connected films as thin as 5 nm, corresponding to 95% transmittance, that have sheet resistances of about $4000 \Omega/\square$.

Changing the composition of the EVA copolymer allows tuning the mechanical and chemical resilience of the resulting CNT-EVA films while leaving the TCF performance unaffected. Exposing CNT-EVA films to repeated bending and folding strain leads to small increases in the sheet resistance, following a logistic function with upper bounds below twice the initial resistance for all samples. Further, no significant difference in the wrapping selectivity of Tuball SWCNTs could be identified for the different EVA polymers.

Finally, several halogenated metals were tested for their ability to chemically p-dope the SWCNT-EVA films. While gold chloride-based dopants performed best, achieving FoM improvements of factors up to 8, several low-cost alternatives could be identified. The dopants under investigation also suggested a correlation between the electron affinity of the dopant metal and the dopant performance with higher electron affinities leading to a stronger p-doping effect. This can be rationalised with the doping mechanism proposed in literature [131].

7

Application of Carbon Nanotube-Ethylene-Vinyl Acetate Films in Touch-Sensitive and Photovoltaic Devices

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7.1 Introduction

Contrary to many emerging material systems in research, the motivation behind CNT-EVA films is not based on the expectation to outperform state-of-the-art

materials, but rather on the abundance, versatility and scalability of the system. In fact, the material cost of Tuball CNT-EVA films ($\approx 2 \text{ €/m}^2$) is already more than an order of magnitude lower than for standard TCF materials like ITO [121, 201], even at lab scale. This opens the door to a number of applications for CNT-EVA films as transparent conductors.

In the previous chapter, we have established several approaches to improve the transparent conductive film performance of SWCNT-EVA thin films. The combined effect of these optimisation steps lead to a TCF figure of merit improvement by a factor of 100, meaning that the electrical conductivity of our films is now 100 times higher at the same optical transmittance. To put this into context, equi-performance lines of CNT-EVA films and other TCF materials are displayed in Fig. 7.1a.

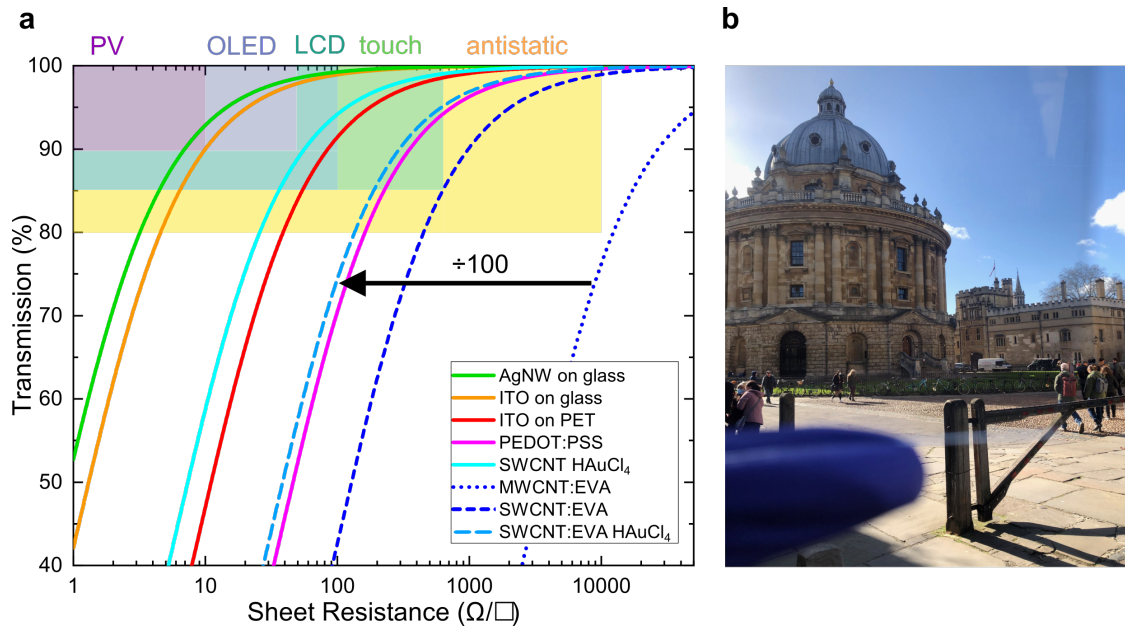


Figure 7.1: Performance of transparent conductors and requirements for applications. **a)** Transmission and sheet resistance of various TCF materials [102, 135, 203, 231–233] compared to CNT-EVA films before (MWCNT-EVA) and after optimisation (SWCNT-EVA) as well as after doping (HAuCl_4). The coloured areas indicate performance requirements of different TCF applications [121]. **b)** Picture of a doped SWCNT-EVA film on a PET substrate with 80% transmittance in front of the Radcliffe Camera.

The shaded areas in Fig. 7.1a highlight the transmission and sheet resistance ranges required for different TCF applications. The CNT-EVA films before (dark blue dotted line) and after optimisation (dark blue dashed line) as well as after

doping (blue dashed line) show that these improvements push CNT-EVA films into commercially relevant performance regions. While previously the performance was insufficient even for the lowest performance requirement of antistatic films, optimised films are on the edge of touch-sensitive applications and doped films even outperform the widely used material PEDOT:PSS. This is a significant result, as the current industry standard ITO has inherently poor performance in flexible applications [234]. In contrast, our SWCNT-EVA films perform equally well on glass and PET substrates and are resilient against mechanical strain (Sec. 6.5), while maintaining high optical clarity, see Fig. 7.1b.

The results of the previous chapter, therefore, make CNT-EVA films suitable for a whole new type of application, touch-sensitive films. In this chapter, we investigate the applicability of SWCNT-EVA films and produce working flexible touch-sensitive devices. In addition, we combine our CNT-EVA films in a hybrid hole transport layer (HTL) with spiro-OMeTAD in perovskite solar cells. This removes the need for extrinsic p-doping to enhance the conductivity of spiro-OMeTAD, which is known to cause rapid device degradation [45].

Solar cell devices in this chapter have been prepared and characterised with the help of Suer Zhou.

7.2 SWCNT-EVA as Transparent Touch-Sensitive Thin Films

To demonstrate the high performance of our optimised films, we designed flexible touch-sensitive SWCNT-EVA thin film devices.

This can be done with a *SparkFun Electronics Teensy 3.2 K20* microcontroller that contains a touch-sense function measuring the ground-coupled capacitance connected to a pin. Upon touching the CNT film, its capacitance is increased and the touch-sense function prints a larger output value. For a proof of concept device, we sprayed a 4x4 pixel matrix of SWCNT-EVA film on a 20 by 13 cm² PET substrate and connected the individual rows and columns to the microcontroller with conductive carbon tape contacts, see Fig. 7.2a.

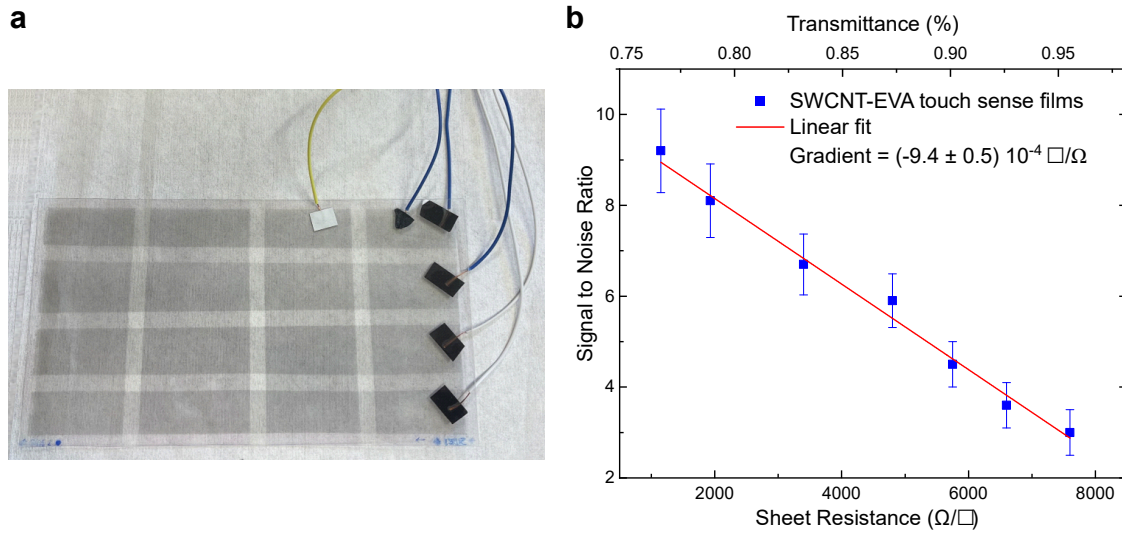


Figure 7.2: touch-sense devices based on SWCNT-EVA thin films. a) Picture of a SWCNT-EVA 4x4 pixel touch-sense device on a 20x13 cm² PET substrate. b) The signal-to-noise ratio of different SWCNT-EVA touch-sense films plotted as a function of the thin film sheet resistance together with a linear fit. Signal-to-noise is defined as the ratio of the signal amplitude when a pixel was touched to the baseline.

The pixel layout allows us to identify where the film was touched and replicates the design of standard touchscreen devices. Typically, the rows and columns are separated by an insulating layer to prevent interference. Here, we could remove this requirement by simply depositing on the front and back sides of the thin PET substrate. The resulting devices performed well and did not show signs of degradation after being touched with gloves for extended periods of time. In fact, the sensitivity of the device was sufficient to detect the change in capacitance produced by the proximity of the finger several centimetres away, allowing it to be used without being physically touched.

The upper limit for the sheet resistance of touch-sensitive transparent conductors is typically given as 1000 $\Omega/\square$ [121]. Since undoped SWCNT-EVA films typically have sheet resistances of just under 1000 $\Omega/\square$ at 85% transmittance, we tested up to which transmittance undoped films produce working touch devices. For this purpose, we fabricated several touch-sensitive devices with increasing transmittance and consequently increasing sheet resistances, see Fig. 7.2b. We found that for sheet resistances above 1000 $\Omega/\square$, the signal-to-noise ratio, defined as the ratio between the voltage signal amplitude when a pixel was touched and the baseline

amplitude, correlates linearly with the sheet resistance of the SWCNT-EVA thin film in the probed range. The CNT film with $7600\ \Omega/\square$ had a signal-to-noise ratio of 3 at a transmittance of 95% and a thickness of less than 10 nm, demonstrating that undoped SWCNT-EVA thin films can produce working touch-sense films at extremely low thicknesses and transmittance values well above 85%.

7.3 SWCNT-EVA as Transport Layer in Perovskite Solar Cells

An exciting application of CNT thin films is in photovoltaic devices. We deploy our SWCNT-EVA films in the hole transport layer (HTL) of perovskite solar cells. As Habisreutinger *et al.* have demonstrated, the combination of SWCNTs with spiro-OMeTAD forms high-performing hole transport layers [235].

Typically, the hole conductivity of spiro-OMeTAD needs to be enhanced by the addition of p-dopants like Li-TFSI. Abate *et al.* describe the doping mechanism as a redox reaction in which the presence of the lithium salt allows oxygen to act as a p-dopant [236]. The high electron affinity of molecular oxygen and the low ionization potential of spiro-OMeTAD lead to electron transfer from spiro to oxygen. The addition of LiTFSI results in the presence of Li^+ cations. These cations form lithium oxide complexes under the consumption of O_2^- and therefore stabilise the spiro-OMeTAD cations. The additional positive charges act as mobile holes in spiro-OMeTAD and enhance the hole transport properties of the material.

However, the doping mechanism consumes Li^+ during device operation and therefore severely limits long-term stability [236]. In addition, the presence of oxygen is required for the doping mechanism but may have detrimental effects on the overall device stability [237, 238].

Habisreutinger *et al.* showed that the combination of SWCNT thin films with an undoped spiro-OMeTAD layer enhances device stability compared to devices using Li-TFSI and provides excellent hole transport properties [45, 235]. This is based on the rapid extraction of holes from the absorber layer via carbon nanotubes in synergy with the charge selectivity of the spiro-OMeTAD layer. The

hybrid layer consists of a thin network of carbon nanotubes, which is deposited directly on top of the perovskite absorber. Consecutively, the SWCNT layer is embedded in a continuous spiro-OMeTAD film, preventing direct contact between perovskite and metal electrode.

This device layout has been modified by Mazzotta *et al.* to include SWCNT-EVA instead of the previously used SWCNT-P3HT layers [102]. To investigate whether our optimised SWCNT-EVA films can improve the overall PV device performance, we fabricate analogous devices but with FAPbI₃ as the absorber material. This is based on the superior performance of FAPbI₃ devices in recent reports, achieving world record efficiencies of up to 25.7% [239]. The Tuball SWCNTs used in this work have slightly larger diameters than previously used SWCNTs [45, 102, 235], resulting in less favourable energy levels for hole extraction. However, in combination with the charge-selective spiro-OMeTAD, this might be less relevant than the strongly enhanced electrical conductivity of our SWCNT films. The layout of our devices is shown in Fig. 7.3a together with experimentally determined approximate layer thicknesses. Upon photoexcitation, electrons are injected into the electron transport

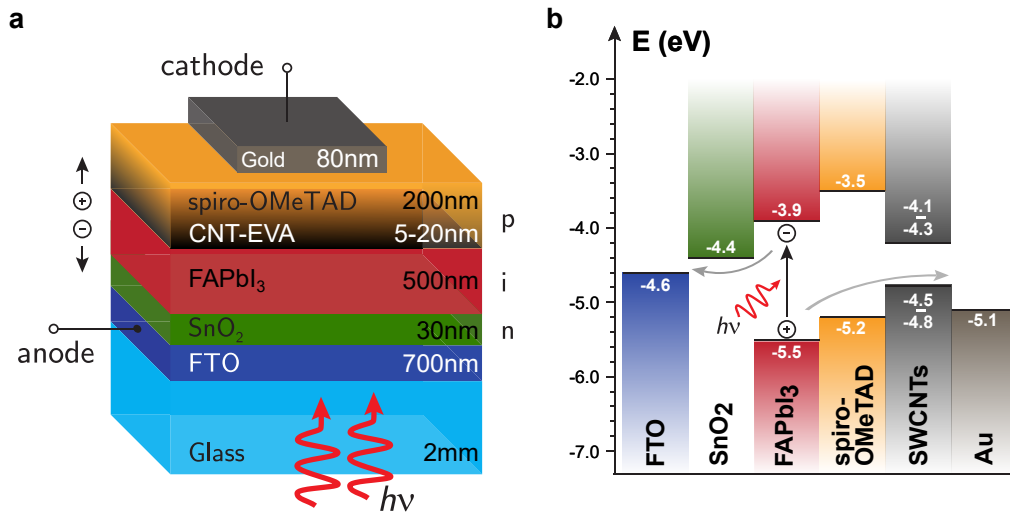


Figure 7.3: PV device layout. a) The individual layers comprising the photovoltaic devices. CNT-EVA films have been deposited before spiro-OMeTAD as part of the hole transport (p) layer. Layer thicknesses are provided but layers are not drawn to scale. b) Schematic of the energy levels involved in the charge extraction from the perovskite absorber layer. The energy levels are aligned in a way that electrons and holes can only move into the electron and hole transport layers, respectively.

layer (ETL), consisting of SnO_2 , and extracted via the anode. The anode consists of fluorinated tin oxide (FTO) and the transparent conductor is deposited on a glass substrate. Similarly, photogenerated holes move from the absorber layer into the CNT-EVA and spiro-OMeTAD hybrid layer acting as the hole transport layer (HTL). Holes are then extracted via the gold cathode. The energy levels of the hole transport and electron transport layers are positioned in a way that supports charge transport in the preferred direction but prevents holes from entering the ETL and electrons from entering the HTL, as described in Sec. 2.2.4. The energy levels of all layers in our device stack are displayed in Fig. 7.3b.

7.3.1 Optimising HTL layer thicknesses

As a first step, we wanted to establish the optimal CNT-EVA layer thickness. The CNT layer needs to be thick enough to improve the vertical conductivity of the spiro-OMeTAD layer sufficiently. At the same time, the CNT-EVA layer needs to be thin enough that it is covered entirely by the spiro-OMeTAD layer. The mesh-like structure of the CNT-EVA layer requires the polymer layer to fill structural gaps to prevent direct contact between the absorber layer and the anode, which would create shunting pathways and impede device performance. Consequently, there is a trade-off between low series resistance and high shunt resistance when varying the CNT-EVA layer thickness.

In initial device runs we found that SWCNT-EVA layer thicknesses above 20 nm suffer from a reduced shunt resistance but provide low series resistances. Therefore, we chose thicknesses of 5, 10 and 15 nm for the CNT-EVA layer. For each condition, we compared two concentrations of the spiro-OMeTAD in chlorobenzene solution that was spin-coated on top of the SWCNTs, 85 and 100 mg/ml, which produces film thicknesses of 190 nm and 220 nm, respectively. To avoid confusion with CNT layer thicknesses, we adopt the convention to label the spiro layers by their concentration. As control devices, LiTFSI doped and pristine spiro layers deposited from 85 mg/ml solutions were used as hole transport layers. The results of this device run are shown in Fig. 7.4.

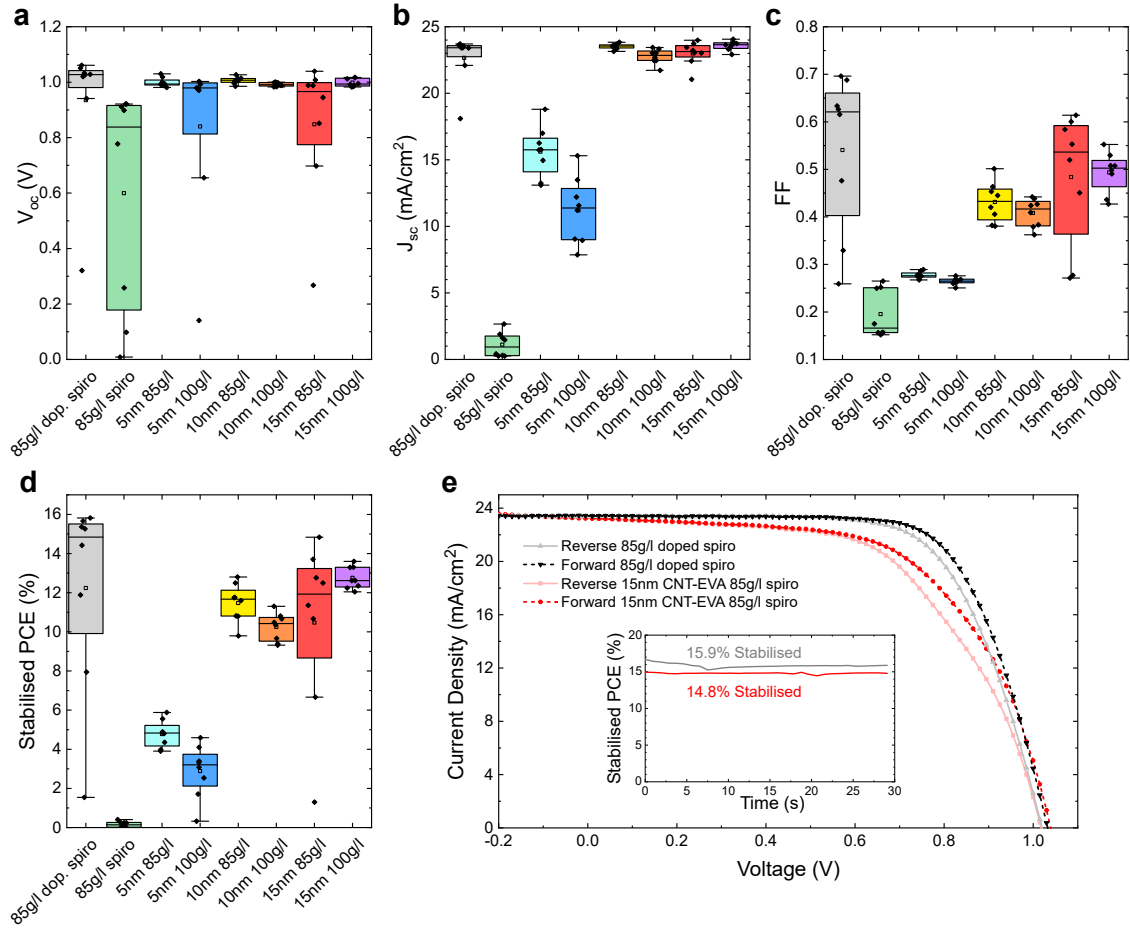


Figure 7.4: PV devices with varying SWCNT-EVA layer thickness and spiro-OMeTAD concentration. The thickness of the CNT-EVA layer was 5, 10 or 15 nm, and the spiro-OMeTAD layer was deposited from chlorobenzene solutions with 85 or 100 mg/ml concentration, resulting in 190 nm and 220 nm thick spiro films. Control devices had pristine and LiTFSI doped spiro-OMeTAD layers deposited from 85mg/ml solution as HTLs. The resulting devices are shown in terms of their **a)** open circuit voltage (V_{oc}), **b)** short circuit current density (J_{sc}), **c)** fill factor (FF) and **d)** stabilised power conversion efficiency (PCE). **e)** JV curves of the champion CNT device and the champion control device. The inset provides the stabilised PCE for a 30s measurement.

The open circuit voltage (V_{oc} , Fig. 7.4a) is comparable for the doped spiro control and all SWCNT-EVA devices, as is expected for devices with an identical absorber material. The CNT devices with 85 mg/ml (190 nm) spiro-OMeTAD layers have a slightly higher V_{oc} than their 100 mg/ml (220 nm) counterparts, which might be related to additional recombination in the thicker spiro-OMeTAD layers. The pristine spiro control has a reduced V_{oc} due to the insufficient conductivity of the spiro-OMeTAD layer.

A similar pattern is present in the short circuit current (J_{sc} , Fig. 7.4b). Devices with 10 and 15 nm of SWCNT-EVA give about $J_{sc} = 23 \text{ mA/cm}^2$, matching the current of the doped spiro control. The 5 nm devices have a reduced J_{sc} , which we attribute to the sparser CNT networks providing insufficient carrier pathways through the spiro-OMeTAD layer and thus lower carrier mobility. As a result, charges are extracted slower from the absorber layer, which leads to a loss of current. This is confirmed by the fact that 5 nm devices with a thicker spiro layer (100 mg/ml) perform worse than those with a thinner layer (85 mg/ml) at 5 and 10 nm. The pristine spiro control has nearly zero current which is again due to its low conductivity.

The fill factor (FF , Fig. 7.4c) is clearly lower for the CNT devices than for the doped spiro control, hinting at the presence of parasitic resistive losses in the CNT devices. The nature of the resistive losses is revealed by comparing the fill factors of the different CNT devices. Since thinner SWCNT-EVA films consistently produce lower fill factors and thicker spiro-OMeTAD layers at the same SWCNT layer thickness equally show reduced fill factors, we conclude that the resistive losses are due to an increased series resistance rather than the presence of shunt pathways. A comparison of the parasitic resistances and fill factors of all champion devices presented in this chapter is given in Tab. 7.1.

The multiplication of V_{oc} , J_{sc} and FF divided by the power of incoming light yields the power conversion efficiency (PCE). The stabilised PCE is given in Fig. 7.4d. The overall trend is similar to the fill factor, with a larger gap between 5 nm and remaining CNT devices, as both FF and J_{sc} are reduced. Control devices with undoped spiro do not show the rectifying behaviour typical for a diode but had the JV curve of a resistor instead. This highlights the positive effect of just 5 nm SWCNT-EVA on the hole transport characteristics of spiro-OMeTAD.

The CNT devices with the highest mean of stabilised PCE (12.7%) are the 15 nm 100 mg/ml. The best performing individual SWCNT-EVA device is a 15 nm with 85 mg/ml spiro-OMeTAD device at 14.8% stabilised PCE. The JV curves of this device and the champion control device are presented in Fig. 7.4d, and

the stabilised PCE data is given as an inset. The JV data suggest that while an increased series resistance causes most of the fill factor loss, the slope of the JV curve near V_{oc} also demonstrates a lower shunt resistance of the CNT devices compared to the doped spiro controls (Tab. 7.1).

We have shown that SWCNT-EVA layers thinner than 15 nm result in increased series resistances and SWCNT-EVA layers thicker than 20 nm suffer from low shunt resistances. Therefore, our next batch of devices compares SWCNT-EVA layer thicknesses of 15 and 20 nm with all remaining parameters unchanged. The results are presented in Fig. 7.5 in the same format as before. The pristine spiro controls are not shown since their performance was equally poor as in the previous batch and we rather focus on the smaller differences between the remaining samples.

For this batch, the mean V_{oc} of the doped spiro controls is about 40 meV higher than for the best SWCNT-EVA devices (Fig. 7.5a). V_{oc} is the main indicator of charge recombination, but given the similarity of the device stacks, we hypothesize that the difference originates from recombination at the perovskite/SWCNT interface.

In terms of J_{sc} , the mean of the 15 nm SWCNT-EVA devices with 100 mg/ml spiro is 0.1 mA/cm² above the doped spiro controls, with a 0.4 mA/cm² gap between the champion devices (Fig. 7.5b). This highlights the excellent hole extraction of the SWCNT-EVA/spiro-OMeTAD hybrid layer.

The fill factor is remarkably consistent between the different SWCNT-EVA configurations, with the means varying between 0.53 and 0.56 (Fig. 7.5c). In comparison, the doped spiro controls show fill factors with a mean of 0.56 and a larger standard deviation, which is mainly due to one pixel failing.

Comparing the stabilised PCE (Fig. 7.5d), we find that the mean of the doped spiro controls is only about 0.2% higher than the mean of the 15 nm 100 mg/ml CNT-EVA devices (13.8%). A 20 nm 100 mg/ml SWCNT-EVA device achieves the highest stabilised PCE (16.3%) of all SWCNT-based devices and the JV curves are compared to the champion control device in Fig. 7.5e.

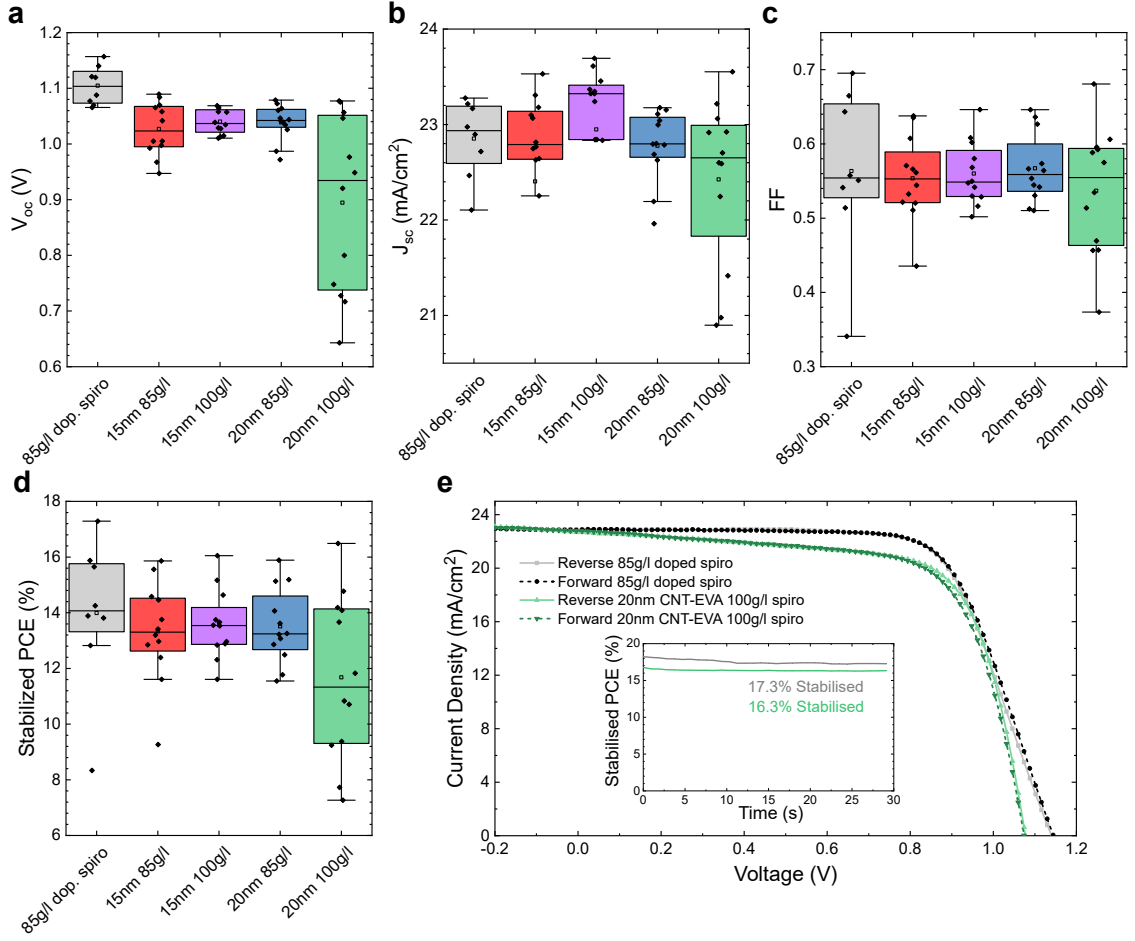


Figure 7.5: PV devices with refined CNT-EVA and spiro-OMeTAD layer thickness. PV devices with 15 or 20 nm SWCNT-EVA thin films with a spiro-OMeTAD layer deposited from either 85 or 100 mg/ml chlorobenzene solution (190 or 220 nm). Devices with LiTFSI doped and pristine (not shown, but similar to Fig. 7.4) spiro-OMeTAD layers deposited from 85mg/ml solution were used as controls. Resulting devices are shown in terms of their **a)** open circuit voltage (V_{oc}), **b)** short circuit current density (J_{sc}), **c)** fill factor (FF) and **d)** stabilised power conversion efficiency (PCE). **e)** JV curves of the champion CNT device and the champion control device. The inset gives the stabilised PCE for a 30s measurement.

The slope of the JV curves around V_{oc} suggests that the champion SWCNT-EVA device still suffers from shunting pathways (Tab. 7.1). By contrast, the series resistance of the SWCNT-EVA device appears to be lower than for the doped spiro control shown in Fig. 7.5e. This confirms our previous hypothesis that thicker CNT layers decrease series and shunt resistances alike. While the 20 nm 100 mg/ml champion device is close in performance to the doped spiro control, the data suggest that the 20 nm layer is too thick to be covered entirely by the spiro-OMeTAD

layer and shunting pathways remain.

To overcome this issue, we will try adding an inert transparent polymer layer on top of spiro-OMeTAD to reduce shunting in the following section.

7.3.2 Introducing a PMMA top layer

Much like EVA, poly(methyl methacrylate) (PMMA) is an insulating, transparent polymer. For our additional layer, we have chosen PMMA over EVA due to its higher melting point. This additional layer of PMMA has the purpose of filling any remaining spatial holes or gaps in the HTL and thereby increasing the shunt resistance while maintaining a low series resistance. It will hence be deposited last and sit just below the gold cathode, as depicted in Fig. 7.6b.

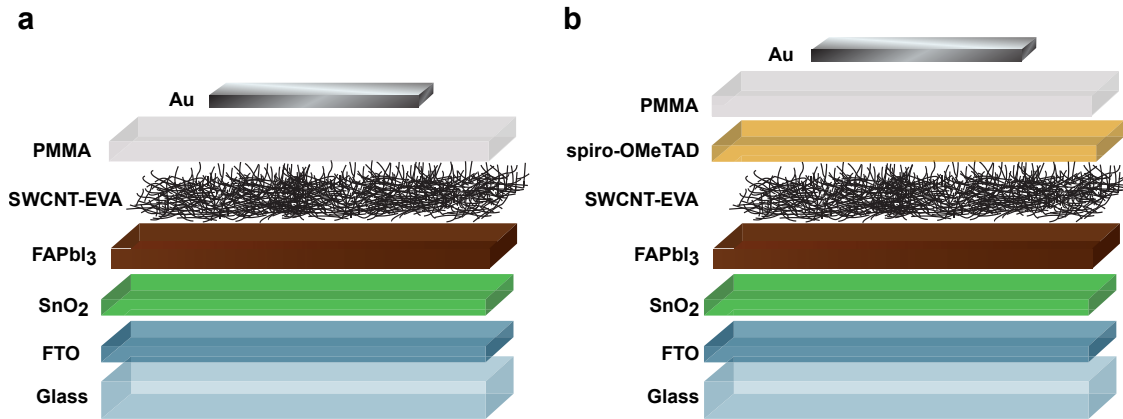


Figure 7.6: Device stack of PV devices including a PMMA layer as part of the HTL. The inert PMMA layer fills spatial holes in the layers underneath and thus increases the shunt resistance of the device. Layer thicknesses are identical to Fig. 7.3a. **a)** Layout of PV devices with a hole transport layer consisting of SWCNT-EVA and PMMA. **b)** Layers of devices with SWCNT-EVA, spiro-OMeTAD and PMMA as combined HTL.

To investigate the hole selective transport capabilities of Tuball SWCNT-EVA layers directly, we have also prepared devices with SWCNT-EVA and PMMA as HTL, without a spiro-OMeTAD layer in between, see Fig. 7.6a. The results of this device run are given in Fig. 7.7.

The SWCNT-EVA layer thickness was kept at 15 nm for all CNT devices as this thickness gave the most consistent results in previous runs. The spiro-OMeTAD concentration was 90 mg/ml for all devices labelled spiro, producing a 200 nm film intermediate between the previous two configurations.

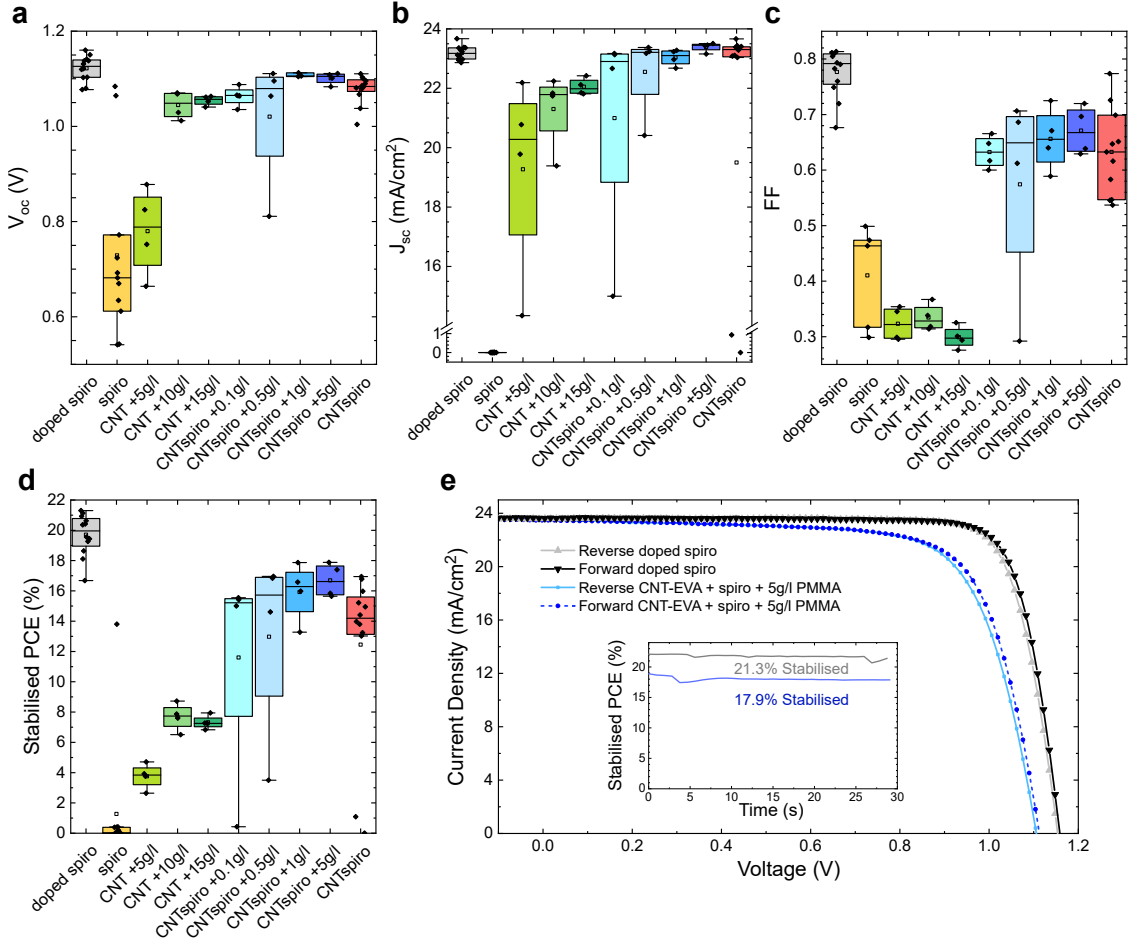


Figure 7.7: PV devices with SWCNT-EVA and an additional PMMA layer. All CNT devices have a 15 nm SWCNT-EVA layer, devices labelled spiro have a 90 mg/ml (200 nm) spiro-OMeTAD layer and the concentrations correspond to PMMA in toluene solutions used to deposit PMMA layers (1 – 50 nm). Resulting devices are shown in terms of their **a)** open circuit voltage (V_{oc}), **b)** short circuit current density (J_{sc}), **c)** fill factor (FF) and **d)** stabilised power conversion efficiency (PCE). **e)** JV curves of the champion CNT device and the champion control device. The inset gives the stabilised PCE for a 30s measurement.

The PMMA layer was spin-coated from toluene solution at concentrations of 0.1 to 5 mg/ml on top of spiro-OMeTAD and at a concentration of 5 to 15 mg/ml without spiro. This corresponds to PMMA film thicknesses between ~ 0.5 nm and 50 nm, respectively. Similarly to the previous section, we indicate the PMMA layer thickness via the concentration in Fig. 7.7. LiTFSI doped and pristine spiro-OMeTAD control devices without CNT or PMMA layers were prepared as before.

Fig. 7.7a shows that the SWCNT-EVA devices with 5 mg/ml (10 nm) PMMA are the only CNT batch with severely reduced V_{oc} . This can be attributed to severe

shunting from the slope of the JV curves (not shown). The other two SWCNT-EVA samples with solely 10 mg/ml (25 nm) and 15 mg/ml (50 nm) PMMA on top achieve open-circuit voltages above 1 V. However, their fill factors are just above 0.3, suggesting that the charge selectivity of the HTL suffers without the presence of spiro-OMeTAD. This can be explained by the narrow bandgap of the SWCNTs, providing preferential energy levels for photogenerated electrons and holes alike (Fig. 7.3b). Still, the short-circuit currents of the SWCNT-EVA with PMMA devices are above 20 mA/cm² for most pixels, suggesting that the SWCNT-EVA-PMMA HTLs provide sufficient hole-extraction characteristics.

The PV devices with SWCNT-EVA, spiro-OMeTAD and PMMA layers combined show a clear trend of improved performance with higher PMMA thickness in J_{sc} , FF and stabilised PCE. This agrees well with the filling of spatial holes in the HTL and increased shunt resistances upon adding more PMMA. This becomes more obvious when comparing these devices to the samples with SWCNT-EVA and spiro-OMeTAD. While the PMMA layer seems to have a negligible effect on V_{oc} and J_{sc} , the fill factor increases upon adding 1 and 5 mg/ml PMMA, which is reflected in the stabilised PCE as well.

For devices with 0.1 and 0.5 mg/ml PMMA, the effect of the additional PMMA layer appears statistically insignificant considering the number of devices prepared.

Finally, the JV curves for the champion devices are shown in Fig. 7.7e. The best SWCNT-EVA + spiro + 5 mg/ml PMMA device has a stabilised PCE of 17.9%, which is 2% higher than the highest stabilised PCE previously achieved with CNT-EVA-based hole transport layers [114]. The JV curves show that the shunt resistance of the champion CNT device is significantly increased compared to the previous CNT devices, with a $V_{oc} = 1.11$ V and $J_{sc} = 23.6$ mA/cm² for the champion device. The difference in PCE to the champion doped spiro control device is mainly caused by a lower V_{oc} . We hypothesize that this difference might be linked to increased interfacial recombination caused by the presence of CNTs.

A summary of the series and shunt resistances as well as fill factors of best-performing devices with different SWCNT-EVA layer thicknesses is given in Tab. 7.1.

There is an overall trend of decreasing R_s and increasing fill factor with higher SWCNT-EVA layer thicknesses. The comparison of the 15 and 20 nm champion devices is not straightforward, as the devices originate from different batches. However, the 15 nm devices achieving fill factors of 0.73 come remarkably close to the overall doped spiro control champion (0.817).

Table 7.1: Champion devices and their corresponding HTL layer thicknesses shown with the series resistance (R_s), shunt resistance (R_{sh}) and fill factor. Batches 1, 2 and 3 refer to device data in Fig. 7.4, Fig. 7.5 and Fig. 7.7, respectively.

Batch	Layer thickness (nm)			R_s ($\Omega \cdot \text{cm}^2$)	R_{sh} ($\Omega \cdot \text{cm}^2$)	Fill factor
	SWCNT-EVA	spiro-OMeTAD	PMMA			
1	5	190	-	38.5	76.6	0.289
1	10	190	-	12.4	1530	0.501
1	15	190	-	7.50	827	0.600
3	15	200	-	4.13	859	0.730
3	15	200	15	4.86	1800	0.728
2	15	220	-	6.58	495	0.649
2	20	220	-	6.08	410	0.635
3	doped spiro	190	-	3.72	6320	0.817

7.4 Summary

In this chapter, we have demonstrated that their improved TCF performance makes SWCNT-EVA films suitable for applications in perovskite solar cells and transparent touch-sensitive devices. By making several of these touch-sensitive devices, we have found a linear relationship between the sheet resistance and the signal-to-noise ratio of the touch sensing that can be used to determine a threshold film thickness. With 10 nm SWCNT-EVA films of 95% transmittance still able to function reliably at a sheet resistance of $7600 \Omega/\square$, this clearly demonstrates the potential of CNT-EVA films for transparent touch-sensitive applications.

In addition, we have tested SWCNT-EVA films in the hole transport layer of perovskite solar cells. By optimising the CNT-EVA layer thickness, we could minimise parasitic resistive losses and achieve a stabilised PCE of 16.3%. Adding an additional top layer of PMMA reduced shunting and boosted the stabilised PCE

to 17.9%, nearly 2% higher than the highest previously achieved value with CNT-EVA films (16.0%) [114]. We found that in combination with the hole-selective polymer spiro-OMeTAD, SWCNT-EVA films provide effective hole extraction from the absorber layer and have the potential to replace the short-lived Lithium based dopants of spiro-OMeTAD. Interestingly, the unfavourable energy level positions of Tuball SWCNTs do not seem to have significant detrimental effects on device performance when used in combination with spiro-OMeTAD.

However, devices with just SWCNT-EVA and PMMA as HTL were clearly affected by the lack of charge selectivity in this configuration, achieving a maximum stabilised PCE of only 8.9%. These results highlight the potential of hybrid transport layers that combine a highly conductive with a highly charge-selective material, bringing the potential for cost reduction and stability improvements.

8

The Effect of MDACl₂ on the Phase Stability FAPbI₃ Single Crystals

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8.1 Introduction

Hybrid organic-inorganic metal halide perovskites are a promising class of emerging semiconductor materials for optoelectronic applications based on their tuneable bandgaps [240], high absorption coefficients [241] and long charge-carrier diffusion lengths [242]. For single-junction photovoltaic applications, FAPbI₃ (FA⁺ is formamidinium, HC(NH₂)₂⁺) is the most promising candidate out of all the ABX₃ lead-halide perovskites reported to date [36]. This is because FAPbI₃ has the narrowest achievable bandgap ($E_g = 1.4\text{ eV}$) for a Pb₂⁺ based halide perovskite [29], allowing for the highest theoretical photovoltaic PCE in a single-junction architecture according to the Shockley-Queisser limit (see Sec. 2.1.2) [26]. This is reflected in the majority of recent world record PCE perovskite PV devices employing FAPbI₃-based materials as their photo-absorbing layer [243–245].

There is however one major challenge with the use of FAPbI₃. The cubic α -phase of the FAPbI₃ crystal (Fig. 8.1a) is thermodynamically unstable in ambient conditions and tends to transform into a photo-inactive hexagonal δ -phase (Fig. 8.1b,c). This hexagonal phase has a wider band gap, larger defect density and poor PLQE and is thus unsuitable for photovoltaic applications [246–248]. This phase transition is kinetically inhibited at ambient conditions and thus occurs

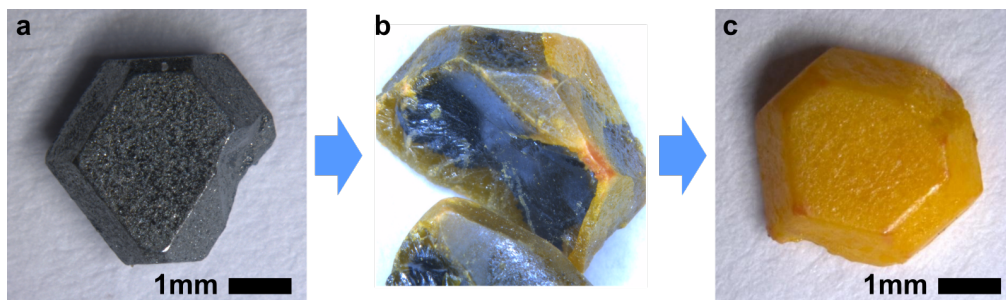


Figure 8.1: Degradation of α -phase FAPbI₃ single crystals into the δ -phase under ambient exposure. **a)** Pristine FAPbI₃ single crystals are in the cubic α -phase characterised by its black colour. **b)** A FAPbI₃ crystal that was cleaved after 8 hours of ambient exposure. The orange colouring at the surface indicates the starting degradation into the photo-inactive hexagonal δ -phase, while the bulk is still in the α -phase. **c)** A crystal that has degraded entirely into the δ -phase. Typically the phase transition is completed within days or weeks of ambient exposure.

within time frames of hours up to weeks, allowing a metastable α -FAPbI₃ to exist.

The lifetime of α -FAPbI₃ has been shown to depend strongly on the atmospheric conditions during processing and storage [29, 249]. To be of practical relevance, the long-term phase stability of FAPbI₃ has to be improved. Finding ways to stabilise the α -phase is thus a key challenge in the field.

Extensive research has been conducted aiming to suppress the α - to δ -phase transition. In particular, smaller A-site cations have been shown to stabilise the perovskite lattice by alloying with FA⁺ [38–41]. This is often done in combination with I[−], Br[−] or Cl[−] X-site alloying. Although promising for their stability, these approaches are accompanied by undesired side effects. The inclusion of smaller A-cations widens the band gap lowering the theoretical limit for the PCE in single-junction PV devices [250]. In addition, compositional inhomogeneities in the mixed-ion perovskites introduced during growth can render materials susceptible to ion segregation [39, 251] and non-radiative recombination losses [252] during operation. Strategies to improve stability without impeding other properties of α -FAPbI₃ are thus required.

In 2019, Min *et al.* [138] reported highly efficient α -FAPbI₃ solar cells based on polycrystalline thin films by incorporating a small amount of methylenediammonium dichloride (MDACl₂, 3.8 mol%) into the precursor solution, while maintaining the inherent bandgap of FAPbI₃. The authors attribute the high certified PCE of 23.7% to the addition of MDACl₂ and report that MDA₂⁺ leads to structural stabilization of α -FAPbI₃ via partial replacement of FA⁺ with MDA₂⁺. Subsequently, Kim *et al.* [253] proposed that concurrent substitution of 3 mol% of Cs⁺ and MDA₂⁺ on FA⁺ sites lowers the lattice strain and trap density in perovskite solar cells. In two more recent studies, again by Seok and co-workers, MDA₂⁺ was used alongside FAPbI₃ to reach the highest ever reported efficiency for single-junction perovskite solar cells of first 25.8% (certified 25.5%) and earlier this year 26.1% (certified 25.7%) [239, 243].

Here, we study the effect of the additive MDACl₂ on FAPbI₃ in single crystals rather than polycrystalline thin films. Single crystals have several advantages such as lower defect densities, longer carrier diffusion lengths, and better-defined structure since the influence of interfaces and grain boundaries can be eliminated [254–257].

Therefore, single crystals provide a more reliable platform to study the optoelectronic properties and phase transitions of FAPbI₃ [258, 259].

In this chapter, we present evidence that the beneficial effect of MDACl₂ addition to FAPbI₃ does not originate from MDA²⁺ A-site alloying as was previously proposed [138, 253]. Further, we derive a method to describe the α - to δ -phase transition in FAPbI₃ quantitatively via Raman spectroscopy. We then compare the phase stability of single crystals grown with MDACl₂ and hexamethylenetetramine (HMTA) additives to pristine FAPbI₃ crystals. Finally, we investigate the effect of the additives on the optoelectronic properties of FAPbI₃ single crystals, to ensure the stability enhancement is not accompanied by detrimental effects on other PV device-relevant properties.

8.2 Instability of MDACl₂ in Solution

The origin of the beneficial effects of MDACl₂ on FAPbI₃ single crystals has been proposed to be the incorporation of MDA²⁺ into the A-sites of the perovskite, as discussed above. In contrast to these reports, nuclear magnetic resonance (NMR) experiments performed and analysed by Benjamin Gallant, Silvia Collavini and Dominik Kubicki as part of this project show that the highly acidic MDA²⁺ is unstable in solution and degrades rapidly into ammonium (NH₄⁺) and hexamethylenetetramine (HMTA), see Fig. 8.2. The latter parts of this chapter are based on these results and they will thus be summarised below.

Fig. 8.2a shows the ¹H solution NMR spectra acquired from a solution of MDACl₂ dissolved in DMSO-d₆ at between 5 and 120 minutes after initial dissolution. Fig. 8.2b shows an expanded view of the earliest of these spectra, emphasising the presence of a number of signals that appear to correspond to intermediate species that exist only transiently. At the shortest time after dissolution, the ¹H NMR spectrum already shows several unexpected species. We attribute the distinctive 1:1:1 triplet at 7.34 ppm to ammonium (NH₄⁺, shaded in purple), with the splitting due to spin-spin coupling of ¹H to the quadrupolar ($I = 1$) ¹⁴N nucleus (¹J_{14N-1H} = 50.8 Hz). The signal, initially at 7.34 ppm, rapidly shifts and stabilises

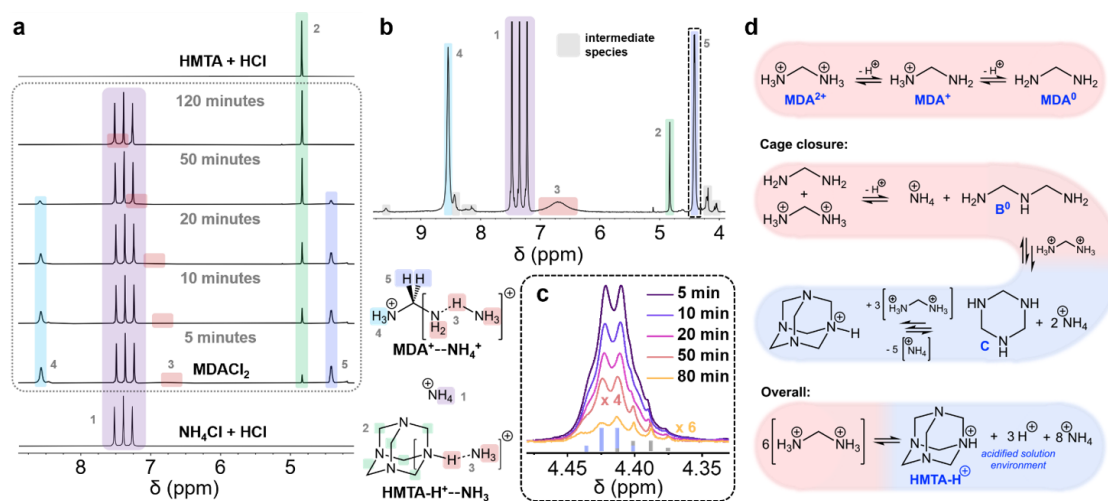


Figure 8.2: Degradation of MDACl_2 in solution. **a)** ^1H solution nuclear magnetic resonance (NMR) spectra tracking the evolution of MDACl_2 upon dissolution in DMSO-d_6 . Bottom: Spectra acquired from acidified solution of ammonium chloride. Top: Spectra acquired from acidified solution of Hexamethylenetetramine (HMTA). The colour scheme correlates detected signals with ^1H chemical environments in detected species. **b)** Expanded ^1H NMR spectrum of five minutes after initial dissolution of MDACl_2 in DMSO-d_6 . **c)** Evolution of ^1H NMR quartet signal corresponding to methylene environment in dominant degradation intermediate. **d)** Degradation pathway of MDA^{2+} upon dissolution in a polar solvent. HMTA and ammonia (NH_4) are represented in their protonated forms in line with our observations and on account of the acidic environment generated in solution as a result of the degradation. Experiments performed and analysed by collaborators B. Gallant, S. Collavini and D. Kubicki.

at 7.37 ppm, as is typical for ammonium species under varying pH conditions [260]. This assignment is confirmed by comparison with the solution ^1H NMR spectra of NH_4Cl in DMSO-d_6 at the bottom of Fig. 8.2a.

Fig. 8.2c highlights the coupling of one of these signals (4.42 ppm), which we find is superposed on top of another low-intensity signal, both of which we interpret as quartets. Given C-C bond formation is unlikely under the conditions, resolution of this spin-coupling along with the chemical shift suggests a CH_n environment adjacent to a $^+\text{H}_3$ group.

From these data, we infer that the most likely assignment for the dominant intermediate observed is MDA^+ in which the amine group is undergoing rapid chemical exchange with acidic NH_4^+ in solution (Fig. 8.2b). Accumulation of this species is mechanistically justified. When the charge-dense MDA^{2+} cation is dissolved in pH-neutral, aprotic polar solvents such as DMF, DMSO and GBL it

is expected to act as a Brønsted acid, rapidly releasing H^+ to become MDA^+ and acidifying the solution environment, as shown in Fig. 8.2d.

Release of a second acidic H^+ is possible, although less favourable in the acidified solution environment. However, this second deprotonation event yields neutral MDA^0 , a potent nucleophile. The presence of both MDA^0 and MDA^{2+} , a strong electrophile, renders both species unstable in solution with respect to formation of NH_4^+ and bis(aminomethyl)ammonium (B^+). Thus, under these conditions, MDA^+ is the most stable form of this species. MDA^+ can also act as an electrophile, however, its single charge renders it less reactive than MDA^{2+} . It may also eliminate to produce NH_3 and methaniminium ($\text{CH}_2=\text{NH}_2^+$). However, elimination reactions are typically slow, and production of methaniminium – itself a highly reactive electrophile – does not alter the course of the degradation.

Transient deprotonation of B^+ produces B^0 , another nucleophile, which reacts with further MDA^{2+} before rapidly cyclizing to form 1,3,5-triazinane (C). Repeated reaction of C with MDA^{2+} in conjunction with rapid cage-closure, driven entropically by release of additional NH_4^+ , is expected to lead to formation of protonated hexamethylenetetramine (HMTA-H^+), as shown in Fig. 8.2d. Experimentally, between 5 and 50 minutes after initial dissolution of MDACl_2 , a singlet signal of increasing intensity is observed in the ^1H solution NMR spectra at 4.83 ppm. By 120 minutes after initial dissolution, the spectrum consists only of this singlet, the 1:1:1 triplet corresponding to ammonium and a broad singlet at 8.00 ppm. HMTA dissolved in DMSO-d_6 at neutral pH shows a singlet at 4.56 ppm. However, incremental addition of hydrochloric acid (HCl) to this solution produces a downfield shift of this singlet to 4.83 ppm in line with the reported monoprotic $\text{pK}_{a\text{H}}$ value for HMTA (4.93) [261], confirming the identity of the final product of MDA^{2+} degradation as HMTA-H^+ . Integration of the relevant ^1H NMR signals confirms the stoichiometric 8:1 ratio of $\text{NH}_4^+:\text{HMTA-H}^+$ expected by the proposed degradation route. As observed with MDA^+ , rapid chemical exchange between the acidic H^+ of HMTA-H^+ and ammonium leads to a broadened ^1H NMR signal at a chemical shift corresponding to the weighted average of the contributing chemical environments

(7.45 ppm). We emphasise that despite the bias toward the formation of HMTA-H^+ and NH_4^+ , as all reaction steps are mechanistically reversible, it should be expected that the system at dynamic equilibrium will include small quantities of all intermediates. Overall, these findings suggest that the previously proposed incorporation of MDA^{2+} into the bulk crystal is unlikely.

Ongoing NMR experiments suggest that the stability improvement is instead based on the selective incorporation of tetrahydrotriazinium (THTZ-H^+) at 0.5 mol% into the crystal. A combination of liquid- and solid-state NMR techniques revealed that THTZ-H^+ is formed by the reaction of HMTA with FA^+ in the precursor solution.

8.3 Raman Spectroscopy of FAPbI_3 Single Crystals

Quantifying the phase stability of single crystals requires a technique that can be applied many times to the same sample without changing its properties. Standard characterisation via X-ray diffraction requires single crystal samples to be ground up into powder or smaller crystallites and is thus not an option. The different symmetries of the δ - and α -phases of FAPbI_3 suggest Raman spectroscopy as a powerful tool for the characterisation of FAPbI_3 single crystals regarding their phase.

The Raman activity of lead halide perovskites can be divided into two regions. The low wavenumber region ($< 500 \text{ cm}^{-1}$) contains modes of the inorganic framework and coupled modes, whereas the individual molecular modes of the organic part are represented in the higher wavenumber region ($500 - 3000 \text{ cm}^{-1}$) [262]. Consequently, only wavenumbers below 500 cm^{-1} have to be considered to distinguish the δ and α -phase of FAPbI_3 .

8.3.1 Perovskite Modes

The hexagonal space group of the δ -phase gives rise to four expected Raman modes in the low-frequency region: Octahedral distortion (35 cm^{-1}), molecular in-plane rotation around a corner H (63 cm^{-1}), molecular out-of-plane rotation around the

N-N axis (90 cm^{-1}) and molecular translation (108 cm^{-1}) [263]. These four distinct modes make the δ -phase easy to identify.

However, the literature is surprisingly inconsistent in the assignment of Raman modes to the α -phase. Han *et al.* were the first to report Raman signatures for both phases, assigning peaks at 111 cm^{-1} and 135 cm^{-1} to the δ - and α -phase, respectively [248]. This assignment has been used in numerous studies [264–266] since, even though the cubic $\text{Pm}\bar{3}\text{m}$ symmetry of the α -phase is predicted to be Raman inactive by group theory. Two recent reports by Driscoll *et al.* [267] and Ibaceta-Jana *et al.* [268] dissent previous assignments and provide experimental data supporting that the α -phase is Raman inactive.

This discrepancy in the literature is surprising, as FAPbI₃ crystals can, once degraded into the δ -phase, be transformed back into the α -phase via heating to temperatures above 145°C (see Appendix Sec. A.3) and α -phase Raman peaks should therefore be easy to identify. The origin of this issue can be found in the experimental details of the Raman measurements. The high absorption coefficient ($1 \times 10^5\text{ cm}^{-1}$ at $E_{\text{laser}} = 2.33\text{ eV}$ [269]) and low thermal conductivity [270] of α -FAPbI₃ make the single crystals sensitive to laser-induced heating. In the presence of oxygen, this has been shown to cause the formation of Raman active PbO_x compounds with a peak at 138 cm^{-1} and a wider two-phonon peak at 276 cm^{-1} [271, 272]. Chemical decomposition of FAPbI₃ single crystals occurs at temperatures above $320 - 360^\circ\text{C}$ (hydrogen iodide) and $375 - 420^\circ\text{C}$ (FA^+) [248, 273]. This results in low wavenumber peaks of lead iodide (PbI_2), polyiodides (I_x^-) and molecular iodine (I_2) in the range of $40 - 110\text{ cm}^{-1}$ [272].

To validate this, we showcase all of these degradation stages on a FAPbI₃ single crystal in Fig. 8.3. Initially, the freshly grown and annealed sample is in the α -phase (Fig. 8.3a). Apart from the laser line background, there is only a small shoulder present at 110 cm^{-1} which we attribute to the presence of traces of PbI_2 which can be formed as a side effect of annealing [272]. No peak is observed at 135 cm^{-1} and we conclude that the α -phase of FAPbI₃ is Raman inactive as predicted by theory.

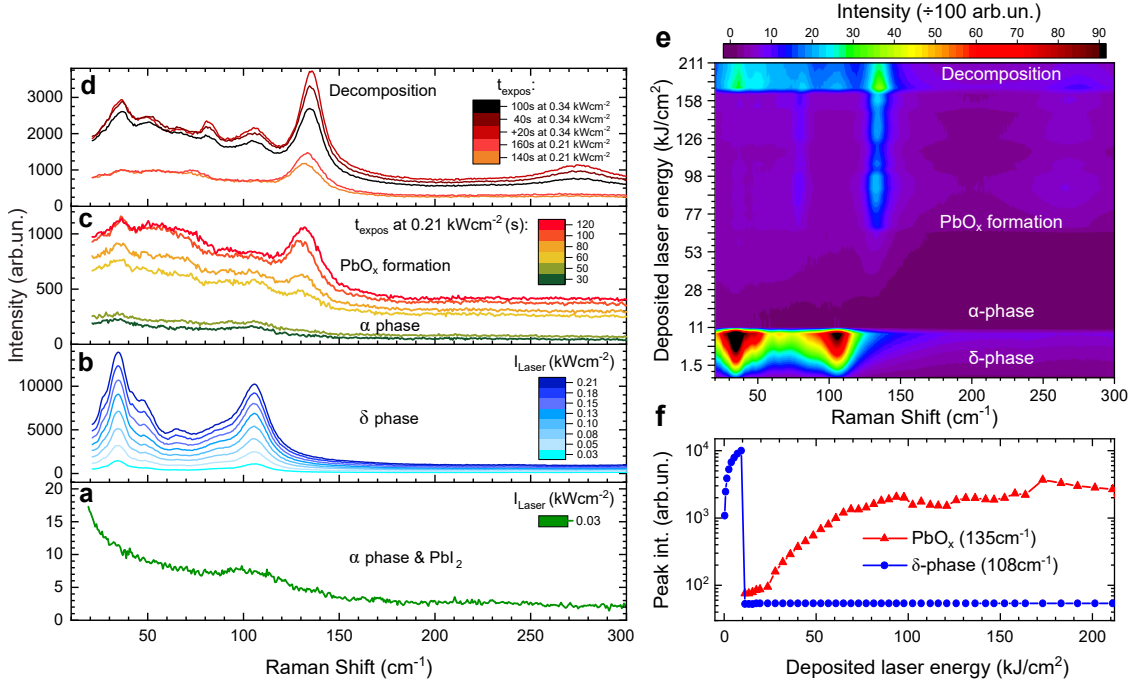


Figure 8.3: Raman spectra of a FAPbI_3 single crystal at different degradation stages. Raman spectra were taken with $2 \times 5 \text{ s}$ exposure time at $E_{\text{laser}} = 2.33 \text{ eV}$ with denoted laser intensities. **a)** In the α -phase, no Raman peaks are present. The wide peak at 110 cm^{-1} is caused by residual PbI_2 . **b)** After 14 days of ambient exposure, the crystal shows a strong δ -phase Raman signature, increasing linearly with the laser intensity. **c)** At a threshold laser intensity of $I_{\text{Laser}} = 0.21 \text{ kWcm}^{-2}$, the Raman intensity is strongly reduced as the crystal surface layer transforms into the α -phase. With continuous exposure at the same laser intensity, the formation of a PbO_x related peak at 135 cm^{-1} can be observed. **d)** The PbO_x peak continues to grow over time at 0.21 kWcm^{-2} . The laser intensity is then further increased to 0.34 kWcm^{-2} . The PbO_x peak intensity decreases as the crystal decomposes and the crystal surface moves out of focus. Further decomposition peaks emerge. **e)** False colour map summarising the data shown in b)-d). The Raman shift is plotted against the cumulative deposited laser energy. **f)** Peak intensity of the strongest δ -phase and PbO_x peaks plotted against the cumulative deposited laser energy.

Raman spectra of the same crystal after ambient exposure for 14 days are given in Fig. 8.3b. The FAPbI_3 crystal has now degraded into the δ -phase and shows the characteristic four peaks. Upon increasing the laser intensity, the Raman intensity of the δ -phase peaks grows linearly.

However, at a threshold laser intensity of 0.21 kWcm^{-2} , we observe a 100-fold intensity drop of the Raman modes (Fig. 8.3c) that happens faster than the 5 s acquisition time used. We assign this to laser-induced heating causing a δ - to α -phase transition. The weak remaining peaks at 35 cm^{-1} and 108 cm^{-1} originate

from the remaining δ -phase in the periphery of the laser spot on the crystal surface that has not reached the phase transition temperature. Apart from this, there are no modes visible, as expected for the α -phase. This shows that the Raman scattering cross-section of the α -phase is at least two orders of magnitude weaker than the δ -phase [264].

Under continuing exposure at the same laser intensity, the PbO_x mode at 135 cm^{-1} becomes visible within 60 seconds of the phase transition. This can be explained by the much higher absorption coefficient of the α -phase, resulting in the laser energy being deposited in a smaller volume of the crystal. About 90% of the laser energy is deposited in the first 200 nm of an α -phase crystal (using $\alpha = 10^5\text{ cm}^{-1}$), resulting in a rapidly increasing temperature in this surface layer and the formation of PbO_x . Note, that due to the low thermal conductivity of FAPbI_3 [270] this is a local effect and limited to a small area around the laser spot on the surface (see next section).

At even higher laser intensities (0.34 kWcm^{-2}), additional modes arise at 36, 50, 67, 82 and 106 cm^{-1} , see Fig. 8.3d. The overall signal intensity decreases over time, a clear indication of decomposition which results in the crystal surface moving out of focus. The additional modes are caused by the formation of PbI_2 , I_x^- and I_2 upon decomposition [272, 274]. Fig. 8.3e provides a visualisation of the laser-induced phase transition and consecutive degradation of the Raman data in Figs. 8.3b-d. In the false-colour map, the Raman shift is plotted against the cumulative laser energy deposited into the single crystal. The peak intensities of the δ -phase peak at 108 cm^{-1} and the PbO_x peak at 138 cm^{-1} are plotted against the cumulative deposited laser energy in Fig. 8.3f. The peak at 108 cm^{-1} was picked over the stronger peak at 35 cm^{-1} as it is less affected by the laserline background. Tracking the peak intensity of these two peaks highlights the drop in Raman intensity when the surface of the crystal is transformed into the α -phase, even on a logarithmic scale.

8.3.2 Defocused Raman Spectroscopy

In the last section, the sensitivity of FAPbI_3 to laser-induced degradation was discussed in detail. This requires the laser intensity to be reduced as far as possible, which can be done by reducing the laser power or, alternatively, increasing the laser spot size on the sample. Lowering the laser power is accompanied by a proportional decrease in Raman signal intensity, such that longer acquisition times are required to maintain sufficient signal-to-noise ratios (SNRs). This is of course no ideal solution, as the longer laser exposure at a lower intensity might still degrade the crystal surface.

Therefore, increasing the laser spot size is the better option. Since the FAPbI_3 samples investigated are all single crystals, the outcome of the Raman measurement is not affected by the spot size. We have increased the spot size from a diameter of $d = 10 \pm 3 \mu\text{m}$ to $d = 65 \pm 5 \mu\text{m}$ by repositioning a focusing lens. The spot size was measured by moving the spot across the edge of a Silicon wafer with a micrometre stage. Our Raman spectrometer consists of two separate optical systems, one to focus the laser onto the sample and the second to focus the scattered light onto the detector. We can thus adapt the optical detection system to the larger focal spot which allows us to retain 50% of the original SNR. Since the area of the defocused spot is about 40 times larger than before, the defocused Raman setup should produce a 20-fold increase in the SNR at the same laser intensity.

To confirm this, we performed Raman measurements on a δ -phase crystal in the defocused setting and gradually increased the laser power, until the Raman response indicated a phase transition into the α -phase, similar to the experiment described in Fig. 8.3b-c. The threshold laser intensity for the δ - to α -phase transition $I_{\text{Laser}} = 0.21 \text{ kWcm}^{-2}$ was found to be the same as before, now occurring at a laser power 40 times higher. In addition, we can now effectively utilise the small laser spot as a probe and move it across the crystal surface that was irradiated with the larger spot, see illustration in Fig. 8.4a. This allows us to sample the Raman response across the large spot on the crystal surface. Since the intensity distribution across a focal spot follows a Gaussian distribution, we can observe the effect of a continuum of laser intensities on the δ -phase FAPbI_3 crystal. The false-colour map in Fig. 8.4b

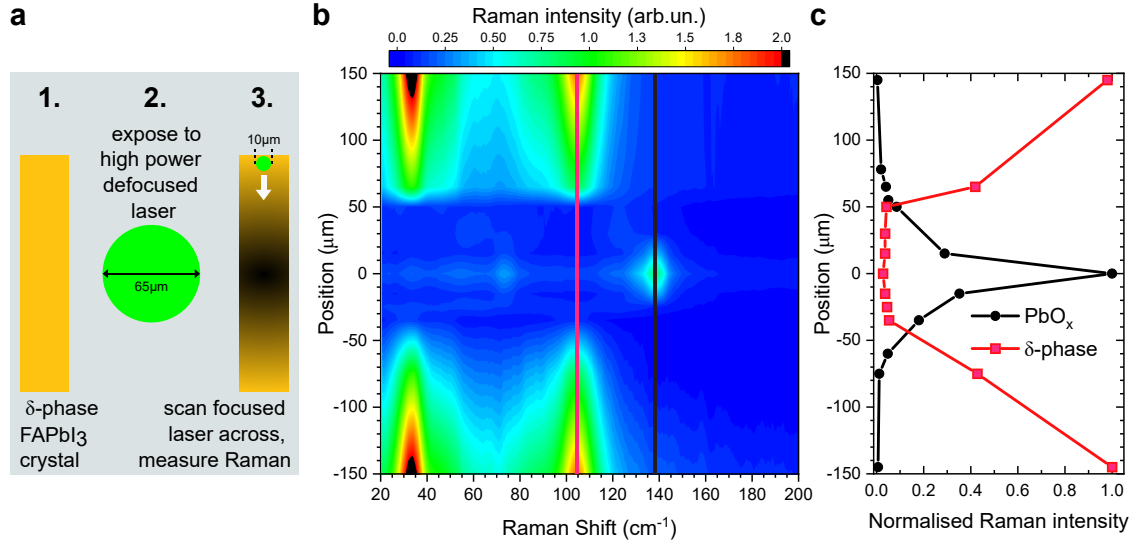


Figure 8.4: Spatial resolution of laser-induced FAPbI_3 phase transition via defocused Raman spectroscopy. a) Working principle. A δ -phase FAPbI_3 single crystal (1.) is exposed to a high-power laser with a defocused focal spot (2.). The laser-induced changes are detected with a low-power focused laser spot via Raman measurements with spatial resolution (3.). b) False-colour plot of the resulting Raman data. Coloured lines highlight the position of modes used in c). c) Raman peak intensities as shown in b) for a δ -phase and a PbO_x mode.

reflects the Raman scattering intensity across the defocused laser spot. Far away from the laser spot, the crystal is still entirely in the δ -phase. Starting at about 150 μm from the spot centre, the δ -phase Raman intensity decreases until it vanishes entirely at 50 μm from the centre. Inside this area with diameter $d = 100 \mu\text{m}$, the crystal is completely transformed into the α -phase. The fact that the transformed area is much larger than the irradiated area suggests laser-induced heating rather than photodegradation as the driving mechanism behind the phase transition, in accordance with previous observations on MAPbI_3 [270].

Towards the centre of the large spot, from about 20 μm out, a strong PbO_x peak emerges at 138 cm^{-1} , see Fig. 8.4c. At the centre of the focal spot, the iodine peaks indicative of crystal decomposition are detected. This shows that the presence of the PbO_x peak is uncorrelated to the phase of the FAPbI_3 sample. At sufficient laser intensity, it can be observed in both α -phase and δ -phase crystals, either, via degrading the α -phase sample directly, or, by first transforming the δ - into the α -phase and then degrading it. The PbO_x peak is thus not suited as

an indicator for the presence of the α -phase.

Even so, the fraction of the crystal that is in the δ -phase can be estimated from the intensity of the δ -phase peaks compared to a perfect δ -phase crystal. In the absence of degradation-related peaks, the missing fraction of the δ -phase peak intensity can be assumed to be in the α -phase. This insight will be used for tracking the phase stability of FAPbI_3 single crystals in the following.

8.3.3 Molecular Modes of the Organic Cation

The 20-fold increase in the Raman signal-to-noise ratio allows us to resolve the much weaker molecular modes of the organic cation without damaging the FAPbI_3 crystals with the defocused laser spot. To our knowledge, this is the first time the FA^+ modes have been resolved via Raman spectroscopy for laser energies above the band gap [264, 265].

There exist four modes of the FA^+ cation that we can detect via Raman spectroscopy, NCN bending (520 cm^{-1}), NH_2 torsion (598 cm^{-1}), CN stretching (1118 cm^{-1}) and NH_2 rocking (1386 cm^{-1}). These modes have been shown to be insensitive to halide mixing in FAPbX_3 perovskites [275] but are sensitive to mixing of the organic A-site cation. In the presence of additional organic cations such as MDA_2^+ or methylammonium (MA^+), we would expect to observe additional Raman peaks in the $500 - 1500\text{ cm}^{-1}$ region [275].

In Fig. 8.5, the organic molecular modes of FAPbI_3 crystals grown with different additives are compared. Details of the single crystal synthesis are given in Sec. 4.1.5. Raman spectra of FAPbI_3 (pristine), $\text{FAPbI}_3\text{-M}$ (3.8%mol MDACl_2), $\text{FAPbI}_3\text{-H}$ (0.63%mol HMTA) and $\text{FAPbI}_3\text{-H-NH}_4\text{Cl}$ (0.63%mol HMTA + 5%mol NH_4Cl) all show the four FA^+ related peaks. No further modes indicating the presence of organic cation mixing are detected at the achieved resolution, suggesting FA^+ as the sole A-site cation. However, we note that at the observed signal-to-noise ratio, cation mixing at the single per cent level would be hard to resolve and this possibility can not be ruled out.

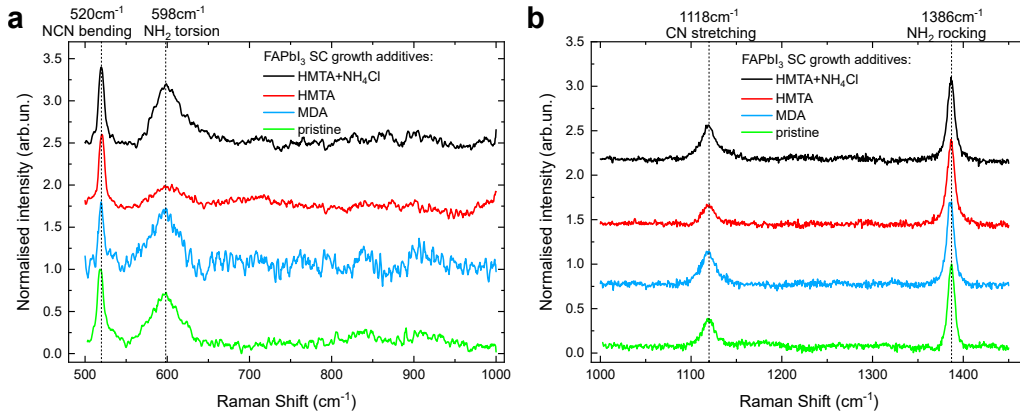


Figure 8.5: Raman spectra of the molecular FA⁺ modes of FAPbI₃ single crystals. Raman spectra of FAPbI₃ (pristine, green), FAPbI₃-M (MDACl₂, blue), FAPbI₃-H (HMTA, red) and FAPbI₃-H-NH₄Cl (HMTA+NH₄Cl, black) in the wavenumber region in which vibrational modes of the organic cation are observed. The spectra are normalised and vertically shifted for the sake of clarity. **a)** In the 500 – 1000 cm⁻¹ region, NCN bending and NH₂ torsion are observed. **b)** At Raman shifts of 1000 – 1450 cm⁻¹, a CN stretching and a NH₂ rocking mode are detected.

8.3.4 Quantifying the Phase Stability of FAPbI₃

We have shown that the Raman scattering cross-section of α -phase FAPbI₃ is at least two orders of magnitude weaker than for the δ -phase. The overall Raman response of any given FAPbI₃ sample will consequently be dominated by δ -phase peaks as soon as a small fraction of the probed layer is degraded. This allows us to track the degraded fraction of the probed surface layer by monitoring the δ -phase peak intensities, even if the crystal is predominantly in the α -phase. We note that peak area is always proportional to the amount of δ -phase present in the crystal and, as is the case here, if peak width is constant then peak intensity correlates directly with peak area.

To quantitatively track the phase stability of crystals grown with different additives, we monitor the absolute Raman intensity of the best resolved δ -phase peak (at a Raman shift of 108 cm⁻¹) under ambient conditions, see Fig. 8.6. Crystals were used directly after growth and consecutive annealing. All spectra were taken on the same crystal and reflect the average of multiple spots on the crystal surface. Crystals were kept in the sample holder of the Raman spectrometer under exposure to ambient air for the duration of the experiment to ensure consistent experimental

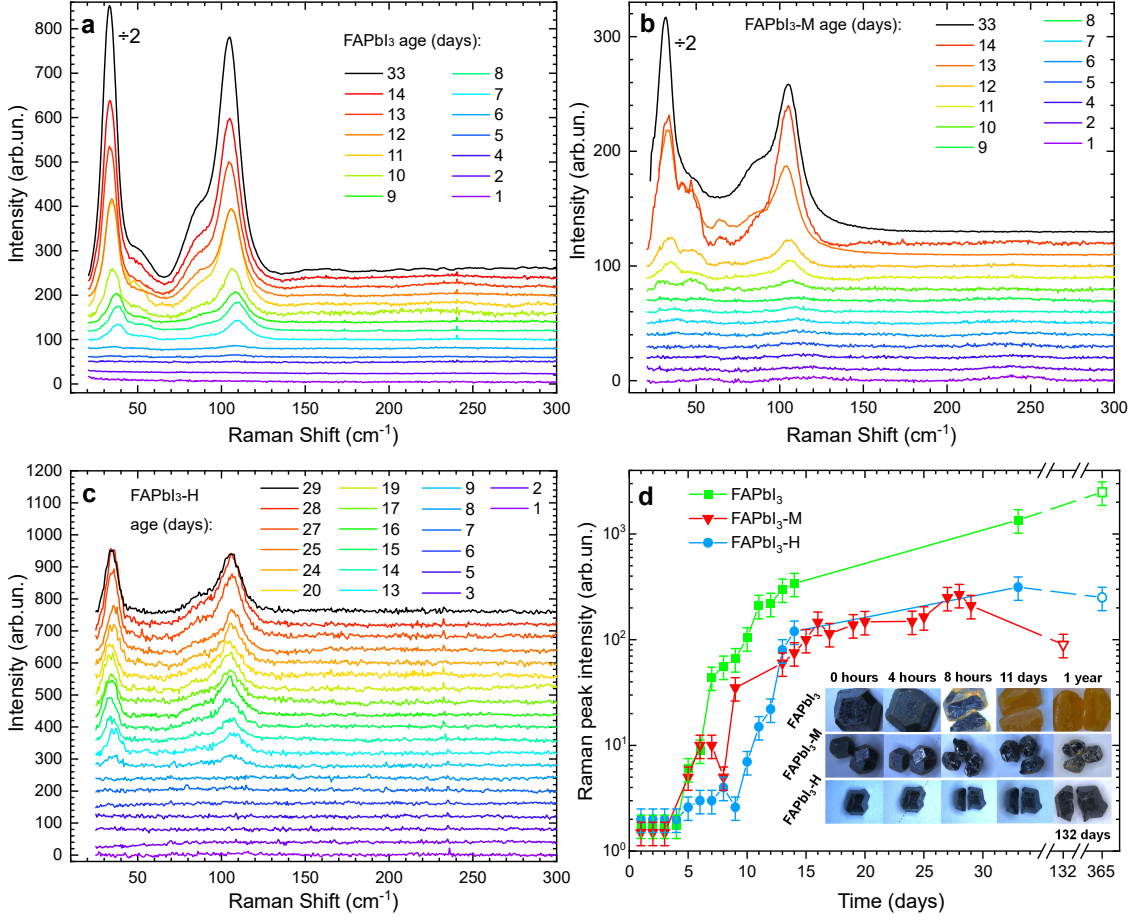


Figure 8.6: Phase stability of FAPbI_3 single crystals with different additives. **a-c)** Raman spectra of neat FAPbI_3 crystals (a) and crystals grown with MDACl_2 ($\text{FAPbI}_3\text{-M}$, b) or HMTA ($\text{FAPbI}_3\text{-H}$, c) additives taken at increasing exposure time to open-air ambient conditions. Crystals were used directly after growth and consecutive annealing. All spectra were taken on the same crystal and reflect the average of multiple spots on the crystal surface. **d)** The peak intensity of the best resolved δ -phase peak at 108 cm^{-1} is plotted against the ambient exposure time on a logarithmic scale. The hollow data points correspond to crystals from the same batches that were stored in air-filled vials for the denoted time. The inset shows photographs of the three types of crystals at various stages of the degradation process. Crystals are of similar size as in Fig. 8.1.

conditions. We observed the formation of the PbO_x Raman peak at laser intensities as low as 25 Wcm^{-2} . The defocused Raman setup allows us to keep the laser intensity in our Raman measurements strictly below 5 Wcm^{-2} .

In addition to crystals grown with the additive MDACl_2 ($\text{FAPbI}_3\text{-M}$, Fig. 8.6b), we performed the same measurements on crystals grown with HMTA ($\text{FAPbI}_3\text{-H}$ Fig. 8.6c) and HMTA + NH_4Cl , since these are the molecules MDACl_2 degrades into when put in solution (see Sec. 8.2). The addition of ammonium chloride

caused rapid degradation of crystals into the δ -phase and the experiment was thus aborted after 5 days (data not shown). We hypothesize that this is related to the easily degradable nature of ammonium and conclude that the single crystal stability improvement is not driven by ammonium.

Neat FAPbI₃ (Fig. 8.6a) undergoes detectable δ -phase formation after 7 days. This onset occurs after 9 and 10 days for FAPbI₃-M and FAPbI₃-H, respectively (Fig. 8.6b). After 30 days, the δ -phase peak intensity of $1.4 \pm 0.4 \times 10^3$ counts is about 5 times higher for the neat FAPbI₃ crystal than for both FAPbI₃-M and FAPbI₃-H. This suggests that while neat FAPbI₃ is nearly entirely degraded into the δ -phase, for the other two crystals merely a fraction of the surface layer is degraded.

In Raman spectra of crystals from the same batch that were stored for 1 year in air-filled vials we detect $(2.5 \pm 0.5) \times 10^3$ and $(0.25 \pm 0.06) \times 10^3$ δ -phase peak counts for FAPbI₃ and FAPbI₃-M respectively.

The peak intensity is directly proportional to the fraction of the probed surface layer in the δ -phase. In a predominantly α -phase crystal, Raman scattering is detected from the top 100 nm only, since the scattered photons have to travel back to the surface. Thus, the onset of the δ -phase peak in Fig. 8.6 corresponds to the degradation of only the top surface of the crystals. We obtain complementary degradation data of the bulk crystal by carrying out the same Raman measurement on the inside of freshly cleaved crystals.

Cleaving a FAPbI₃-M crystal after 285 days of ageing in air-filled vials gives a peak intensity ratio of $I_{bulk}/I_{surface} = 0.10 \pm 0.03$ for the δ -phase peak. This confirms that the observed δ -phase formation occurs in only a thin surface layer of FAPbI₃-M crystals, while the bulk remains largely unaffected. By contrast, the neat FAPbI₃ crystal is entirely converted to the δ -phase.

The peak splitting in the broad δ -phase peaks at 55 cm^{-1} and 83 cm^{-1} that occurs in some of the FAPbI₃-M spectra in Fig. 8.6b indicates a structural change within the δ -phase [268]. The peak splitting has been observed in all crystal types independent of additives and does not affect the peak at 108 cm^{-1} used in our analysis.

Notably, the $\text{FAPbI}_3\text{-H}$ crystals demonstrate a similar stability improvement to $\text{FAPbI}_3\text{-M}$. This confirms our NMR results, suggesting that the stability improvement is not based on alloying of MDA^+ or MDA^{2+} with FA^+ .

8.4 Single Crystal Optoelectronic Characterisation

Just as important as improving the stability of FAPbI_3 is to make sure that the extraordinary properties of this material are not lost in the process of doing so. In this section, we compare the optical and electronic properties of FAPbI_3 single crystals grown with and without additives.

First, the impact of MDACl_2 on the charge transport through the single crystals was investigated via pulsed-voltage space-charge-limited-current (PV-SCLC) measurements. These PV-SCLC measurements were performed by Elisabeth Duijnste in the group of Henry Snaith, details are described elsewhere [276, 277].

For this purpose, gold electrodes were deposited on the crystals and the dark current-voltage (JV) characteristics were measured under vacuum, see Fig. 8.7a.

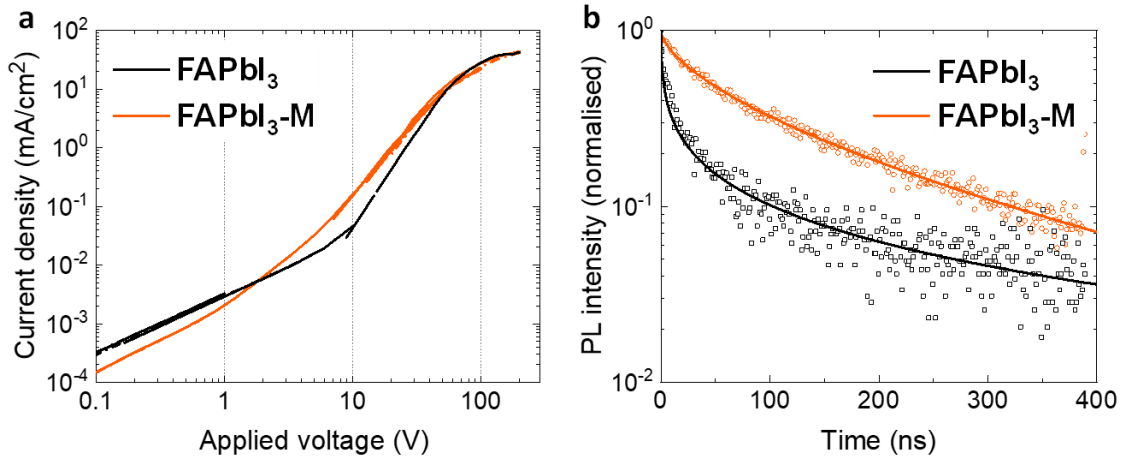


Figure 8.7: Pulsed-voltage space-charge-limited-current (PV-SCLC) and time-resolved Photoluminescence (TRPL) measurements on FAPbI_3 and $\text{FAPbI}_3\text{-M}$ single crystals. **a)** Two regimes with different slopes are observed for both samples, linear fits are shown for both regimes. The onset voltage of the higher slope is used to calculate a lower bound for the trap density of the crystal. **b)** TRPL decay curves are fitted with stretched exponentials in line with [278, 279]. PV-SCLC and TRPL experiments were conducted and analysed by collaborators E. Duijnste and A. Wright, respectively.

The pulsed JV traces of both samples show an Ohmic region at low voltages, where the slope, $m = \frac{d(\log(J))}{d(\log(V))} = 1$. From this region, the dark DC conductivity of FAPbI₃ and FAPbI₃-M crystals can be estimated to 8.5×10^{-6} S/m and 5.3×10^{-6} S/m, respectively. The slope of the JV curve increases to $m > 2$ if the trap density is larger than the density of static ionic space charge [276, 277, 280]. From the voltage point at which this occurs, (V_{onset}), we can calculate a lower bound trap density (n_t) via

$$n_t = \frac{2V_{\text{onset}}\epsilon_0\epsilon_r}{eL^2} \quad (8.1)$$

where ϵ_0 is the vacuum permittivity, L is the crystal thickness, e is the electron charge and ϵ_r is the low-frequency dielectric constant of the material, reported as 49.4 for FAPbI₃ [248]. We assume the same value of ϵ_r for FAPbI₃-M. We find that adding MDACl₂ to the precursor solution significantly reduces the trap density, from a lower bound of $1.1 \times 10^{12} \text{ cm}^{-3}$ for FAPbI₃ to $4.3 \times 10^{10} \text{ cm}^{-3}$ for FAPbI₃-M. The trap density of FAPbI₃-M is more than an order of magnitude lower than reported literature values [248].

The superior optoelectronic quality of FAPbI₃-M single crystals is supported by time-resolved photoluminescence (TRPL) measurements (Fig. 8.7b) performed by Adam Wright. Fitting the TRPL decay reveals a significant increase in lifetime from 47 ns for the FAPbI₃ single crystal to 121 ns for the FAPbI₃-M single crystals. Data was acquired at a fluence of 18 nJ cm^{-2} and fitted with a stretched exponential [278, 279].

To measure the band gap of single crystals, absorbance measurements are typically not an option due to their large thickness. PL measurements of perovskites are prone to be affected by trap-assisted emission shifting the PL peak downwards in energy. This effect was observed in our samples as well and we thus chose to use reflectivity measurements to determine the band gap as described in Sec. 2.1.3.

The normalised reflectance data of neat FAPbI₃, FAPbI₃-M and FAPbI₃-H is given in Fig. 8.8a. The spectra are normalised and vertically shifted for the sake of clarity. In Fig. 8.8b, the normalised energy derivative of the reflectance $-dR/dE$

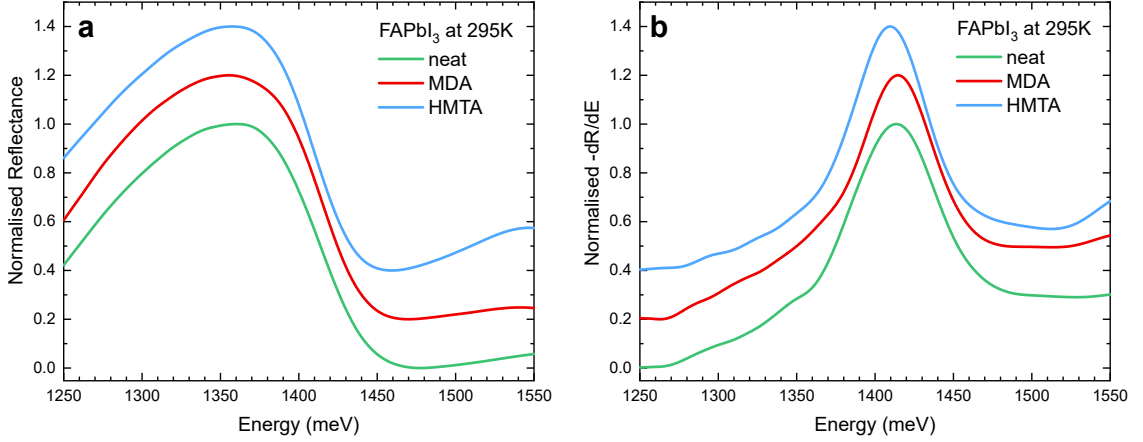


Figure 8.8: Reflectivity Measurements of FAPbI_3 single crystals to determine the band gap. Spectra are vertically shifted for the sake of clarity. **a)** Normalised reflectance of neat FAPbI_3 , FAPbI_3 -M (MDA) and FAPbI_3 -H (HMTA). **b)** Normalised negative energy derivative of the data shown in a). The peak indicates the position of the band gap.

is plotted against energy. The position of the peak provides a good estimation of the sample band gap. This yields $E_g = 1413 \pm 3 \text{ meV}$, $E_g = 1414 \pm 3 \text{ meV}$, and $E_g = 1410 \pm 3 \text{ meV}$ for FAPbI_3 , FAPbI_3 -M and FAPbI_3 -H, respectively. The errors reflect the precision of the peak position and the accuracy of the energy axis calibration. The three results agree with each other within their error range. This confirms that the addition of both MDACl_2 and HMTA does not affect the band gap of the resulting FAPbI_3 single crystals.

8.5 Summary

In this chapter, we have studied the effect of the additive MDACl_2 on FAPbI_3 single crystals. In NMR experiments, we demonstrate that MDACl_2 is unstable in solution and leads to the formation of NH_4^+ and HMTA-H^+ in an 8:1 ratio. This suggests that the beneficial effects of MDACl_2 do not originate from A-site alloying of MDA^{2+} , as was previously suggested [138, 253]. This was confirmed by reproducing the beneficial effects of the MDACl_2 additive by adding HMTA instead.

Further, we demonstrate that Raman spectroscopy is a powerful tool for the characterisation of FAPbI_3 if applied correctly. By devising the defocused Raman spectroscopy method, we achieve a 20-fold increase in the signal-to-noise ratio

that allows us to study both the molecular modes of the organic cation and the perovskite modes without the risk of laser-induced damage to the samples. We deploy this method to quantify the phase stability of FAPbI₃ crystals grown with different additives and demonstrate that the addition of MDACl₂ and HMTA both lead to significant improvements of the α -phase stability under ambient conditions from several days to over 1 year.

Finally, we compare the electronic and optical properties of the different FAPbI₃ crystals. We find that the MDACl₂ additive reduces the trap density significantly from $1.1 \times 10^{12} \text{ cm}^{-3}$ for FAPbI₃ to $4.3 \times 10^{10} \text{ cm}^{-3}$ for FAPbI₃-M. The lifetime of excited carriers is increased from 47 ns to 121 ns by the MDA additive, while the band gap at room temperature appears at $1414 \pm 4 \text{ meV}$ and does not seem to be affected by the addition of MDACl₂ or HMTA.

9

Conclusion & Outlook

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This final chapter summarises the findings presented in this thesis, puts them into a broader perspective, and provides an outlook of possible future developments.

9.1 Brightly Fluorescent States in Molecular GNRs

Chapter 5 covered the investigation of 4-cove-edged graphene nanoribbons via optical spectroscopy. The molecular-like resolution of the optical states seen in these GNRs is made possible by bulky *N*-*n*-octadecylmaleimide side groups and has not been previously achieved. The NOMI-GNRs demonstrate strong Franck–Condon coupling to radial breathing-like (31.6 meV) and G-mode (200 meV) phonons and a weaker, temperature-independent, Herzberg–Teller coupling. The variation of the band gap energy with temperature is driven by internal coupling to the RBLM phonon rather than thermal expansion and exciton lifetimes are limited by defects and finite-size effects rather than phonon scattering. We detect the brightening of a

previously dark excitonic state located 6 meV below the bright excitonic state. This previously dark state carries about four times as much spectral weight as similar dark excitons in carbon nanotubes and is thus labelled *twilight state*. The newly observed twilight states lead not only to high PL efficiency (7.7% PLQE) but also to a superior resolution of the spectral features, offering access to the fundamental optical processes that is unprecedented in extended carbon nanostructures. Notably, this is achieved both in solutions and thin films, as relevant for devices. The chemical versatility of GNRs is also significant, allowing the efficiency and spectral optical response to be tuned chemically. Moreover, the GNR side groups can be modified to bind to biological structures or bear quantum coherent units, making these systems an exceptionally versatile optical platform.

Overall, the higher accessible quantum yield enabled by twilight states and the versatility of graphene nanoribbons make them a promising material for future applications in bio-imaging, optoelectronics and quantum technologies. The outstanding spectral resolution and distinct presence of the zero-phonon line open up the pathway to further investigations of graphene nanoribbons, for example of the excitonic structure in high magnetic fields or in different chemical environments. We are currently considering several follow-up studies to this project.

9.2 CNT-EVA Transparent Conductive Films

Chapter 6 presents a detailed study of the connection between processing and optoelectronic properties of carbon nanotube–ethylene-vinyl acetate thin films. The dispersion technique and polymer removal steps were identified as crucial steps for improving TCF performance, allowing deposition of connected films as thin as 5 nm, corresponding to 95% transmittance that have sheet resistances of about $4000 \Omega/\square$. Changing the composition of the EVA copolymer allows tuning the mechanical and chemical resilience of the resulting CNT-EVA films while leaving the TCF performance unaffected. Exposing CNT-EVA films to repeated bending and folding strain leads to small increases in the sheet resistance, following a logistic function with upper bounds below two times the initial resistance for all samples.

Finally, several halogenated metals were tested for their ability to chemically p-dope the SWCNT-EVA films. While gold chloride-based dopants performed best, several low-cost alternatives such as copper chloride and nickel chloride could be identified and a correlation between the electron affinity of the dopant metal and the dopant performance was found.

The advances made in this chapter led to a 100-fold improvement of the electrical conductivity at a given transmittance in CNT-EVA films compared to the best results previously reported. This lays the groundwork for the large-scale application of low-cost CNT-EVA conductive films. Since they can be synthesised from cheap abundant materials, and even carbon waste, CNT-EVA films can reduce the environmental impact of conductive films and contribute to a more circular economy.

Further research into the interactions between CNTs and EVA polymer could lead to a deeper understanding of the wrapping process that ultimately allows the solubilisation of the nanotubes. This could help identify greener solvents, achieve higher performances, and lead to the isolation of monochiral SWCNTs on a large scale.

9.3 Applications of SWCNT-EVA Films

Chapter 7 demonstrated that the improved TCF performance makes SWCNT-EVA films suitable for transport layers in solar cells and transparent touch-sensitive applications. We demonstrated a touch sensor with 4x4 pixels and identified a linear relationship between the sheet resistance and the signal-to-noise ratio of the touch sensing that can be used to determine a threshold film thickness. Working touch-sense devices were produced with SWCNT-EVA films at 95% transmittance and film thicknesses less than 10 nm.

In addition, SWCNT-EVA films were deployed in the hole transport layer of perovskite solar cells. Tuning the CNT-EVA layer thickness and adding an additional top layer of PMMA reduced shunting and boosted the stabilised PCE to 17.9%, the highest value achieved with CNT-EVA films to date. We found that in combination with the hole-selective polymer spiro-OMeTAD, SWCNT-EVA films

provide effective hole extraction from the absorber layer and have the potential to replace the short-lived Lithium based dopants of spiro-OMeTAD that are currently used. These results highlight the potential of hybrid transport layers that combine a highly conductive with a highly charge-selective material, bringing the potential for cost reduction and stability improvements.

This chapter demonstrated the applicability of CNT-EVA films and their tremendous potential for large-scale usage. As the next steps towards this goal, up-scaling of the solution batch size from currently 200 ml to 2000 ml and prototype testing for conformity with industry standards such as IEC 62908-12-20:2019 for touch screens are planned.

9.4 The Effect of Additive MDACl₂ on FAPbI₃

In chapter 8, we studied the effect of the additive MDACl₂ on FAPbI₃ single crystals. In NMR experiments, we demonstrate that MDACl₂ is unstable in solution and the beneficial effects of MDACl₂ do not originate from A-site alloying of MDA²⁺, as was previously suggested. This was confirmed by reproducing the effects of the MDACl₂ additive by adding degradation product HMTA instead. Further, we establish Raman Spectroscopy as a powerful tool for the quantitative characterisation of the phase stability of FAPbI₃ by devising the defocused Raman spectroscopy method. This achieved a 20-fold increase in the signal-to-noise ratio that allows us to study both the molecular modes of the organic cation and the perovskite modes without the risk of laser-induced damage to the samples. With this method, we demonstrated that the addition of MDACl₂ and HMTA both lead to significant improvements of the α -phase stability from several days to over 1 year.

While the mechanism behind the stabilising effect of MDACl₂ remains a key point of current research, we established that the additive does not impede PV device-relevant optoelectronic properties. The MDACl₂ additive reduced the trap density and increased the excited carrier lifetime significantly, whereas the band gap at room temperature appears at 1414 ± 4 meV independent of the addition of MDACl₂ or HMTA.

Finding ways to stabilise perovskites under ambient conditions is the main challenge to overcome before they can be applied on a large scale. Characterisation techniques that can distinguish different crystal phases non-destructively during ageing studies are an important tool for this process. Defocused Raman scattering offers a solution that can be extended to other perovskites and materials prone to laser-induced degradation in general in the future.

Appendices

A

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A.1 Franck–Condon Modelling of NOMI-GNRs

Franck–Condon modelling was performed according to previous studies [281, 282]. The intensity of a single FC progression coupled to a single phonon mode is calculated as

$$I(\hbar\omega) \propto (\hbar\omega)^3 e^{-S_i} \sum_{v_i} \frac{S_i^{v_i}}{v_i!} \Gamma(\hbar\omega - E_0 + v_i \hbar\omega_i) \quad (\text{A.1})$$

with the intensity I , the photon energy $\hbar\omega$, the Huang-Rhys factor S , the 0-0 transition energy E_0 (E_{ZPL}), phonon energy $\hbar\omega_i$, and the line shape function Γ , which is assumed to be Gaussian. For our material, the optical response can be modelled with the RBLM and G phonons as well as the zero-phonon line, see Fig. A.1.

Note that the model does not include emission above or absorption below the ZPL energy which is thus excluded. In addition, the PL data contains a wide Gaussian

contribution from low energy emission due to defects and excimers. Similarly, the absorption has an additional wide Gaussian contribution at higher energies and a narrow Gaussian representing the second interband transition E_{21} . Results of the modelling are given in Tab. A.1 and Tab. A.2.

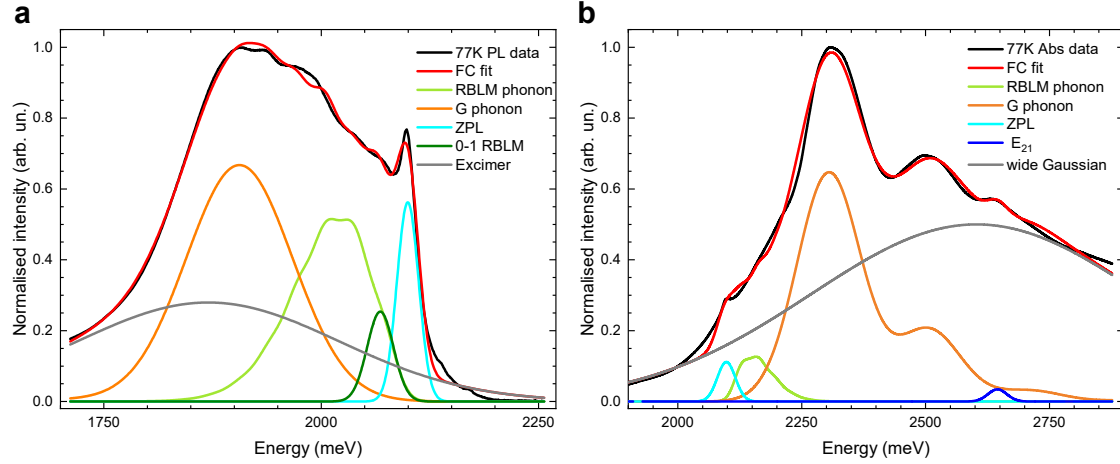


Figure A.1: Franck–Condon modelling of NOMI-GNR at 77 K. a) Photoluminescence spectrum excited with 2.33 eV excitation together with the Franck–Condon model and its individual contributions. **b)** Absorption spectrum and Franck–Condon model results.

Table A.1: Franck–Condon modelling results for 77 K PL data.

PL contribution	A	centre (meV)	S	σ (meV)
ZPL	0.63	$X_0 = 2100$		13
RBLM	0.32	X_0	3.4	17
G	0.26	X_0	0.66	57
0-1 RBLM	0.23	$X_0 - 31.6$		16
Excimer	0.30	1844		62

Table A.2: Franck–Condon modelling results for 77 K absorption data.

Abs contribution	A	centre (meV)	S	σ (meV)
ZPL	0.25	$X_0 = 2089$		20
RBLM	0.07	X_0	1.88	15
G	0.20	X_0	0.78	71
E_{21} peak	0.08	2629		29
Wide Gauss	0.35	2739		300

A.2 Small-Angle Neutron Scattering (SANS)

SANS data was analysed in SASView [283]. Initial Porod plot ($\log(Q)$ vs $\log(I)$) analysis showed one or two linear regions, pointing to a hierarchical, fractal system. Similar systems also displaying fractal behaviour [214] are often described in terms of the multiscale Beaucage model [284, 285]. We were not successful in applying this model due to the four different fitting parameters per level making the physical interpretations of the fit values difficult and the investigated Q range not covering the low Q Guinier regime. Instead, data showing one linear regime was fitted as a power law

$$I(q) = \text{scale} \cdot q^{-P} + \text{background} \quad (\text{A.2})$$

where P is the Porod exponent and the scale and background are empirical fitting parameters. The background of fits was determined by fitting a constant value for the intensity between $1\text{-}3 \times 10^{-1} \text{ \AA}^{-1}$. Scattering data showing two linear regimes were fitted as

$$I(q) = \begin{cases} A q^{-P} + \text{background}, & q \leq q_c \\ B q^{-P_{\text{high}Q}} + \text{background}, & q > q_c, \end{cases} \quad (\text{A.3})$$

where P , $P_{\text{high}Q}$ are the Porod exponents, q_c the cross over point between the regimes and A and B are scaling constants with $B = A q_c^{P_{\text{high}Q}} / q_c^P$ to ensure the values match at the boundary. Reported parameter uncertainties correspond to those calculated by the DREAM algorithm which is used for fitting.

A.3 High-Temperature PL of FAPbI₃

The temperature of the δ - to α -phase transition was reported as 125° C [37, 286] and 110° C [268] recently, but values as low as 77° C [287] and high as 185° C [248] have been reported. This large discrepancy was assigned to differences in the kinetics of the methods used as well as the respective synthesis ramp rate [288].

We measured the phase transition temperature in temperature-dependent PL measurements, see Fig. A.2. The temperature was ramped up at a rate of 5 K/min.

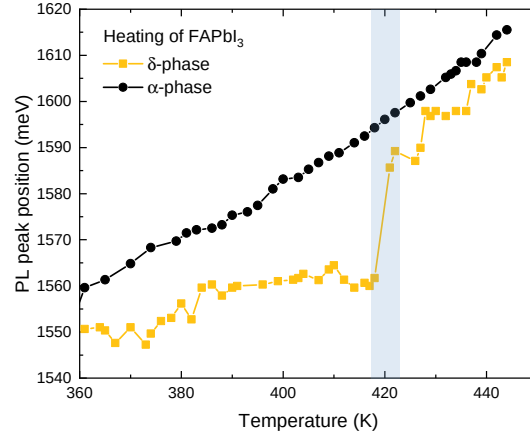


Figure A.2: Photoluminescence peak position of FAPbI_3 single crystals in the δ - and α -phase upon heating. A shift in the δ -phase sample can be observed at 420 K indicating the transformation into the α -phase.

The PL peak position of the δ -phase FAPbI_3 crystal shifts upwards in energy sharply at 420 K, following the behaviour of the α -phase sample at higher temperatures. We conclude that the phase transition occurs at 420 K in our FAPbI_3 single crystals.

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