

DISSERTATION

Titel der Dissertation

"Photoluminescence studies on double-walled carbon nanotubes:

Filling with long linear carbon chains and extraction of inner tubes."

Verfasser Mag. Philip Rohringer

angestrebter akademischer Grad Doktor der Naturwissenschaften (Dr. rer. nat.)

Wien, 2014

Studienkennzahl It. Studienblatt:A 791 411Dissertationsgebiet It. Studienblatt:PhysikBetreuerin / Betreuer:Univ.-Prof. Mag. Dr. Thomas Pichler

"I may not have gone where I intended to go, but I think I have ended up where I needed to be."

> Douglas Adams, The Long Dark Tea-Time of the Soul

Abstract

In this thesis, double-walled carbon nanotubes were investigated as they combine the outstanding properties of both multi-walled and single-walled nanotubes, e.g. shielding of the inner tube from external influences. Such a shielding can be used for example for the growth of very small inner tubes that are very hard to obtain when grown as single-walled carbon nanotubes. On the other hand, the optical properties of the inner tubes are heavily influenced by the presence of an outer tube although they are not completely suppressed as many studies have shown. Especially the basic capability of inner tubes to exhibit photoluminescence is highly debated, since tubetube interactions are believed to prohibit fluorescence from inner tubes and that any measured photoluminescence signal comes from single-walled carbon nanotubes abundant as impurities in the sample. An obvious problem in the whole debate is the high variation of methods for the sample preparation, preventing an objective comparison of different studies.

To resolve this question, samples of double-walled carbon nanotubes made from the same synthesis procedure were solubilized in different ways. Differing observations reported in the literature could be reproduced very well, confirming that the optical response from a sample of double-walled carbon nanotubes strongly depends on the sample preparation. By applying density gradient ultracentrifugation to solutions of carbon nanotubes, inner tubes can be extracted from their outer tube hosts. However, this process is also highly dependent on the sonication power used when solubilizing the sample, as a low sonication power only cuts small nanotubes, whereas bigger tubes stay uncut. Consequently, only inner tubes from cut nanotubes are extracted. The photoluminescence quantum yield of double-walled carbon nanotubes was found to be very low, 50 times weaker than their single-walled counterpart, indicating strong nonradiative exciton relaxation pathways.

Another approach to further support the assignment of photoluminescence from doublewalled carbon nanotubes to their inner tubes is to use filling of double-walled carbon nanotubes as a tool to selectively enhance the photoluminescence intensity of specific tubes. This aspect is based on two recent studies performed in our group: Firstly, the optical properties of singlewalled carbon nanotubes can be altered by filling them with ferrocene. The photoluminescence intensity of the tubes is increased, depending on their diameter. The inner tubes of double-walled carbon nanotubes are too small to contain ferrocene but they can be used as nanoreactors to stabilize linear carbon chains (polyynes). In the second study we showed that these long linear carbon chains inside the double-walled carbon nanotubes can be grown with very high yield and up to 150 carbon atoms being linked together. This filling with polyynes as long as possible is another focus of our group's current research and I contributed in the optimization of the growth parameters.

For this PhD study, I analyzed how charge transfer and growth yield of the carbon chains can influence the photoluminescence response of different inner tubes. By a combination of Raman, optical absorption and photoluminescence spectroscopy it was found that the amplification of the photoluminescence intensity compared to non-filled samples is highly correlated with the length distribution of carbon chains and it is also diameter dependant. The maximum of the amplification was seen (8,3) inner tube species with a diameter of $d_t = 0.78$ nm when being annealed at 1400 °C and the intensity of these tubes is up to 6 times stronger than for untreated tubes. This is attributed to a local charge transfer from the carbon chains to the inner tubes of the double-walled carbon nanotubes that reduces the number of nonradiative pathways for the exciton relaxation, therefore increasing the photoluminescence quantum yield. These findings may contribute in the developement of optoelectronic devices such as solar cells based on nanotubes or in the application of nanotubes as contrast agents for biological imaging.

Zusammenfassung

Diese Arbeit beschäftigt sich mit doppelwandigen Kohlenstoff-Nanoröhren, welche die herausragenden Eigenschaften von mehrwandigen und einwandigen Nanoröhren verbinden, da die äußere Röhre die Innere vor externen Einflüssen schützt. Solch eine Abschirmung kann zum Beispiel für das Wachstum sehr dünner Nanoröhren genützt werden, deren Synthese als einwandige Nanoröhre nur schwer durchzuführen ist. Auf der anderen Seite wiederum werden die optischen Eigenschaften der inneren Röhren maßgeblich durch die äußeren Röhren beeinflusst. Speziell die Frage, ob innere Röhren Photolumineszenz zeigen können, wird seit Jahren heftig debattiert. Wechselwirkungen zwischen den beiden Nanoröhren sollen verantwortlich sein, dass Fluoreszenz von inneren Röhren nicht stattfinden kann und dass jegliche gemessene Photolumineszenz tatsächlich von einwandigen Nanoröhren stammt, die als Verunreinigungen in Probe vorhanden sein können. Ein offensichtliches Problem in der Einschätzung dieses Problems liegt bei den vielen, sehr unterschiedlichen Methoden, wie Kohlenstoff-Nanoröhren hergestellt beziehungsweise in Lösung gebracht werden, was einen objektiven Vergleich der Studien zu diesem Thema unmöglich macht.

Um dieser Frage nachzugehen wurden Proben aus doppelwandigen Kohlenstoff-Nanoröhren, welche mit der selben Synthesemethode hergestellt wurden, auf verschiedene Arten in Lösung gebracht. Die erwähnten unterschiedlichen Resultate in der Literatur konnten reproduziert werden, was die Abhängigkeit der optischen Eigenschaften der inneren Röhren von der Probenpräparation bestätigt. Durch die Anwendung von Dichtegradienten-Zentrifugierung auf Lösungen von doppelwandigen Kohlenstoff-Nanoröhren können die inneren Röhren aus den äußeren Röhren extrahiert werden. Dieser Prozess hängt stark von der vorausgehenden Ultraschallbehandlung der Nanoröhren ab. Niedrige Ultraschallleistung bewirkt, dass dünne Nanoröhren zwar geschnitten werden, größere und daher stabilere Nanoröhren aber nicht. Dies wiederum führt dazu, dass nur diejenigen inneren Röhren extrahiert werden können, deren Durchmesser gering ist. Des weiteren konnte gezeigt werden, dass die Effizienz der Photolumineszenz von doppelwandigen Nanoröhren etwa 50 mal niedriger ist als jene von einwandigen Nanoröhren. Daraus folgt, dass es in diesem Fall wesentlich mehr nicht-radiative Zerfallskanäle für die beteiligten Exzitonen gibt.

Ein alternativer Ansatz um Photolumineszenz von inneren Röhren nachzuweisen besteht darin, diese zu füllen um so selektiv die Intensität von Nanoröhren zu verstärken. Diese Herangehensweise basiert auf zwei kürzlich durchgeführter Studien unserer Arbeitsgruppe: Erstens konnte gezeigt werden, dass die optischen Eigenschaften von einwandigen Kohlenstoff-Nanoröhren modifiziert werden, wenn sie mit Ferrozen gefüllt werden. Abhängig von ihrem Durchmesser wird die Intensität der Photolumineszenz erhöht. Die inneren Röhren von doppelwandigen Kohlenstoff-Nanoröhren sind zwar zu eng um sie mit Ferrozen zu füllen, allerdings können sie als Reaktoren für das Wachstum von linearen Kohlenstoffketten (Polyyne) eingesetzt werden. In einer zweiten Studie konnte unsere Gruppe zeigen, dass auf diese Art Kohlenstoffketten in groer Anzahl hergestellt werden und diese aus bis zu 150 miteinander verbundenen Kohlenstoffatomen bestehen können. Das Füllen von doppelwandigen Kohlenstoff-Nanoröhren mit Polyynen maximaler Länge ist ein weiterer Forschungsschwerpunkt unserer Arbeitsgruppe und mein Anteil bestand in der Optimierung der Parameter für das Kettenwachstum.

Für diese Doktorarbeit analysierte ich, wie Ladungstransfer und Wachstumsrate der linearen Kohlenstoffketten die Photolumineszenzeigenschaften von verschiedenen inneren Röhren beeinflussen. Mit Hilfe von Raman-, Absorptions-, und Photolumineszenzspektroskopie konnte ich nachweisen, dass die Verstrkung der Intensität der Photolumineszenz im Vergleich zu nicht gefüllten Nanoröhren stark mit der Längenverteilung der Polyyne zusammenhängt und dass diese Verstärkung vom Durchmesser der Nanoröhren abhängt. Das Verstärkungsmaximum konnte bei den (8,3) inneren Röhren ausgeheizt bei 1400 °C beobachtet werden und die Lumineszenz dieser Spezies ist bis zu 6 mal höher als jene der ungefüllten Nanoröhren. Dies kann durch einen lokalen Ladungstransfer von den Ketten zu den inneren Röhren erklärt werden, was bewirkt, dass die Anzahl der nicht strahlenden Zerfallskanäle für Exzitonenrelaxation reduziert wird und somit die Effizienz der Photolumineszenz erhöht wird. Diese Erkenntnisse können Eingang finden in der weiteren Entwicklung optoelektronischer Bauelemente wie zum Beispiel Solarzellen basierend auf Nanoröhren oder im Einsatz von Nanoröhren als Kontrastmittel für bildgebende Verfahren im biologischen oder medizinischen Bereich.

Acknowledgements

This thesis could not have been accomplished without the help of several people. First of all I am very grateful to Professor Thomas Pichler who gave me the opportunity to work in the prosperous field of carbon nanotube research and also for his advice throughout the years. Being part of the "Electronic Properties of Materials" group was a fascinating experience that is barely explainable in just a few words. My sincerest appreciation I give to my fellow PhD colleagues Markus, Georgina, Lei, Antonio, Julio, Georg, Carlos, Oleg and Filippo who not only were colleagues but became true friends during this interesting venture. I also want to thank Paola, Hide, Feri, Toma and Jani for fruitful discussions and of course Stefan, Andreas and Eva, without whom basically nothing would work in our group.

To Professor Kazuhiro Yanagi I am truly thankful as he gave me the privilege of working in his laboratory at the Tokyo Metropolitan University. From him I learned an inconceivable amount of knowledge on the preparation of solubilized nanotube samples and the separation of carbon nanotube species.

My sincerest appreciation belongs to my family, especially to my parents Christa and Wolfgang Rohringer, as their unconditional support throughout the studies helped me in achieving my goals.

I feel extremely lucky to have so many great friends and it needs to be said that I am thankful for all the time, thoughts and laughs we shared. Vielen herzlichen Dank to Christian, Leni, Lena, Bernhard, Uwe, Marlene and Sonja! A special Danke schön belongs to Johanna Aigner who not only believed in me and supported me in these years, but who has the miraculous gift to ask precisely the right questions that are both challenging and inspiring at the same time.

In the course of researching for this thesis I had the chance to work, meet and spend time with many interesting people from all over the world. I am deeply grateful for this experience and it is hard for me to grasp the whole magnitude of this great opportunity. All I can say is

Gracias, Xièxiè, Arigatō, Köszönöm, Kiitos, Grazie, Merci, Spasibo, Danke!

Contents

Acknowledgements vi			vii	
\mathbf{C}	ontei	nts	ix	
\mathbf{Li}	st of	Figures	xiii	
A	bbre	viations and Nomenclature	$\mathbf{x}\mathbf{v}$	
1	Inti	roduction	1	
	1.1	Motivation and goals	1	
	1.2	Carbon in nature and science	3	
	1.3	Carbon nanotubes: Overview	5	
		1.3.1 Structural parameters of nanotubes	5	
		1.3.2 Band structure of single-walled carbon nanotubes	7	
		1.3.3 Double-walled carbon nanotubes	11	
		1.3.4 Synthesis of carbon nanotubes	14	
		1.3.5 Purification and sorting of carbon nanotubes	17	
	1.4	Modifications of the electronic properties of nanotubes	19	
		1.4.1 Intercalation	19	
		1.4.2 Sidewall functionalization	19	
	1.5	Applications for carbon nanotubes	23	
N	omer	nclature	1	
2	Bac	ekground of the experimental techniques	27	
	2.1	Optical properties of carbon nanotubes: Exciton photophysics	27	
		2.1.1 Concept of excitons	27	
		2.1.2 Exciton fine structure	29	
	2.2	Photoluminescence spectroscopy	30	
		2.2.1 Photoluminescence of carbon nanotubes	30	
		2.2.2 $$ Photoluminescence of inner tubes from double-walled carbon nanotubes $$.	34	
	2.3	Optical absorption spectroscopy	35	
		2.3.1 Absorption spectra of single-walled carbon nanotubes	35	
		2.3.2 Absorption spectra of double-walled carbon nanotubes	36	
	2.4	Raman spectroscopy	40	
		2.4.1 Vibrational modes in carbon nanotubes	40	

		2.4.2	Raman spectroscopy of double-walled carbon nanotubes	43
		2.4.3	Linear carbon chains investigated by Raman spectroscopy	44
3	San	nple p	reparation & experimental setups	47
	3.1	Synth	esis of double-walled carbon nanotubes filled with linear carbon chains	47
		3.1.1	Growth of pristine double-walled carbon nanotubes	47
		3.1.2	Growing long linear carbon chains inside double-walled carbon nanotubes	49
	3.2	Suspe	nsions of pristine and filled double-walled carbon nanotubes	50
	3.3	Exper	imental setup for absorption measurements	51
	3.4	Exper	imental setup for photoluminescence measurements	52
	3.5	Exper	imental setup for Raman measurements	54
4	Res	ults &	discussion	57
	4.1	Purifi	cation, separation and extraction of inner tubes from double-walled carbon	
		nanot 4.1.1	ubes by tailoring density gradient ultracentrifugation using optical probes . Comparison of the optical absorption spectrum to single-walled carbon	57
			nanotubes	57
		4.1.2	Abundance of semiconducting inner tube species	58
		4.1.3	Selective extraction of inner tubes by density gradient ultracentrifugation	59
		4.1.4	Analysis of the photoluminescence intensity difference from double-walled	
	4.0		to single-walled carbon nanotubes	62
	4.2	Enhar	icing the photoluminescence quantum yield by controlled growth of long	CT.
		inear	Carbon chains inside double-walled carbon nanotubes	60
		4.2.1	a different temperatures	65
		422	Optical absorption spectroscopy of filled double-walled carbon nanotubes	00
		1.2.2	in solution	74
		4.2.3	Photoluminescence spectroscopy of double-walled carbon nanotubes filled	
			with linear carbon chains	77
		4.2.4	Discussion on the physical process behind the luminescence signal and	
			enhancement	84
5	Cor	nclusio	ns and outlook	89
-				
Bi	bliog	graphy		93
$\mathbf{A}_{\mathbf{j}}$	ppen	dix		109
Cı	urric	ulum	Vitae	113

List of Figures

1.1	Schematic of a carbon nanotube with a luminescent local state	2
1.2	Allotropes of carbon in different dimensions	3
1.3	Model of an SWCNT filled with a linear carbon chain with alternating bond lengths	4
1.4	The honeycomb-lattice of an unrolled carbon nanotube, definition of the unit	
	vectors in carbon nanotubes	5
1.5	Structure of nanotubes with different chiral angles: Armchair, zigzag and chiral	
	nanotubes	6
1.6	Real space and reciprocal space unit vectors in carbon nanotubes	7
1.7	First Brillouin Zone of graphene and quantized unit cell vectors of different nan-	
	otubes	8
1.8	Energy dispersion relation of graphene throughout the whole Brillouin zone and	
	along the high symmetry points Γ , K and M	9
1.9	Energy dispersion relation and density of states for a metallic and a semiconduct-	
	ing nanotube	10
1.10	Chirality map of nanotube species marked by their metallicity	11
1.11	HR-TEM of DWCNT	12
1.12	Calculated band structure for two different DWCNT	13
1.13	Schematic of the Arc Discharge synthesis process	15
1.14	Schematic of the Laser Ablation synthesis process	15
1.15	Schematic of a CVD synthesis process	16
1.16	Sorting of SWCNT by different chiralities by applying density gradient ultracen-	
	trifugation	18
1.17	Intercalation of SWCNT	20
1.18	Sidewall functionalization	21
1.19	Filling of carbon nanotubes	22
1.20	TFT made from carbon nanotubes	23
1.21	Schematic of a SWCNT-Si solar cell	24
1.22	In vivo near-infrared photoluminescence imaging of mice	25
0.1		
2.1	Polarization-dependence of exciton formation in carbon nanotubes and schematic	20
0.0	Fractions for structure in each or prositions	20
2.Z	Exciton line structure in carbon nanotubes	29
2.3 9.4	Schematic of the photoluminescence process in carbon nanotubes	პ∪ 91
2.4	Photoluminescence map of SWON1	ა1 ეი
2.5	PL images of suspended and free-standing carbon nanotubes	32

2.6	Effect of water filling on the emission wavelength of carbon nanotubes	33
2.7	Amplification of the PL signal by filling SWCNT with ferrocene	34
2.8	Optical absorption spectra of SWCNT	37
2.9	Contributions of inner and outer tubes to optical absorption spectra of DWCNT	38
2.10	Conceptual image of different light scattering processes	40
2.11	Example of a typical Raman measurement of a SWCNT powder	41
2.12	Dependence of the shape and position of the G^+ and G^- line on the nanotube	
	type and diameter	42
2.13	Raman spectra of DWCNT	44
2.14	Raman map of a DWCNT filled with linear carbon chains and Raman shift of the	
	carbon chain signal as function of the chain length	45
2.15	Example of a typical Raman measurement of a DWCNT powder at room tem-	
	perature after an annealing treatment	46
0.1		40
ა.1 ე.ე	And service of the service in called and liquid form	40
ა.2 ე.ე	Experimental for the samples in solid and inquid form	48
ა.ა ე_4	Furnace for high temperature annealing Outcome of different colubilities to being the being to be annealing	49
3.4 2 5	Seture for a sufficient solubilization techniques	51
3.0 2.6	Setup for performing optical absorption spectroscopy	02 52
3.0 9.7	Setup for Domon measurements	55
3.7	Setup for Raman measurements	94
4.1	Comparison of the absorption spectra of double walled carbon nanotubes and a	
	control sample containing single walled carbon nanotubes	58
4.2	PL Line scans at two different excitation wavelengths for a DWCNT sample not	
	treated by DGU	59
4.3	Outcome of a process of density gradient ultracentrifugation with samples of	
	double walled carbon nanotube solution solubilized by different sonication powers	60
4.4	Photoluminescence line scans of different layers from a sample treated with low	
	sonication power and subsequent application of density gradient ultracentrifugation $% \mathcal{A}$	61
4.5	Line scans of the photoluminescence signal of (6,5) nanotubes from samples	
	treated by different sonication and centrifugation procedures	63
4.6	Comparison of the photoluminescence response of samples treated either with or	
	without applying density gradient ultracentrifugation	64
4.7	RBM of DWCNT annealed after synthesis in high vacuum at different temperatures	65
4.8	G-Band and carbon chain signal of double-walled carbon nanotubes annealed in	
	high vacuum at different temperatures	67
4.9	Fitting procedures for the LCC Raman response of the sample annealed at 1480 $^{\circ}\mathrm{C}$	68
4.10	Integrated area of the chain signal as a function of the LCC growth temperature	70
4.11	Raman map of a DWCNT sample annealed at $1480 ^{\circ}\text{C}$	71
4.12	Adapted model for the relationship between observed Raman shift and the chain	
	length of polyynes inside carbon nanotubes	72
4.13	Absorption spectroscopy performed on solubilized pristine and filled DWCNT	74
4.14	Comparing the optical absorption spectra of pristine and filled DWCNT	75
4.15	PL map of pristine DWCNT	77
4.16	Difference in the PL intensity between DWCNT and SWCNT	78

4.17	Photoluminescence line scans showing the amplification of $(6,5)$, $(8,3)$ and $(10,2)$	
	inner tubes due to the presence of linear carbon chains	79
4.18	PL fitting procedure and amplification of all measured inner tube species filled	
	with LCC	80
4.19	Amplification of DWCNT filled with carbon chains as function of the inner tube	
	diameter	81
4.20	Amplification of the PL intensity of DWCNT as function of the annealing tem-	
	perature	82
4.21	Shift in the emission wavelength for inner tubes filled with LCC	85
4.22	Schematic of mobile excitons being prevented to interact with quenching sites and	
	reduction of nonradiative pathways	86

Abbreviations and Nomenclature

Abbreviations:

BZ	brillouin zone
CVD	chemical vapour decomposition
DCM4-(dicyanomethylene)-2-	-methyl-6-(4-dimethylaminostyryl)-4H-pyran (laser dye)
DGU	density gradient ultracentrifugation
DOC	sodium deoxycholate
DWCNT	double-walled carbon nanotubes
НіРсо	high pressure CO conversion
HR-TEM	high resolution transmission electron microscopy
LCC	linear carbon chains
MWCNT	multi-walled carbon nanotubes
NIR	near-infrared
PL	photoluminescence
PL QY	photoluminescence quantum yield
SWCNT	single-walled carbon nanotubes
vdW radius	van der Waals radius
vHs	van Hove singularities

Nomenclature:

C_h	chiral vector
\mathbf{d}_t	nanotube diameter
η_{PL}	
Θ	chiral angle
τ_R	radiative lifetime
τ_{NR}	non-radiative lifetime
τ_{PL}	photoluminescence lifetime

Chapter 1

Introduction

1.1 Motivation and goals

Carbon nanotubes are very interesting materials due to their remarkable electronic and mechanical properties which give them the potential of being an important keystone for future technological advances. The quasi-one-dimensional structure gives rise to many interesting effects, for example their optical response is highly dependent on the behaviour of excitons [1] which for conventional semiconductors are only seen at low temperatures. A plethora of different types of nanotubes with different bandgaps enables to tune the electronic properties of a device. Their intrinsic strength [2, 3] makes them less vulnerable for mechanical wear than it is the case for commonly used semiconductors. Also, their small size and electronic structure might aid in the ongoing search for smaller and faster electronic devices, boosting current developements, since Moores law for the exponential growth of microchip power is predicted to become unsustainable in the next few years due to inevitable physical barriers arising from the miniaturization of devices working with conventional semiconductors. The optical properties of carbon nanotubes inherit many positive advantages for their potential use in imaging applications within live cells and tissue. Their unique photostability for exhibiting photoluminescence allows for longer and stronger excitation compared to standard fluorophores as well as the fluorescence range of nanotubes which is ≈ 800 - 1400nm largely overlaps with the transparency window of organic tissue [4]. The incorporation of nanotubes in solar cell arrays [5] is also a promising application in times with an ever increasing need for clean energy with high efficiency. The optical properties of carbon nanotubes are not yet fully understood and complete control of the optical response has not been achieved by now. Photoluminescence of carbon nanotubes is highly sensitive to environmental effects [6] and therefore it is very important to completely understand the consequences of different perturbations to the intrinsic electronic structure.

In this thesis, double-walled carbon nanotubes were mainly investigated, as they combine the outstanding properties of both multi-walled and single-walled nanotubes, for example shielding of the inner tube from external influences whilst preserving the inner tubes optical properties [7]. However, the basic capability of inner tubes to exhibit photoluminescence is highly debated, since tube-tube interactions are believed to completely suppress fluorescence from inner tubes [8]. Therefore, systematic studies are needed to elucidate this question.



Figure 1.1: Schematic of a carbon nanotube with a luminescent local state, from [9]: A photoexcited intrinsic exciton is mobile along the nanotube axis (blue spot). When the mobile exciton collides with a local state (red spot), where the exciton energy becomes lower than that of the intrinsic state, the mobile exciton can be trapped by the local state. If the local state has no efficient non-radiative decay paths, it should work as a luminescence center, and the exciton can decay radiatively by emitting a photon.

The second goal involves the tailoring of the photoluminescence of inner tubes of doublewalled carbon nanotubes. It has been shown that filling of single-walled carbon nanotubes with the organometallic compound ferrocene leads to an amplification of the photoluminescence intensity by establishing a charge transfer to the tubes which reduces nonradiative decay channels [10]. Ferrocene is too big (diameter 0.9nm) to be introduced into the inner tubes of double-walled carbon nanotubes (diameter 0.7-0.8nm), therefore linear carbon chains were chosen as filling material. Theoretical studies predict that the chains can interact with the nanotube [11] and that the strength of this interaction is determined by the length of the chain [12]. A recent study of our group has shown that these chains can be grown inside double-walled carbon nanotubes with high yield and different chain lengths by changing the growth temperature [13]. This can be used for systematically analyzing the influence of linear carbon chains with different growth yield and lengths on the photoluminescence properties of inner tubes from double-walled carbon nanotubes.

1.2 Carbon in nature and science

Carbon is one of the most abundant and versatile elements in nature although it makes up much less than 1% of planet earth's matter. Being part of every lifeform it is an essential element when it comes to the importance for the biosphere. This pure presence of carbon can already be used in a practical matter: Carbon has three isotopes abundant in nature, among which two are stable, ¹²C, making up around 98,9% of carbon atoms and ¹³C, making up around 1,1% of carbon atoms and the radioactive ¹⁴C with very small abundance. ¹³C can be distinguished from ¹²C by magnetic spin resonance measurements which is also applied and frequently used in hospitals for biological imaging. The detection of ¹⁴C on the other hand is the key element for the radiocarbon dating method. Because of a radioactive half-life of about 5730 years, ¹⁴C actually serves as a facilitator for assigning various archeological findings to different periods in human history.



Figure 1.2: Allotropes of carbon in different dimensions. The quotation marks for nanotubes and fullerenes mean that although they are structurally three-dimensional, their electronic behaviour shows 1D or 0D behaviour.

For this work however, the electronic configuration of carbon is more important. The electrons are arranged in $1s^2$, $2s^2$ and $2p^2$ orbitals and can show three different hybridisations: sp, sp^2 and sp^3 . This results in a huge diversity of materials as it shows the highest diversity in chemical compounds compared to other elements and it has allotropes ranging from the three to the (basically) zero dimensional space as seen in Figure 1.2. Graphite is a layered material and the carbon atoms form a honeycomb lattice showing sp^2 hybridization. In this case, one of the 2s electrons hybridizes with two of the 2p electrons to give the three sp^2 orbitals that arrange circularely in a plane seperated by 120° . The remaining orbital has a p_z (or π) configuration, oriented perpendicular to this plane. The sp^2 orbitals form strong σ bonds between the carbon atoms, resulting in a very high in-plane Young modulus, whereas the overlap of the π orbitals from adjacent carbon atoms is the reason for the high electric conductivity of graphite.

The carbon atoms in diamond form a tetrahedral structure, where they have sp³ hybridization and are bound covalently. This gives diamond its enormous hardness and its good thermal and electrical insulating properties. However, it is less stable than graphite as it is transforming into the latter above $1500\,^{\circ}\mathrm{C}$ at normal pressure.

Graphene, the 2D-allotrope of carbon, can basically be seen as a single layer of graphite. It has received much attention since Novoselov and co-workers first isolated this material in 2004 by simply rubbing two freshly cleaved graphite surfaces against each other [14]. In doing so, some flakes were dispatched and some of them turned out to be single sheets of graphene. Graphene exhibits remarkable electronic properties and shows a great potential for nanoelectronic devices.

The C_{60} molecule, representing a "0D"-allotrope of carbon, consists of carbon atoms forming twenty hexagons and twelve pentagons which are arranged in a football-like structure. The atoms are essentially sp² hybridized, however, the structure gains a little bit of a sp³ character due to the curvature of the molecule.



Figure 1.3: Model of an SWCNT filled with a linear carbon chain with alternating bond lengths (as indicated by the colors) [13].

The focus of this work lies on the 1D carbon allotropes, namely carbon nanotubes and linear carbon chains ("LCC") which are illustrated in Figure 1.3. Carbon nanotubes can be seen as graphene sheets rolled up into a cylindrical form. They were first reported by Iijima et al. [15], which triggered worldwide investigation of this novel nanoscale material. Nanotubes can appear in two different versions: Either as a Single-Walled Carbon Nanotube (SWCNT) with a diameter of about 1-2nm or as a Multi-Walled Carbon Nanotube (MWCNT) with 10-20nm in diameter, where the nanotubes appear as several concentric cylinders with an interlayer space of 0.34nm, similar to the graphite interlayer distance. Nanotubes exhibit a very high aspect ratio since they usually have a length of several micrometers. However, they can be grown to be up to several centimeters long [16] what gives them a quasi 1D form. Despite their small diameter and weight, carbon nanotubes also exhibit outstanding mechanical properties and are among the strongest materials known to exist in nature. The Young modulus can reach about 1TPa, outperforming high tensile steel by a factor of 5 [2] whereas their tensile strength is within 100-200 GPa which makes them more than 30 times stronger than high quality kevlar [3] while having less density than both materials.

Linear carbon chains (also called "polyynes") are the carbon allotrope closest possible to being one dimensional. These chains are expected to have very interesting properties, e.g. acting as a spin-filter usable for quantum computing [17]. By covalently connecting carbon chains with zigzag-edged graphene electrodes, a large magnetoresistance effect is observed for the whole system, interesting for spintronics [18]. Also, Mikhailovskij et al. found that the inherent strength of the carbon chains exceeds even the previously mentioned strength of graphene and carbon nanotubes [19].

1.3 Carbon nanotubes: Overview

The following sections on describing the structural and electronic properties of carbon nanotubes follows in great part the books of Harris [20], Jorio [21] and Saito [22].

1.3.1 Structural parameters of nanotubes



Figure 1.4: The honeycomb-lattice of an unrolled carbon nanotube. By connecting the points O and A along the vector \vec{C}_h while connecting B and B', a nanotube is constructed. \vec{C}_h is then the circumferential vector of the nanotube, whereas the translational vector \vec{T} is normal to \vec{C}_h and therefore parallel to the tube axis. The two basevectors of this systems are \vec{a}_1 and \vec{a}_2 [22].

A simple way of describing the carbon nanotube structure is by the imagination of rolling up the 2D graphene sheet into a tube. Graphene has a hexagonal "honeycomb" lattice as shown in Figure 1.4 with two independent base vectors, \vec{a}_1 and \vec{a}_2 . These unit vectors have a length of $|\vec{a}_1| = |\vec{a}_2| = a\sqrt{3} = 2.46\text{\AA}$, with a being the C-C bond length of 1.42Å, and are given by

$$\vec{a}_1 = \frac{1}{2}(a\sqrt{3}, a), \ \vec{a}_2 = \frac{1}{2}(a\sqrt{3}, -a)$$
 (1.1)

The structure of a nanotube is defined by the way how the vector \vec{OA} is oriented along which the nanotube is rolled up. \vec{OA} corresponds to a structure perpendicular to the nanotube's axis \vec{OB} . The vector \vec{OA} defines the chiral vector $\vec{C_h}$, the so-called Hamada-vector, that can be written as multiple integers of the unit vectors. The nanotube is then defined as a set of these integers:

$$\vec{C}_h = n\vec{a}_1 + m\vec{a}_2 \equiv (n, m) \text{ (n, m are integers, } 0 < m < n)$$
(1.2)

The diameter of the nanotube is then given by L/π , with L being the length of the circumferential vector \vec{C}_h





Figure 1.5: Three different kinds of nanotubes with different chiral angles, with the source of the names from the extreme cases are marked in blue: (a) the (5,5) species, an "armchair" nanotube with a chiral angle $\theta = 30^{\circ}$, (b) the (9,0) species, a "zigzag" nanotube with $\theta = 0^{\circ}$ and (c) the (10,5) species, a "chiral" nanotube. These have chiral angles between 0° and 30° [23].

$$d_t [nm] = L/\pi = |\vec{C}_h|/\pi = \frac{a}{\pi}\sqrt{n^2 + nm + m^2}$$
(1.3)

The chiral angle θ is defined as the angle between \vec{C}_h and \vec{a}_1 . Due to the symmetry of the hexagonal lattice, the values of θ can only be in the range of $0^\circ < \theta < 30^\circ$. Expressed in terms of the integers n and m, we get

$$\cos\theta = \frac{\vec{C}_h \vec{a}_1}{|\vec{C}_h||\vec{a}_1|} = \frac{2n+m}{2\sqrt{n^2+nm+m^2}}$$
(1.4)

for the value of θ . In Figure 1.5, three different sorts of nanotubes in relationship to their chiral angles are shown. The names of the two extrem cases, "armchair" with $\theta = 30^{\circ}$, so m = n and "zigzag" with $\theta = 0^{\circ}$, where m = 0, are derived by the appearance of the chiral vector \vec{C}_h (marked blue). All tubes with angles in between are called "chiral" nanotubes.

The translational vector \vec{T} is the unit vector of a 1D carbon nanotube and lies parallel to the tube axis and perpendicular to \vec{C}_h as seen in Figure 1.4. \vec{T} can be described as

$$\vec{T} = t_1 \vec{a}_1 + t_2 \vec{a}_2 \equiv (t_1, t_2) \ (t_1, t_2 \text{ are integers})$$
(1.5)

The values of the integers t_1 and t_2 can be calculated from the relation $\vec{C}_h \cdot \vec{T} = 0$. By dividing these two resulting values by their greatest common divisor d_R , we can obtain the shortest lattice vector which is then the correct unit vector \vec{T} with $t_1 = (2m + n)/d_R$ and $t_2 = -(2n + m)/d_R$. Now we can easily calculate the number of hexagons N within the unit cell that is created by the rectangle $\overline{OBB'A}$.

$$N = \frac{|\vec{C}_h \times \vec{T}|}{|\vec{a}_1 \times \vec{a}_2|} = \frac{2(n^2 + nm + m^2)}{d_R}$$
(1.6)

As each hexagon contains two carbon atoms, the total number of carbon atoms within the unit cells is given by 2N.

1.3.2 Band structure of single-walled carbon nanotubes



Figure 1.6: Real space (a) and reciprocal space (b) honeycomb lattice of a graphene sheet. Marked are the unit vectors \vec{a}_i and \vec{b}_i as well as the unit cells (dashed lines) constructed by the unit vectors. The first Brillouin zone is indicated in dark gray, the second in light gray. The high symmetry points are marked as Γ , K and M, being the middle, the corner and the center of the edge, respectively.

The electronic properties of single-walled carbon nanotubes can also be derived from the graphene sheet and subsequent zone-folding. In Figure 1.6 the hexagonal lattice in real space (a) as well as in reciprocal space (b) are shown with the corresponding unit vectors. The unit cells are marked by the dotted rhombus, the first Brillouin Zone (BZ) in reciprocal space is marked by the black hexagon and the second BZ by the grey six-pointed star. With this selection of the first two BZ, we can define a triangle of high symmetry points, for which the energy dispersion relation will be calculated. These points are marked as the Γ point being in the center of the first BZ, M in the middle of the edge and K on the corner. The unit vectors in reciprocal space can be calculated from their real space counterparts as described in equation 1.1 and be written as

$$\vec{b}_1 = \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, 1), \ \vec{b}_2 = \frac{2\pi}{a}(\frac{1}{\sqrt{3}}, -1)$$
 (1.7)

As mentioned above in Figure 1.4, the unit cell in real space is given by the rectangle $\overline{OBB'A}$ created with the Hamada vector \vec{C}_h and the translation vector \vec{T} . Their reciprocal space counterparts are given by the relation $\vec{R}_i \cdot \vec{K}_j = 2\pi \delta_{ij}$, where the \vec{R}_i represent the real space vectors and the \vec{K}_i the reciprocal space (often referred to as "k-space") vectors. Therefore, the relations can be written down as

$$\vec{C}_h \cdot \vec{K}_1 = 2\pi, \ \vec{T} \cdot \vec{K}_1 = 0; \ \vec{C}_h \cdot \vec{K}_1 = 0, \ \vec{T} \cdot \vec{K}_2 = 2\pi$$
 (1.8)

where the circumferential vector $\vec{K_1}$ and $\vec{K_2}$ as the reciprocal unit vector parallel to the tube axis can then be expressed as

$$\vec{K}_1 = \frac{-t_2\vec{b}_1 + t_1\vec{b}_2}{N}, \ \vec{K}_2 = \frac{m\vec{b}_1 - n\vec{b}_2}{N}$$
 (1.9)

Since there are 2N carbon atoms in the unit cell, we can expect N pairs of π bonding and π^* anti-bonding energy dispersion bands. As carbon nanotubes are (quasi) one-dimensional objects, the first BZ collapses into a straight line. Considering equation 1.5 and the relations for t_1 and t_2 , we can see that they both do not have a common divisor except unity. By applying this to equation 1.9, this means that only $\vec{K_2}$ does fulfill the requirements for being a reciprocal vector in 2D graphene. Hence, the N wavevectors $\mu \vec{K_1}$ give rise to N parallel line segments in the carbon nanotube unit cell and as $N\vec{K_1}$ does represent a reciprocal vector in graphene, wavevectors differing by $N\vec{K_1}$ are equivalent. The length of all these "cutting lines" can be received by the relations between real space and reciprocal space vectors, leading to $|\vec{K_1}| = 2\pi/|\vec{T}|$ which is the length of the first BZ. Therefore, a reciprocal vector for the 1D structure can generally be written as

$$\vec{k} = \kappa \frac{\vec{K}_2}{|\vec{K}_2|} + \mu \vec{K}_1 \ \mu = 0, \dots N - 1 \text{ and } -\pi/|\vec{T}| < \kappa < \pi/|\vec{T}|$$
 (1.10)

Due to the symmetry of the lattice, we obtain continuous wave vectors in the direction of \vec{K}_2 for a carbon nanotube of infinite length, as sketched in Figure 1.7:



Figure 1.7: First Brillouin zone (Here: PZB) of graphene and the quantized vectors of (a) a (5,5) nanotube and (b) a (9,0) nanotube. The q indices correspond to the zone folding method indices [24].

These definitions enable us to perform a simple tight-binding calculation to obtain the energy dispersion relation with the orbital energy (not equal to the atomic energy value due to the lattice constraint of the carbon atoms) as well as nearest neighbour interactions being considered. This procedure is given in full detail elsewhere [22], however, by executing this approach for the graphene sheet we get

$$E_{g2D}^{\pm}(\vec{k}) = \frac{\epsilon_{2p} \pm \gamma_0 \omega(\vec{k})}{1 \pm s\omega(\vec{k})}$$
(1.11)

 ϵ_{2p} is the orbital energy of the 2p level, γ_0 is the so called transfer integral that is received by calculating the Hamiltonian for nearest neighbours and s denotes the overlap of electronic wave functions from adjacent sites, giving an indicator for the asymmetry of the system (i.e. s = 0 represents symmetry). The + signs in the numerator and in the denominator arises from the bonding π energy band (valence band), whereas the - signs correspond to the anti-bonding π^* energy band (conduction band). The function $\omega(\vec{k})$ is given by

$$\omega(\vec{k}) = \left\{ 1 + 4\cos\left(\frac{k_x a}{2}\sqrt{3}\right)\cos\left(\frac{k_y a}{2}\right) + 4\cos^2\left(\frac{k_y a}{2}\right) \right\}^{\frac{1}{2}}$$
(1.12)



Figure 1.8: Left: Plotted energy dispersion of graphene throughout the whole Brillouin Zone. Right: Energy dispersion along the directions of the triangle created by the high symmetry points Γ , K and M with s=0.129 (solid line) and s=0 (dashed line).

In the left panel of Figure 1.8, the energy dispersion relation of the two-dimensional graphene is plotted as a function of the 2D wavevector \vec{k} in the hexagonal BZ. We set the values for $\gamma_0 = 3.013 eV$, s = 0.129 and $\epsilon_{2p} = 0$ as this best fits both the first-principles calculations of the energy bands of 2D turbostratic graphite and experimental data [22, 25]. The right panel shows the energy dispersion relation along the high symmetry points Γ , K and M, where the π^* conduction band and the π valence band are degenerate at the K point in the hexagonal BZ which corresponds to a Fermi-Energy $E_F = 0$. The dashed line on the right panel represents a symmetric \vec{k} vector, i.e. s = 0, that gives an almost similar result for the energy dispersion relation as for the aforementioned non-zero value for s up to an energy difference of π and $\pi^* \approx 6 eV$. Since the physical phenomena investigated in this thesis only involve small energies it is convenient to use the symmetric approximation. By implementing this case for equation 1.11 as well as the aforementioned zone-folding of graphene, meaning $\psi(\vec{x} + n\vec{C}_h) = \psi(\vec{x})$, we get for the energy dispersion relation of a SWCNT

$$E_{1D}^{\pm}(K) = E_{g2D}^{\pm} \left(\kappa \frac{K_2}{|K_2|} + \mu K_1 \right)$$
(1.13)

with the same possible values for k and μ as in equation 1.10. Using the x,y values for the vectors \vec{K}_1 and \vec{K}_2 , we finally obtain

$$E_{1D}^{\pm}(K) = \pm \gamma_0 \left\{ 1 + 4\cos\left[\frac{a_0\sqrt{3}}{2} \left(\kappa \frac{K_{2x}}{|K_2|} + \mu K_{1x}\right)\right] + \cos\left[\frac{a_0}{2} \left(\kappa \frac{K_{2y}}{|K_2|} + \mu K_{1y}\right)\right] + 4\cos^2\left[\frac{a_0}{2} \left(\kappa \frac{K_{2y}}{|K_2|} + \mu K_{1y}\right)\right] \right\}^{\frac{1}{2}}$$
(1.14)

Considering the relation between the chirality (n,m) and the reciprocal vector \vec{K} given in equation 1.10, it is possible to determine the band structure of a carbon nanotube from equation 1.14. From that, the density of states D can be expressed as

$$D(E) = \frac{T}{2\pi N} \sum_{\pm} \sum_{\nu=1}^{N} \int \frac{1}{\frac{dE_{1D}^{\pm}(k)}{dk}} \delta\left(E_{1D}^{\pm}(k) - E\right) dE$$
(1.15)

The first summation sign stands for the N conduction (+) and valence bands (-), respectively.



Figure 1.9: Electronic dispersion for (a) a (9,9) and (b) a (16,0) tube, where a clear bandgap arises for the latter. (c) Density of states for both tubes: The spikes are typical for 1D systems, and for the (9,9) species (black), the density of states is finite at the Fermi energy, resulting in metallic behaviour [26].

Figure 1.9 shows the calculated energy dispersion relation and density of states for a (9,9) and a (16,0) nanotube which both have a similar diameter of $d_t \approx 1.2nm$. Due to the symmetry of the K points all subbands are doubly degenerate. The corresponding density of states (Figure 1.9c) present van Hove singularities (vHs) typical of 1D systems at the onset of each new subband. It can be seen in Figure 1.9b that a clear bandgap arises for the (16,0) nanotube. The reason for this can be found by comparing the cutting lines in Figure 1.7 to the energy dispersion relation of graphene illustrated in Figure 1.8. The conduction and the valence band touch each other at the K points, so the density of states at the Fermi-Level is non-zero giving graphene its semi-metallic behaviour. This is only true for sufficiently large nanotubes. For small nanotubes the curvature of the nanotube invokes a orbital rehybridization effect [27] which causes metallic nanotubes to become small-bandgap semiconductors (10meV for a nanotube with a diameter of

1.4nm). Still, this small bandgap can be neglected at room temperature as the thermal energy ($\approx 27 \text{meV}$) is bigger than the bandgap.

If the cutting lines of the SWCNT representing its electronic states do not go through a K point, they have a large bandgap and therefore show semiconducting behaviour. The bandgap is chirality dependent ($\propto \cos(3\theta)$) and scales with $1/d_t$ since the cutting lines are separated by $2\pi/|\vec{T}|$ as already mentioned, hence, every nanotube has a unique band structure. In Figure 1.10 a chirality map of small-diameter nanotubes is illustrated where blue dots represent metallic and red dots semiconducting carbon nanotube species.



Figure 1.10: Chirality map of nanotube species marked by their metallicity. The red dots indicate nanotubes showing semiconducting behaviour and the blue dots represent metallic species.

The distribution of the metallic species shows a clear pattern where those tubes are metallic that have a divisor of 3 for (n-m). From there a simple rule for the metallicity of carbon nanotubes can be derived:

$$if (n-m)mod3 = \begin{cases} 0, & \text{metallic} \\ 1, 2 & \text{semiconducting} \end{cases}$$

Thus, in a sample containing a random distribution of nanotube chiralities, we can expect 1/3 to be metallic and 2/3 to be semiconducting. Put in a nutshell, the electronic properties of carbon nanotubes depend sensitively on their chirality.

1.3.3 Double-walled carbon nanotubes

General aspects and synthesis of double-walled carbon nanotubes

Double-walled carbon nanotubes (DWCNT) can be seen as the simplest manifestation of MWCNT, where one smaller SWCNT is nested inside a bigger SWCNT lying parallel to its tube axis. This can be observed by high resolution transmission electron microscopy (HR-TEM) illustrated in Figure 1.11. In this sense they combine the outstanding properties of SWCNT, allowing to study intertube interactions and the resulting influence on the properties of nanotube systems. Generally speaking, they have several advantages over simple SWCNT. For example, they exhibit

higher stability than SWCNT which can be of substantial help in high performance environments, e.g. for usage as tips in field emission experiments [28]. The protective nature of an outer tube can aid in the growth of very small diameter inner tubes that are usually very hard to obtain when growing SWCNT [29] and therefore allow to study high-curvature effects as well as the optical properties of these small tubes. The extremely low inter-shell friction force also opens the possibility of developing wear free nano-bearings [30]. The geometry of nanotubes allow the growth of heterotubes when the outer and the inner tube are not grown simultaneously, like a ¹³C carbon nanotube inside a ¹²C outer tube [31].



Figure 1.11: HR-TEM of a DWCNT grown by transforming C_{60} inside SWCNT by annealing in vacuum at high temperatures [32].

Electronic and optical properties of double-walled carbon nanotubes: Interwall interactions

DWCNT basically consist of two coaxially arranged SWCNT whose electronic properties where already described in section 1.3.2, however, these properties also depend on tube-tube interactions. As we have two sets of different (n,m) indices for inner and outer tubes, the unit cells of DWCNT (compare equation 1.6) can be extremely large and therefore very difficult to calculate. As a consequence, these calculations are usually performed on relatively simple pairs of nanotubes, like armchair-armchair or zigzag-zigzag tubes. Such cases represent only a fraction of nanotube pairs when it comes to the symmetry of DWCNT, as they are all commensurate which gives small unit cells. Commensurability of DWCNT means that the ratio of unit cell lengths between inner and outer tube is either a rational number (commensurate) or an irrational number (incommensurate) [33]. Zólyomi et al. calculated the band structure of several commensurate DWCNT by using density-functional theory and the intermolecular Hückel model [34]. They found that a charge transfer from inner to outer tube as well as orbital mixing between the layers occurs. These effects lead in some cases to a transition from semiconducting to metallic behaviour but not in all cases as illustrated in Figure 1.12.

On the other hand, by studying such symmetry effects, Damnjanovic et al. found that (infinite, defect free) incommensurate nanotube pairs only show negligible interaction. It is very hard to generalize on the electronic and optical properties of DWCNT as also the interwall-



Figure 1.12: Calculated band structure for two different DWCNT with c being the lattice constant of the nanotubes, the green and blue lines representing inner and outer tube and the red lines the calculated band structure for the whole DWCNT. Originally, all shown tubes are semiconducting if no other perturbations are present. For the (7,0)@(16,0) system (a) the bandgap closes making this DWCNT metallic, whereas for the (8,0)@(17,0) the bandgap becomes smaller but not zero [34].

distance in DWCNT is not uniform; HR-TEM revealed distances between 0.33nm and 0.42nm [35] which differs from the interwall-distance of 0.34nm in MWCNT or graphite layers. This is attributed to the difference of π orbital stacking interaction resulting from the high curvature. By adding these extremes in interval distances to a given inner tube diameter, we get a huge amount of potential outer tube candidates that can be commensurate but are incommensurate for the majority of all cases. Besides this, the tube structures offer many possibilities, for example on the metallicity. Since each tube can be either metallic or semiconducting, four different configurations can exist which has been shown to lead to different transport properties [36].From the experimental point of view, several interesting observations have been made in the past: Pfeiffer et al. observed in Raman measurements that the linewidth of the radial breathing mode from inner tubes grown by C_{60} transformation is much lower than expected for similar tubes, indicating that the outer tube provided a perfect clean room for the growth of an (almost) defect-free inner tube [37]. In a following work they also showed a splitting of the radial breathing mode resulting from the presence of different outer tubes for a given inner tube which depends on the interwall-distance [38]. A very important aspect of their work for the discussion below on photoluminescence of DWCNT is that the tube-tube interaction was weaker than the interactions of tubes in nanotube bundles. Similar observations in more detail were performed by Liu et al. [39] as they were able to investigate quantum coupled radial breathing mode oscillations in chirality-defined DWCNT. Although usually treated as weak perturbations, van der Waals interactions were shown to cause collective vibrational phenomena of both tubes which again were depending on the interwall-distance.

To summarize, the electronic structure of DWCNT is very interesting but it can be very complicated since tube-tube interactions enter the picture as additional factors. This raises the question on the influence of outer tubes on inner tubes for optical transitions, especially concerning the photoluminescence properties that are heavily intertwined with photoluminescence quenching processes but also the Raman response is strongly affected.

1.3.4 Synthesis of carbon nanotubes

As shown in the previous section, carbon nanotubes can have a huge variety of different individual morphologies and properties. All of these aspects are determined by the synthesis method and the further processing of the used sample. Hence, several different methods of carbon nanotube synthesis have been developed over the years to produce nanotubes with desired properties, be it specific length, diameter, wall numbers or metallicity for further scientific analysis or implementation for various kinds of devices. However, no method so far has been optimized in a way that it produces single chirality nanotubes with control over diameter and electric properties. Therefore, all future nanotube-related science will strongly rely on the further optimization of carbon nanotube synthesis. Four main challenges in nanotube synthesis still remain:

- 1. Mass production of high quality carbon nanotubes including SWCNT and MWCNT,
- 2. Selective production so that carbon nanotubes with specific structures and electronic properties can be obtained,
- 3. Growth control, i.e. carbon nanotubes can be grown in specific locations with specific orientation on flat substrates,
- 4. More in-depth understanding of the process of nanotube growth.

The first two points are important for applications such as implementation in other structures to form composites where it is desired to have access to high-quality carbon nanotubes in the kilogram level with methods that are efficient and inexpensive. The third point is very crucial when it comes to nanotube based electronics that require highly organized arrays for controlled and reproducable devices.

In the following subsections, the three synthesis methods used most frequently are highlighted: Arc Discharge, Laser Ablation and Chemical Vapor Deposition.

Arc discharge

Arc Discharge was used in the pioneering work of Iijima et al. [15]. This method was developed as a modification of the Krätschmer-Huffman technique that was used for synthesis of C_{60} . Two graphite electrodes containing metal catalysts like Fe, Ni, Mo or Co are kept at a small distance while arcing, illustrated in Figure 1.13. The current usually applied is between 50-100A with the temperature of the arc reaching up to 3000K while the chamber is flooded with He gas. The breakthrough of this method was reached when Ebbesen et al. demonstrated in 1992 that the growth of MWCNT can be significantly enhanced by optimising the pressure of the He gas. This enabled them to grow MWCNT at the gram level [40]. Bethune et al. first managed to synthesize SWCNT by finding appropriate concentrations of the additives to the graphite electrodes [41]. At the same time, Iijima et al. used similar electrodes but their carrier gas was a mixture of methane and argon rather than helium [42].

This led to quite a different result: Whereas Bethune et al. obtained SWCNT with a mean diameter of $1.2 \text{nm} \pm 0.1 \text{nm}$, Iijima et al. obtained a much broader diameter distribution of 0.7 to 1.6 nm. The growth rate within these processes can be up to 20-100 mg/min but the discharge can only be sustained for a short time. Nevertheless, the downsides of the method of arc discharge are easily found in the requirements for the equipement and the high power



Figure 1.13: Schematic of the Arc Discharge process. Two high quality graphite electrodes doped with metal catalysts are brought to a close distance while arcing, which results in the growth of nanotubes. Varying current and carrier gas can result in the growth of different nanotubes [43].

consumption. Furthermore, the controlled synthesis on substrates has not been possible by now. Also, the yield of CNT growth is often only between 30% and 50% so that other carbon based byproducts and impurities have to be removed in post-synthesis purification processes [26].

Laser ablation



Figure 1.14: Schematic of the Laser Ablation process. A high power laser evaporates the surface of a graphite target so that nanotubes are grown on the collector [44].

The synthesis of SWCNT by laser vaporization was first reported by the group of Smalley in 1995 [45]. The process is illustrated in Figure 1.14: Typically, a furnace is heated up to a temperature between 1100 °C and 1200 °C and an inert gas (for example Argon) flows through

the tube at constant pressure. A cylindrical, rotateable target is positioned in the center of the furnace that, just like in the Arc Discharge method, is composed of high purity graphite with small additives of Co and Ni. Then, the beam of a Nd:YAG laser (or two in the refined process [46]) is focused unto the target to vaporize it. With this technique, the growth conditions are well controlled and can be maintained over a long time allowing for a growth rate of 1-10 gram per day. By using a 1kW free electron laser, Eklund et al. were able to increase the rate to 1.5 gram per hour [47]. Rümmeli et al. found that nanotube growth by laser evaporation can be achieved even at room temperature when metal oxides are used as additional catalysts [48]. However, the high costs of powerful lasers seem to be preventing this technique from wide useage.

Chemical vapor deposition

For up-scaling the production of carbon nanotubes, the synthesis by chemical vapor deposition (CVD) seems to be most promising for it has several advantages compared to the other techniques. CVD does not have as high requirements for the equipement as arc discharge and laser ablation and furthermore it is taking place under relatively mild conditions increasing the level of control over the growth process. Maruyama et al. were able to grow single-walled carbon nanotubes with high purity at reaction temperatures of only 700-800 °C by using ethanol or even at 550 °C with methanol and they also achieved direct growth of nanotubes on conventional semiconducting devices already patterned with aluminum [49]. Patterning substrates with already established nanolithographic techniques also enables single nanotube synthesis [50]. Vertically aligned films with μ m thickness covering large areas (e.g. 25x25mm) were also produced by CVD [51]. Figure 1.15 shows a schematic of the CVD setup used in this thesis for the growth of DWCNT. In high vacuum and at 875 °C, ethanol is decomposed by the catalyst leading to the growth of DWCNT.



Figure 1.15: Schematic of the high vacuum CVD process used in this thesis. A carbon-carrier gas is introduced into the hot zone of an evacuated furnace, where the reaction with the catalyst leads to the growth of nanotubes.

So far there have been many different CVD techniques developed that are successful in the synthesis of SWCNT and MWCNT, all of which are following the process of decomposition of a carbon-carrier gas supported by a metallic catalyst at elevated temperatures. An important representative of CVD is the high pressure catalytic decomposition of carbon monoxide (HiPco) which has been developed by the group of Smalley [52]. It is currently the only process capable of producing SWCNT on a kilogram per day scale. Nanotubes made according to this method were also used in this work as reference samples. Among many other widely used CVD synthesis methods are the "CoMoCat" process, where, as the name implies, a catalyst containing Co and Mo is used and CO as a carbon feedstock which was introduced by the group of Resasco [53] and the DIPS method (Direct injection pyrolytic synthesis) established by Saito et al. that uses carbon sources with different decomposition properties to control the eventual diameter distribution [54].

For the growth of DWCNT another method is available: The growth of inner tubes inside larger tubes by thermal treatment of precursor systems, where a carbon source, be it C_{60} [37] or metallorganic compounds such as Ferrocene [55], is encapsulated in SWCNT and subsequently annealed.

As mentioned earlier, all these methods are not optimized in a way that only the desired nanotube compound, be it SWCNT or MWCNT, but merely a mixture of different nanotubes with different chirality, metallicity or wall numbers mostly accompanied by remaining catalysts and carbonaceous impurities, is produced. There are only few reports on selective growth of nanotubes. The group of Li and co-workers [56] for example used plasma enhanced CVD as growth method enabling them to produce samples containing 85-90% semiconducting SWCNTs, whereas one would expect only 67% of semiconducting species for a random distribution. On the other hand, the group of Bachilo et al. received a sample highly enriched with (6,5) nanotubes by using a special CoMoCat technique [57]. Although these results are not yet fully understood, it seems that the morphology of the metal cluster plays an essential role in this question. However, the selective growth of nanotubes with specific (n,m) distributions is still the holy grail of nanotube synthesis.

1.3.5 Purification and sorting of carbon nanotubes

Purification

The resulting carbon soot of all previously introduced methods always contains impurities leftover from the synthesis process such as amorphous carbon or metallic particles. Hence, purification of the carbon nanotubes as well as sorting them is necessary to exploit their intrinsic properties. There are several different ways of purifying carbon nanotube samples, most of which contain heat and/or acid treatments. Annealing the carbon soot after synthesis in air has the effect of removing carbonaceous impurities, amorphous carbon for example is less stable than carbon nanotubes [58] but also small diameter tubes are more reactive than larger tubes [59]. Additionally, Li-Pook-Than et al. found that within a subset of nanotubes with similar diameter, chirality effects on the etching efficiency are visible [60].

In the same manner few wall CNT including DWCNT samples can be cleansed from SWCNT since they are thermally more stable than SWCNT [61] though this already implies that heat treatment might not be very effective for the purification of SWCNT. High-temperature annealing in vacuum (1600-3000 °C) has been shown to not only evaporate catalyst particles but also improve the structure of MWCNT as defects are reduced in the process [62]. Acid treatments, for example with HCl [58] or HNO₃ [59], are also frequently used to remove catalyst particles. The downside of acid treatments is that they tend to have a destructive effect on the structure of nanotubes and can cause unwanted functionalization of the nanotubes if the solvent is bonding

with the nanotube on reactive sites like defects or tube ends. In an early work, Tsang et al. have shown that nanotubes synthesized by the arc discharge method can be opened by using concentrated nitric acis [63]. Furthermore, Kamarás et al. proved that HNO_3 usage leads to p-type doping of the nanotubes, altering their optical properties [64].

In most procedures oxidation and acid treatment are used sequentially to receive a high purity of nanotube samples. Physical techniques such as filtration, centrifugation or size exclusion chromatography are also commonly involved for purification purposes, with the former two being of special interest for this work. Filtration makes use of the length of the nanotubes: By putting the overall carbon soot after synthesis into solution, they are trapped on a membrane filter whereas catalyst particles are washed out. This process is proven to be quite effective if it is sonication assisted [65]. Centrifugation on the other hand seperates various materials due to different densities. The group of Haddon et al. showed that low-speed centrifugation had the effect of sedimentation of their SWCNT on the bottom of the centrifuge tube, whereas amorphous carbon stayed in suspension [66]. However, if the solution is well dispersed, the carbon nanotubes stay suspended whereas carbonaceous or other nanoparticles are sedimented.

Sorting



Figure 1.16: Sorting of SWCNT by different chiralities by applying density gradient ultracentrifugation [67].

The unavailability of single chirality nanotube growth logically led to the development of various techniques capable of sorting nanotubes. There are various possibilities on doing so, as for example sorting by electronic type (metallic or semiconducting), diameter, length or, if optimized ideally, by a specific (n,m) index. As these are already several parameters that can vary over a sample, the techniques established for sorting purposes are plentiful with each relying on different physical principles making use of nanotube properties. The most frequently used methods are described in the next paragraphs, however, the review of Joselevich provides a comprehensive list [68].

Size-exclusion chromatography is based on the separation of nanotube bundles from individ-
ual tubes on the basis of their hydrodynamic size difference by using a size-exclusive gel. Flavel et al. have shown with the gel they used that monochiral suspensions can be obtained simply by altering the pH of the solution [69]. For dielectrophoresis, the difference of the relative dielectric constants between different species with respect to the solvent results in different movements along the electric field gradient. By doing so, Krupke et al. were able to seperate metallic from semiconducting nanotubes [70]. The group of Kataura was able to achieve chirality sorting by performing single-surfactant multicolumn gel chromatography [71]. Here, the variation of the interaction strength of different SWCNT with an allyl dextran-based gel is utilized. This led them to the seperation of 13 different species. Another interesting pathway to sort nanotubes is the use of single stranded DNA which was shown to wrap around SWCNT, allowing dispersion in aqueous solutions. As different types of nanotubes are differently charged by the DNA, they can be fractionated by ion-exchange chromatography, yielding nanotube suspensions either seperated by electronic type [72] or even specific chirality, if specific DNA sequences are used [73].

By dispersing nanotubes in bile salts and subsequently applying density gradient ultracentrifugation (DGU), they can be differentiated by their density. The method of DGU is also used in this work and will be discussed in more detail later. Modifications on the gradient medium lead to highly different outcomes of the centrifugation process what gives this procedure a high flexibility. In the first report of this method, Arnold et al. received different layers with very narrow diameter distributions (< 0.02nm) [74]. Green et al. were able to seperate nanotubes by their wall numbers [75]. Ghosh et al. improved the procedure of Arnold et al. and were able to obtain layers with nanotubes of single chiralities which is illustrated in Figure 1.16. Nanotubes can also be seperated by their electronic type when using DGU as it has been shown by Yanagi et al. [76]. Eventually, Fagan et al. used a modification of this method to investigate on the optical properties of nanotubes with different lengths [77].

1.4 Modifications of the electronic properties of nanotubes

Carbon nanotubes are amphoteric, meaning that they possess the ability of accepting/donating electrons from/to atoms or molecules and due to their structure, there are several different possibilities on how to tune their electronic properties.

1.4.1 Intercalation

Intercalation of nanotubes, e.g. with alkalimetals like K or Li or other molecules like FeCl₃, is frequently used for doping (Figure 1.17). Here, the atoms/molecules are placed in the free zone between nanotubes and bundles where they act as electron-donors which results in weakening of the C-C bonds in the SWCNT downshifting (upshifting if acceptors like Br_2 are introduced) the vibrational energies of certain modes. Using optical absorption, the disappearence of absorption bands in both types of nanotubes has been observed.

1.4.2 Sidewall functionalization

Sidewall functionalization of carbon nanotubes is very often the method of choice for modifying nanotube properties. This is used when the linking of various molecules to the nanotube's sidewall is desired. In early works, various fullerenes have been subjected to addition reactions



Figure 1.17: Intercalation of SWCNT [78].

to elucidate their reactivity, for example C_{70} , a flatened-out relative of the previously mentioned C_{60} [79]. In this context it has been shown that the reactivity on the poles is much higher than in the flatter equatorial regions, indicating a direct relation between curvature and reactivity. Applying this knowledge to carbon nanotubes, it means that smaller diameter nanotubes have a higher reactivity compared to large diameter tubes like during oxidization as it has been pointed out in the purification section 1.3.5. Although there are many different ways to perform sidewall functionalization, the methods can be devided in the groups of substitutional doping (Figure 1.18a), defect-group chemistry (Figure 1.18b), covalent (Figure 1.18c) and noncovalent sidewall functionalization (Figure 1.18d) [80].

Substitutional doping

The method of substitutional doping (Figure 1.18a) is referring to the implementation of noncarbon atoms into the nanotube lattice. This is mostly done with either B or N but also P since they are neighbours of carbon in the periodic table and therefore easy to build into the nanotube structure. They introduce strongly localized electronic features near the Fermi level, either above (N as it has one electron more than C) or below (B with one electron less than C). On sites where the dopant atoms are localized, the reactivity with either donor or acceptor molecules is enhanced, making further functionalization easier.

Defect-group chemistry

Defects are important as they can serve as anchorpoints for further functionalization (Figure 1.18b). They can be either intrinsic, originating from the synthesis process, or be introduced artificially by using strong acids [84]. Oxygenated functional groups tend to lie at these defect positions [80] and they can be used to tether various kinds of chemical moieties [85]. These functional groups can be used for further chemical reactions such as e.g. silanation [86] or esterification [87] but they can also be used to increase to solubility of nanotubes [88].

Covalent sidewall functionalization

Covalent sidewall functionalization is used to directly link molecules to the nanotube sidewall and is associated with a change of hybridization from sp^2 to sp^3 [85]. This process can be performed with molecules of high chemical reactivity. Successful methods like fluorination [8], chlorination [89], hydrogenation [90] among others have been employed. The drawback of such methods is the possible introduction of defects to the nanotubes as well as the optical and



Figure 1.18: Functionalization of nanotubes by (a) defect-group chemistry: oxygenated functional groups tend to lie at defect positions [80]. (b) Substitution of wall atoms (here for example with N [81], (c) covalent sidewall functionalization by doping with oxygen [82] and (d) noncovalent sidewall functionalization by attaching a surfactant to the nanotube sidewall [83].

electronic properties are altered [85]. However, by fine tuning of this method, this type of functionalization can be exploited for improving nanotube properties. Ghosh et al. were able to improve the photoluminescence intensity by doping nanotubes with oxygen that is illustrated in Figure 1.18c [82].

Noncovalent sidewall functionalization has the advantage of not being destructive to the nanotube structure and therefore (in most part) preserves the nanotube properties. It can be realized either from outside of the nanotube (exohedral) by attaching molecules to the sidewall or from the inside (endohedral) by filling the nanotube.

Exohedral noncovalent sidewall functionalization

Functionalizing nanotubes from the outside of the tubes with substances like aromatic compounds, polymers or surfactants employs π - π stacking or hydrophobic interactions for the most part that enhances the solubility of nanotubes remarkably [85]. The use of surfactants is of great significance for this work. Important representatives for commonly used surfactants which were also used in this thesis are the sodium salt of deoxycholic acid (DOC) and sodium dodecyl sulfate (SDS); the effectiveness of different surfactants is reviewed by Wenseleers et al. [91]. They are often used to individualize carbon nanotubes as two main advantages of the surfactants are exploited: First, the surfactant treated nanotubes overcome the van der Waals attraction of nanotubes within bundles and secondly, the physical absorption of surfactants on the nanotube sidewall lowers the surface tension of the sidewall, preventing re-aggregation of nanotubes into bundles.

Endohedral noncovalent sidewall functionalization

Ultimately, the hollow structure of carbon nanotubes opens the possibility of encapsulating atoms or whole molecules and use the nanotube as a reactor for chemical processes, illustrated in Figure 1.19. All these filling procedures have in common that the maximum degree of filling is in the range where the radius of the molecule plus the van der Waals radius of the C atoms from the nanotube matches the nanotube's diameter. The controlled encapsulation of SWCNT with C_{60} (Figure 1.19a) and a subsequent annealing treatment can lead to the growth of doublewalled carbon nanotubes [32]. Organometallic compounds such as ferrocene have been filled into SWCNT 1.19b to create a local charge transfer for selective enhancement of the photoluminescence signal [10], and by annealing, DWCNT were formed with the remaining iron-nanoparticles residing on the DWCNT with a well-defined intra-tube spacing and doping level [55]. Another interesting issue is the growth of nanowires as it is expected that they show novel electronic properties due to the reduced dimensionality. Linear chains of metals inside carbon nanotubes could be grown, e.g. Ag [92] or Fe [93] but also chains made of rare earths like Eu [94], Gd [95] or Ho [96] among others could be synthesized.



Figure 1.19: Filling of carbon nanotubes with different materials, e.g. (a) C_{60} [97], (b) Ferrocene [10] or (c) linear carbon chains [98]

Long linear carbon chains inside carbon nanotubes

The synthesis of linear carbon chains poses as a challenging task for chemists due to their high reactivity [99] and strong tendency to undergo chain-chain crosslinking reactions [100]. Since for DWCNT the inner tube diameter can be well below 1nm it is possible to encapsulate linear carbon chains. In this way the potential energy of the chains is reduced significantly by the nanotube environment [101, 102]. Several different methods for building such structures have been developped. Zhao et al. opened DWCNT by oxidation of the nanotube caps and inserted $C_{10}H_2$ molecules which, by a subsequent thermal treatment, fused to form linear chains [98], illustrated in Figure 1.19c. Another reported method is the heat treatment of highly pure DWCNT grown by an arc discharge method from Shi et al. [103]. In this work, the growth of long linear carbon chains with high yield was achieved by using purified DWCNT synthesized by the CVD method as nanoreactors and high vacuum thermal annealing to form carbon chains out of the "unused" carbon atoms trapped within the inner tubes of the DWCNT during the synthesis. The interaction with the carbon nanotube wall modifies the electronic properties of the latter. For example, Moura et al. observed a shift of the G-Line in Raman measurements by encapsulation of $C_{10}H_2$ inside DWCNT [104]. An interesting point is the charge distribution depending on the length of the carbon chains. Mölder et al. predict in a theoretical study that the net charges of a carbon chain converge rapidly with increasing chain length, with the central carbon atoms being almost neutral whereas excess charges are located at the chain ends [105, 106]. This will be of great importance for the photoluminescence measurements of DWCNT filled with linear carbon chains in this thesis as it will be shown in the results section.

1.5 Applications for carbon nanotubes

The properties of carbon nanotubes introduced in the former sections make them attractive for a tremendous variety of possible applications. The following points are intended to show a small selection of applications which are related to this thesis.

Integration of carbon nanotubes in electronic devices



Figure 1.20: Carbon nanotube network TFTs on a flexible $50 \times 50 \text{mm}^2$ substrate [107].

The ongoing improvement of nanoscale lithographic techniques is the main driving force behind the rise in speed and power of modern computers, allowing companies to build silicon-based microchips in smaller and smaller dimensions at an exponential rate described by Moores law. However, this process will come to a halt unless alternatives to current processor structures are found. With decreasing size, electromigration becomes a serious problem for silicon, making it less stable and more susceptible to failure. Also, since interconnects are usually made of copper. high currents become a problem as resistivity increases with shrinking size due to surface and grain-boundary scattering. Here, carbon nanotubes enter the picture: Various groups showed that semiconducting SWCNT can be used to build field effect transistors (FETs) and even the integration of such transistors into logic circuits has been achieved [108]. These transistors are capable of showing outstanding properties like high carrier mobility, low switching resistance and allowance of much higher currents when compared to conventional MOS-FETs. Another interesting feature comes to mind when constructing thin-film transistors (TFTs) out of nanotubes as shown in Figure 1.20. These films exhibit similar conductance and transperency performances like commonly used indium tin oxide (ITO) films but show better performance in the infrared range. Also, they don't contain the very expensive indium. Besides transistors, metallic carbon nanotubes are superior to copper in the sense that they are ballistic conductors and capable of current densities more than 1000 times higher than copper.

Improvement of solar cell performance



Figure 1.21: Schematic of a SWCNT-Si solar cell [5].

Despite the low power conversion efficiency (PCE) of pure nanotube based devices, the incorporation of carbon nanotubes into various solar cell structures looks promising. Conventional solar cells made of Si, Cd, Te or As inherit several problems with respect to the cost of the overall device given by the complexity like large scale single crystal growth and/or toxicity. One way to overcome this problem is the use of organic solar cells which have been developed over the last years. Here, the nanotubes are used to form bulk heterojunctions with photoactive polymers, providing a higher charge extraction and therefore increasing the PCE. In this fashion, Dabera et al. have shown a PCE of 7.6% by wrapping semiconducting SWCNT with a conjugated polymer [109]. Another method is the use of nanotubes as scaffolds for dye-sensitized solar cells. There, nanotubes serve a double-purpose, where they act as the scaffold for the small dye-molecules so that much light can be collected, but also as photoanodes. Dang et. al reported that such an architecture increases the elctron diffusion length, therefore the PCE as well and they were able to reach a value of roughly 10% [110]. The combination of nanotubes with Si substrates also provides an interesting approach. Cui et al. recently observed a PCE of 6% in a device similar to the one sketched in Figure 1.21, however, doping the nanotubes by acid treatment led to an increase of the PCE to more than 10% [5]. Although such a treatment does not provide a stable doping of the nanotubes as well as it possibly deteriorates the Si layer, other methods of nanotube modifications as shown in section 1.4 might lead to better and more stable results.

Carbon nanotubes for biological applications

An interesting detail about the optical properties of carbon nanotubes is their potential practicability in biological applications. Organic tissue is opaque in the visible range but exhibits greatly attenuated absorption, autofluorescence and scattering characteristics in the near-infrared (NIR) region. The fluorescence profiles of many different semiconducting nanotubes overlap with this range what shows their potential use as contrast agents in blood and tissue [111]. By sonicating SWCNT in an aqueous sodium cholate solution and a subsequent surfactant exchange to biocompatible phospholipidpolyethylene glycol, Welsher et al. could use an SWCNT suspension for whole-animal in-vivo imaging of mice [4]. Furthermore, in contrast to organic fluorophores or quantum dots, carbon nanotubes exhibit high photostability with no visible photobleaching effect which is usually a great problem for biological imaging [112].



Figure 1.22: In vivo near-infrared photoluminescence imaging of mice, from [4].

Besides biological imaging, the optical properties of carbon nanotubes can also be used to interact with biological organisms. As mentioned, carbon nanotubes absorb strongly at NIR wavelengths and therefore displays local heating upon NIR absorption which can be used for different purposes. The work of Kam et. al showed that DNA-functionalized nanotubes release the DNA upon NIR irradiation, allowing for its transport into the cell nucleus [113]. In the same study, they also functionalized nanotubes using a folate moiety that allowed them to directly address cells marked with a folate receptor tumor marker. The local heating of the nanotubes caused by NIR irradiation then led to tumor cell death. Nevertheless, there is still work left to be done in this field since a controlled and directed transport of nanotubes in organic systems is not yet within reach and the eventual fate of the nanotubes (how or if it even exits the system) is not known.

Chapter 2

Background of the experimental techniques

2.1 Optical properties of carbon nanotubes: Exciton photophysics

The description of the physical background giving carbon nanotubes their optical properties largely follows the reviews by Lefebvre [114] and Miyauchi [115].

2.1.1 Concept of excitons

As mentioned before, the optical properties of carbon nanotubes depend sensitively on the chirality of the nanotube, denoted by its indices (n,m). We have seen that when (n-m) mod 3 = 0, the nanotube is metallic and if else, the nanotube is semiconducting; in the context of this thesis the focus lies on the latter. A semiconducting SWCNT has a direct bandgap in the near-infrared range which is favorable for optoelectronic applications or bioimaging. The quasi-1D structure of the nanotube is responsible for very interesting properties as they show a strong quantum confinement along the circumference which results in the rise of van Hove singularities in the density of states (Figure 1.9c). This results in optical properties being strongly influenced by electronic many-body correlation effects and the optical transitions themselves are dominated by excitons which are bound electron-hole states. In conventional bulk semiconductors excitons are usually only seen at low temperature as their binding energy is very low (in the order of the room temperature thermal energy ≈ 27 millielectron Volts (meV)) [116]. In SWCNT however, the binding energy can be as high as several hundred meV [1], so excitons are quite stable even at room temperature.

Figure 2.1a shows the selection rules for optical transitions in SWCNT for incident light being polarized along the nanotube axis (longitudinal, left picture) or perpendicular (transversal, right picture). As the nanotube band structure consists of a big set of subbands near the K point, however, only the first and second subband is shown as they are the only bands relevant for this thesis. A longitudinal exciton (labeled X_{ii}) consists of an electron and a hole with the same quasi-angular momentum, so the exciton itself has no quasi-angular momentum. Due to the antenna-like structure of the nanotube, longitudinal excitons are responsible for the major optical transitions and all of the optical methods in this thesis are devoted to this type. Never-



Figure 2.1: (a) Polarization-dependence of exciton formation in carbon nanotubes [115]. Light polarized along the nanotube axis creates electron-hole pairs from the same level of conductance or valence band (left, longitudonal excitons, labeled X_{ii}), whereas light polarized perpendicular to the nanotube axis leads to excitons formed from electron-hole pairs from adjacent bands (right, transverse excitons, labeled X_{ij}). Due to the antenna like structure of a nanotube, the most prominent optical response comes from longitudonal excitons. (b) Sketch of the energy relations concerning excitons in k-space. Optical resonances in carbon nanotubes happen at the energy of the exciton E_{EX} , which is smaller than the quasi-particle bandgap E_G due to the exciton binding energy E_B .

theless, transverse excitons (labeled X_{ij}), which posses quasi-angular momentum that connects electron and hole states from different subbands, also exhibit small but distinct optical features from which important informations on the SWCNT band structure can be gained. For example, the intrinsic electron-hole asymmetry of transverse excitons can be used to evaluate the band asymmetry parameter s (see equation 1.11) (the effective overlap integral) for each chirality [117].

In general, under light illumination of a SWCNT, a photon can be absorbed that excites an electron from the valence to the conduction band, leaving a hole behind. The electron with negative charge and the hole with positive charge interact through the attractive Coulomb force and form a bound state, the exciton, which is stabilized by the binding energy E_B of the two particles. In the case of a nearly ideal one dimensional semiconductor that 2/3 of SWCNT are representing, a considerable portion of electrons and holes near the band edge make up excitons due to the rise of van Hove singularities. Consequently, optical resonance in SWCNT predominantly occurs at the wavelength (energy) of the incoming photon that corresponds to the exciton energy E_{EX} . This energy is smaller than the quasi-particle bandgap created by the van Hove singularities owing to the binding energy E_B (Figure 2.1b) [1].

Figure 2.1b shows a schematic of the energy dispersion relation of excitons in momentum space as a function of \vec{K}_{EX} , which stands for the center-of-mass wavenumber of the exciton whereas the energy of the excitons is labeled E_{ii} referring to the i-th subband electrons and holes. Mainly excitons with $\vec{K}_{EX} \sim 0$ are responsible for direct optical absorption and emission due the small momentum of photons; only such transitions were investigated in this thesis. However, by phonon-assisted processes optical transitions for excitons with $\vec{K}_{EX} \neq 0$ become also possible, as it has been shown on samples strongly enriched with (6,5) tubes [118].

2.1.2 Exciton fine structure

Since there are two carbon atoms in the unit cell of graphene there are two equivalent band structures in the momentum space of nanotubes K and K', shown in Figure 2.2a. Electrons and holes can combine directly (KK or K'K') or indirectly (KK' or K'K). Due to a short-range part of the Coulomb interaction which gives rise to electron scattering between the K and K' point, the "direct" excitons are coupled to form a bonding (+) and an anti-bonding (-) state whereas the "indirect" stay decoupled because of momentum conservation [119]. These excitons split into singlet and triplet states again by short-range Coulomb interaction. Hence, there are 16 exciton states in total. Only one of them, the direct bonding exciton (KK-K'K' (+)) is optically allowed and is therefore often called "bright" exciton. All other first order excitons do not contribute to absorption and emission, thus "dark" excitons.



Figure 2.2: Exciton fine structure in carbon nanotubes. (a) The two equivalent carbon sites in the unit cell give rise to four different electron-hole configurations. (b) Relationship of the exciton energy levels to the spectral features observed for PL of SWCNT. Adapted from [115]

These dark excitons are energetically located in the vicinity of the bright exciton state (Figure 2.2b) which affects the optical properties of carbon nanotubes significantly. For instance, the temperature dependence of the photoluminescence intensity at low temperature as well as a non zero intensity at 0K is attributed to a nonequilibrium distribution of excitons between bright and dark states [120]. The brightening of the dark states and therefore luminescence enhancement can be achieved by spin-degeneracy lifting induced by the Aharanov-Bohm effect in strong magnetic fields [119]. Indirect dark excitons can also show luminescent behaviour if an optically allowed phonon (e.g. one seen in Raman measurements, section 2.4) is involved. Scattering between the bright and direct dark state is normally forbidden, however, intrinsic deviations from ideality such as the presence of defects or extrinsic environmental effects can lift this limitation [121]. Also Miyauchi et al. found that due to the intraband and intra-fine-structure thermalization of excitons, the intrinsic oscillator strength of the bright excitons is reduced by a factor of five [122].

2.2 Photoluminescence spectroscopy

2.2.1 Photoluminescence of carbon nanotubes



Figure 2.3: Schematic of the photoluminescence process in carbon nanotubes: Light with an energy E_{22} creates an exciton, which non-radiatively relaxes to E_{11} where electron-hole recombination occurs and a photon with this energy is emitted.

Since its discovery in 2002 by O'Connell et al. [123], photoluminescence of SWCNT has triggered worldwide investigations in this field due to their possible applications, e.g. for usage as biomarkers [4]. Figure 2.3 shows the main process of photoluminescence (PL) in carbon nanotubes: At first, incoming light with an energy similar to E_{22} and polarized parallel to the tube axis is absorbed and a bound electron-hole pair, an exciton, is formed (as mentioned before, the exciton energy is smaller than the bandgap between the conduction (c_i) and the valence band (v_i) due to the exciton binding energy). The exciton then relaxes nonradiatively to the E_{11} level (dotted arrow) where it collapses and a photon, that has less energy than the photon in the beginning, is emitted. A Plot of such a measurement is usually referred to as a "PL map" which is shown for HiPco-SWCNT in Figure 2.4. Here again we can see why debundling is a very important issue for measuring PL or carbon nanotubes. The formed exciton can decay very rapidly via nonradiative processes to either metallic nanotubes or semiconducting nanotubes with smaller bandgap in the same bundle. Since these energies depend sensitively on the specific nanotube chirality, each species will appear in a different region in a measurement of PL emission with varying excitation wavelength which is indicated by the white lines next to these not assigned peaks.

Several different species denoted by their (n,m) values are seen for the HiPco-SWCNT that have a mean diameter of 1nm and a broad diameter distribution. Consequently, semiconducting SWCNT with a diameter near this value appear strongest in the PL map (e.g. the (9,4) tubes with $d_t = 0.91$ nm), whereas smaller species like the (6,5) ($d_t = 0.76$ nm) appear weaker. Also, the effect of bundling can be seen by the presence of vertical lines starting at species with higher excitation wavelengths to lower values. These appear if tubes with a bigger bandgap



Figure 2.4: Photoluminescence map of a HiPco SWCNT sample. As each nanotube has different values for E_{11} and E_{22} , distinct spots appear by measuring a sample of nanotubes with different excitation wavelengths. If the nanotubes are not debundled sufficiently, additional peaks appear which are marked by the white lines. For example the unlabeled spot to the right of the (6,5) species is created by the bundling of a (6,5) tube with a (7,5) tube. For the (n,m) assignment, the work of Bachilo et al. has been used as a reference [124].

are bundled with smaller bandgap tubes where the former is transferring the exciton energy non-radiatively to the latter. Emission of a specific tube, for example the (7,5), then appears at the excitation wavelength of another tube, here the (6,5). Qian et al. observed this effect by tip-enhanced near-field optical microscopy and found that this exciton energy transfer becomes very efficient (up to 90%) for distances < 2nm [125]. These efficiencies were explained by Förster type electromagnetic near-field coupling.

PL mapping is also a very useful tool to see the diameter distribution of semiconducting nanotubes within a sample and in contrast to absorption spectroscopy, each semiconducting species can be resolved seperately due to each nanotubes unique E_{11}/E_{22} signature. However, for an exact analysis and for receiving absolute values in the diameter distribution, the PL quantum yield (QY) of the different species has to be taken into account since nanotubes with big chiral angles (near armchair-like) give a seemingly stronger PL response than near-zigzag tubes [126]. The background of this chirality dependence is the variation of the absorption cross section given for nanotubes with different chiral angles which is used for calculating the absolute quantum yield of a sample. Vialla et al. reported that this value can vary up to a value of 2.2 [127].

The quantum yield of the PL process in nanotubes is of great interest for two reasons: Firstly, basic physics leading to that process can be fathomed; secondly, the process allows for an understanding of photonic and optoelectronic applications. It is defined as the ratio between the number of emitted photons and absorbed photons. Equivalent to that it can also be defined by the excitonic lifetimes [115]: The intrinsic radiative lifetime of an exciton τ_R can be seen as the time an exciton decays into emitted photons due to the coupling to the electromagnetic field in a very long structurally perfect and unperturbed nanotube. In a real nanotube, τ_R is composed of the photoluminescence lifetime τ_{PL} and the complementary non-radiative lifetime τ_{NR} :

$$\eta_{PL} = \frac{\# \text{ emitted photons}}{\# \text{ absorbed photons}} = \frac{\tau_{PL}}{\tau_R} = \frac{\tau_{PL}}{\tau_{PL} + \tau_{NR}}$$
(2.1)

PL Lifetimes for SWCNT are usually in the order of 10-100ps [128, 129, 130] whereas the radiative lifetimes reported are in the range of 10ns [131, 132].



Figure 2.5: (a) Near-field PL spectra taken along several positions indicated in the near-field PL image a micelle-encapsulated SWNT shown in (b) [133]. (c) PL image of a free-standing nanotube [50]. The PL signal is only quenched by contact with the substrate (red) or a possible defect site in the center.

For surfactants, the QY of SWCNT is usually in the order of 1% [122, 134, 135], meaning that the exciton relaxation is dominated by non-radiative processes. On the other hand, for free-standing nanotubes in vacuum, a value of 7-8% has been reported [50, 136]. To understand these low values, one has to consider exciton mobility and the environmental effects they are exposed to during their PL lifetime in carbon nanotubes. The exciton formed in a nanotube is (usually) not bound to a fixed location but it can migrate along the nanotube axis [137]. While the exciton is moving it can experience several forms of perturbations like defects or nanotube ends [77, 135] as well as surface potential variations [138] that lower the PL quantum yield. Figure 2.5a shows near-field PL spectra of a single nanotube suspended in sodium dodecyl sulfate. Hartschuh et al. observed that the PL of their sample was highly localized on short segments of the nanotube [133]. On the other hand, Lefebvre et al. observed almost homogeneous PL intensity from free-standing nanotubes where only those sites did not show PL that were in contact with the substrate.

The PL line width also contains a lot of information, as a broad line width reflects a dephasing process of the exciton faster than the luminescence lifetime [137, 139]. Several groups found that those tubes with narrower line width exhibit brighter luminescence caused by different sample preparation [6, 140]. For samples prepared similarly, the line width also shows temperature dependance which can be explained by decreased electron-phonon interaction at low temperatures, decreasing the line width and increasing the PL intensity [139, 141] (though at even lower temperatures, the exciton fine structure starts playing a role, changing this picture).



Figure 2.6: Water filling of carbon nanotubes leads to a shift in the emission wavelength [130].

Therefore, the photoluminescence of carbon nanotubes can be affected by various sorts of extrinsic effects. Due to the structure of a SWCNT, electron-electron and electron-hole interactions play an important role for the optical transitions. Thus, these transitions are strongly influenced by changes in the dielectric medium surrounding the nanotube, causing a charge transfer from/to the nanotube and modifications of the nanotube sidewall and interior. For example, different surfactant molecules can be used to disperse nanotubes that cause peak shifts in the emission wavelength with varying magnitude. This is attributed to a difference of the area of the nanotube covered by the surfactant [142] and its polarizability [143] which causes an alteration of the dielectric screening for Coulomb interactions in carbon nanotubes. By comparing several bio-compatible and incompatible surfactants, Tsyboulski et al. found the above mentioned relationship between PL linewidth and intensity [140], whereas Duque et al. also found such a relationship for dispersed nanotubes but additionally for samples immobilized either in aqueous gels or substrates [6]. Water-filling is an important issue for nanotube PL since sonication cuts and therefore opens the nanotube which enables water molecules to enter the hollow core. Cambre et al. have shown that water-filling causes a redshift and broader emission lines compared to empty nanotubes of the same type (Figure 2.6) [130]. C_{60} molecules inserted into nanotubes do not show an (obvious) enhancement of the luminescence signal, however, a strong shift of the excitation and emission energies in the PL maps by up to 100 meV is observed, attributed to local strain effects and hybridization of the SWCNTs and the C_{60} [144].

Filling was the choice of functionalization performed in this thesis since it can also lead to an amplification of the PL intensity; encapsulating ferrocene in SWCNT has been proven to enhance the PL QY which is shown in Figure 2.7. This is attributed to a charge transfer from the molecule to the nanotube, cancelling out the charge transfer induced by the surfactant molecule [10]. Oxygen doping has also been shown to increase the PL QY compared to pristine SWCNT [82] and by further development of such a method, a PL QY of 18% has been reached [9]. This increase in the PL QY in both cases was assigned to a localization of the otherwise mobile excitons, partly increasing their PL lifetime by preventing them from interacting with quenching



Figure 2.7: Amplification of the PL intensity due to encapsulation of ferrocene [10]. Note that since the filling procedure involves oxidation steps, the diameter distribution of the sample is altered and small diameter tubes are less abundant in the filled sample, so the effect of the ferrocene to the SWCNT PL can only be seen by the comparison of the opened and the filled tubes.

sites. The other part was attributed to the increased intrinsic oscillator strength (a dimensionless quantity that expresses the probability of absorption or emission of electromagnetic radiation in transitions between energy levels) by squeezing of the excitons in zero-dimension like states caused by the doping which is known as the giant-oscillator-effect [145]. Piao et al. observed PL brightening by covalent sidewall functionalization with aryl diazonium salts which introduces sparsely distributed sp³ defects in the otherwise sp² carbon lattice [146]. There they attribute the amplification to the appearance of a new, low-energy peak that lies below the dark exciton state seen in the exciton fine structure thus increasing the population of possible PL emitters.

2.2.2 Photoluminescence of inner tubes from double-walled carbon nanotubes

This subsection represents the introductory section of the paper published in CARBON: "Purification, separation and extraction of inner tubes from double-walled carbon nanotubes by tailoring density gradient ultracentrifugation using optical probes" [147].

In recent years, DWCNT have come into focus, since they exhibit some superior properties compared to SWCNT, especially mechanical and chemical stability. The optical properties of DWCNT however, regarding their capability of exhibiting PL, remain rather elusive due to a true cornucopia of different or even (apparently) contradictory works in the past. Due to inevitable deviations during the production process, there's always the possibility of SWCNT byproducts what is often seen as the (main) cause of PL from DWCNT samples [8]. Furthermore, there is an ongoing debate concerning the basic physical ability of DWCNT to exhibit PL due to possible similarities of PL quenching in DWCNT caused by the small intertube-distance compared to PL quenching in SWCNT bundles due to small inter-nanotube distances [125]. Additionally, Koyama et al. [148] found that the relative intensity of steady-state luminescence from inner walls in DWCNT is about 700 times weaker than that from SWCNT by comparing the PL decay rates of emitters within their samples. Contradictory to that, Yang et al. [149] state that PL is possible from inner tubes, but only if they have the right diameter. On the other hand, Hertel et al. [150] showed evidence that a majority of inner tubes exhibit PL with a slight red-shift in the exciton transition compared to SWCNT. Jung et al. [151] also observe a red-shift in their PL spectra on samples which have been covered with a mussel protein that is known to eliminate the possibility of emission from SWCNT impurities. Also, by rendering the optical response of the outer tube inactive by fluorination, Hayashi et al. [152] conclude, that their PL signals come from inner tubes.

An obvious problem in comparing these different studies lies within the deviating sample preparations. First of all, the nature of the pristine sample itself is of uttermost importance: different synthesis processes such as CVD [148, 153], HiPco [128] or transformation of C₆₀ [32] or metalorganic compounds such as Ferrocene [55] within an SWCNT to form a DWCNT result in different nanotube properties, be it different diameter and/or length distributions, chirality preferences, number of defects produced etc. Secondly, the importance of the concrete parameters of the solubilization process, i.e. the path to receiving a homogeneous solution of individualized nanotubes with (almost) identical properties as free-standing nanotubes, can not be underestimated; strong sonication is known to cut nanotubes (as seen in the work of Heller et al. [154] for SWNT or the work from Green et al. [75] for DWCNT) and therefore having an impact on the sample quality by introducing defects and as for example short nanotubes exhibit different optical porperties than long nanotubes [155]. And finally, the purification process is evenly crucial: Ultracentrifugation has been shown to extract the inner tube from the DWCNT [29], what in return means, that the source of a measured near-IR PL is from simple SWCNT [156].

On the contrary, Green et al. showed that DGU can be applied to separate nanotube samples with respect to their wall numbers [75]. From another point of view, by nanomanipulation in a scanning electron microscopy (SEM) system equipped with a cantilever, Zhang et al. have recently successfully shown that inner tubes can be pulled out from their host outer tube, if a directed pulling force is applied [30]. The application of DGU on a tip-sonicated DWCNT sample seems to be a crucial factor in the discussion, whether DWCNT are capable of exhibiting PL or not. Interestingly, most works claiming to observe PL from inner tubes did not apply DGU to the sample [32, 150, 151, 152, 153, 157, 158, 159] whereas those claiming that PL from inner tubes does not occur or is severely quenched [8, 29, 75] applied DGU to their samples. The work of Yang et al. [149] represents a special case, i.e. that the selective observation of PL from inner tubes could be caused by the sample preparation.

2.3 Optical absorption spectroscopy

2.3.1 Absorption spectra of single-walled carbon nanotubes

Optical absorption spectroscopy is one of the most fundamental techniques as it directly probes optical transitions. Figure 2.8a shows the spectra measured by Kataura et al. between 0.5 and 6 eV for nanotubes synthesized by the arc discharge method deposited as a film on a quartz substrate [160], so the nanotubes are bundled. The most peculiar peak is seen at ≈ 4.5 eV for the π -plasmon originating from a collective excitation of π electrons of carbon nanotubes which is always present in absorption measurements of nanotubes as a background feature. In Figure 2.8b the absorption spectra received from an aligned SWCNT film are plotted [161]. Here, Murakami et al. investigated the polarization dependence of the π -plasmon and the low energy excitonic transitions of SWCNT. They used light polarized parallel to the substrate and varied the incident angle (amongst other methods). The position as well as size and shape of the π plasmon absorption is affected strongly when the polarization is changed. Concommitantly the signal of the excitonic transitions is either diminished or enhanced by altering the incident angle. Absorption measurements in this thesis were performed with solubilized nanotube samples that were not aligned and non-polarized light was used so this effect is negligible for the subsequent analysis.

In Figure 2.8c the absorption spectra at low energies of nanotube film samples with different mean diameters (A to F) are illustrated [162] after subtracting the background of the π plasmon. From the top to the bottom graph the mean diameter of the nanotubes decreases and the peaks correspond to the first (E_{11}^S) and second (E_{22}^S) excitonic transitions of semiconducting as well as to the first excitonic transition of metallic carbon nanotubes (E_{11}^M) . Using the linear k approximation valid for low photon energies, the background subtraction can be performed by assuming a linear background which is subsequently subtracted so that only the contributions of optically active nanotubes (i.e. showing excitonic transitions) remain. In this way samples containing different amounts of carbon nanotubes can be normalized to the same density by using a minimum of the absorption signal so that their optical properties can be compared, e.g. [10, 77, 165, 166]. Miyata et al. separated SWCNT with a diameter distribution between 1.1 and 1.3nm according to their metallicity, enabling them to observe higher order transitions [163], illustrated in Figure 2.8d. Again the strongest contribution comes from the π plasmon seen for both metallic and semiconducting tubes at ≈ 4.5 eV. The decomposition of the different contributions brings out the third (here S_{33}) and the fourth (S_{44}) excitonic transitions of semiconducting and the second (M_{22}) excitonic transition of metallic carbon nanotubes.

As mentioned in the previous section for nanotubes, these transitions depend heavily on the environment and the degree of bundling. Figure 2.8e shows the absorption spectra of samples containing individualized nanotubes prepared by different techniques [164]: SWCNT synthesized by performing alcohol CVD at different temperatures (a-c) and the reference HiPco sample (d). Each peak in this picture corresponds to an excitonic transition of a specific nanotube with the E_{11} assignement given for the respective tube at lower photon energies. The transition energies depend on the nanotube diameter and chirality, so measuring the optical absorption of a nanotube sample gives an idea of the chirality distribution in each sample. It can be seen that the observed peaks from Figure 2.8a-c shift to lower energies, indicating that the mean diameter grows with increasing synthesis temperature since the transition energies roughly scale with $1/d_t$.

2.3.2 Absorption spectra of double-walled carbon nanotubes

Optical absorption spectra detect signals from both the inner and outer tube simultaneously. Therefore, the resulting spectrum reveals an overlap of both contributions if the E_{11} transitions of the inner tubes are approximately at the same position as the E_{22} transitions of the outer tubes which is sketched in Figure 2.9a. The work of Iakoubovskii et al. shows a way to deconvolute the inner and outer tube signal by an ozone etching technique, rendering the outer tube contribution inactive as illustrated in Figure 2.9b [153]. Consequently, in the total spectrum, the former is influenced by the latter. Since the diameter distribution in their experiments is comparable to



Figure 2.8: Optical absorption spectra of SWCNT: (a) Nanotubes synthesized by the arc discharge technique with a diameter distribution of 1.24-1.58nm deposited on a quartz substrate showing a strong contribution of the π -plasmon at high photon energies and weak features of excitonic transitions at low energies. Adapted from [160]. (b) Absorption spectra of a vertically aligned SWCNT film with light polarized parallel to the substrate plane and the incident angle varied from 0° (\perp to substrate, bottom) to 45° (top) in 7.5° steps. The position of the π -plasmon shifts and the appearance of excitonic transitions at low energies show a clear polarization dependence. Adapted from [161]. (c) Low energy features of the absorption spectra from nanotubes after background subtraction of the π -plasmon with decreasing diameter (from top to bottom) [162]. (d) Absorption spectra of metallicity seperated nanotubes allowing the observation of higher order excitonic transitions for semiconducting (S_{ii}) and metallic (M_{ii}) tubes [163]. (e) Absorption spectra of individualized SWCNT synthesized by alcohol CVD. Due to reduced tube-tube interactions signals of specific chiralities can be observed and are denoted by their (n,m) values. Adapted from [164].

the distribution for the work in this thesis, similar effects can be expected. Miyata et al. used strong sonication and density gradient ultracentrifugation to extract inner tubes of DWCNT [29]. Figure 2.9c shows the absorption spectra of DWCNT before (black curve) and after (red curve) extracting the inner tubes. In the case of unseparated tubes, the inner tubes are nested inside their outer tube host and consequently the absorption spectrum shows an overlap of inner and outer tube contributions. An unambiguous assignment of inner tube species similar as performed by Miyauchi et al. [164] in the previous section is hard to perform since the peaks appear blurred. After the extraction process several distinct peaks emerge in the near-infrared range which can be assigned to different nanotube species.



Figure 2.9: (a) Sketch of the band structure for inner and outer tubes where c_i and v_i are the conduction and valence band, respectively. Since inner and outer tubes show van Hove singularities at similar positions, the optical absorption spectrum will show an overlap from both contributions. (b) Optical absorption spectra of inner and outer tube contribution of a DWCNT sample by using an ozone etching technique to "deactivate" the outer tube contribution [153]. (c) (n,m) assignment for extracted inner tubes (red curve, "Inner S₁₁") by Miyata et al. [29]. The same peaks are hard to identify inside the DWCNT structure (black curve, "Unseparated") making an unambiguous assignment of inner tube species difficult. Only the (7,5) or the (7,6) species show clear peaks in both spectra. Adapted from [29].

For this thesis absorption spectroscopy was used in two ways: first to compare optical properties of pristine DWCNT with DWCNT that were subjected to different solubilization techniques and second to investigate the effect of filling DWCNT with linear carbon chains on their absorption spectra. The latter measurements were also used to normalize all samples to the same optical density which is crucial for comparing the photoluminescence signals of each sample.

2.4 Raman spectroscopy

2.4.1 Vibrational modes in carbon nanotubes

Detailed reviews on the physics on Raman scattering in carbon nanotubes are reported elsewhere [167, 168, 169], so only a short overview is given here. Raman spectroscopy involves the analysis of light scattered inelastically from a sample which has become a powerful tool in solid state physics for material characterization. The advantages are: a) it is a non-destructive method, b) it doesn't require complicated sample preparation and c) it is reasonably fast and can be performed at room temperature and ambient pressure. In general, as depicted in Figure 2.10, an electron can be excited from the ground state to a higher "virtual" level by absorption of a photon. The recombination of the electron with the hole can occur either directly without energy loss so the incoming photon is scattered eleastically (Rayleigh scattering), or inelastically by the emission (Stokes scattering) or absorption (Anti-Sokes scattering) of phonons.



Figure 2.10: Conceptual image of the scattering process where the incoming photon is scattered elastically (Rayleigh), or inelastically, either losing energy (Stokes) or gaining energy (Anti-Stokes).

Usually, the scattered signal is weak if only phonons are involved in the process but the scattering efficiency is enhanced greatly when the incident light matches an electronic transition of a system which is called resonance Raman scattering [170]. The latter is of crucial importance for carbon nanotubes because the density of states can reach very high values at certain energies. The intensity observed in Raman measurements can be expressed as

$$I(E_{Laser}) \propto \left| \frac{1}{(E_{Laser} - E_{ii} - i\Gamma)(E_{Laser} \pm E_{Ph} - E_{ii} - i\Gamma)} \right|^2$$
(2.2)

where Γ represents the width of the resonance window which is also environment dependent as the window is usually broader for nanotubes in bundles than they are when isolated in solution [171]. E_{Ph} is the phonon energy and \pm is selected by either Stokes (+) or Anti-Stokes (-) scattering. Equation 2.2 shows that if the energy of the laser E_{Laser} is close to the energy of an excitonic transition in a carbon nanotube E_{ii} , the denominator reaches a minimum and therefore the intensity is enhanced greatly, allowing for investigation even at the single nanotube



Figure 2.11: Example of a typical Raman measurement of a HiPco SWCNT powder excited with a 633nm laser.

level. In carbon nanotubes, many different vibrational modes are possible, however, only few of them are of significance for this thesis; the most important informations gained by Raman spectroscopy in the present case are the signal of linear carbon chains inside DWCNT, the diameter distribution and the defect density. Figure 2.11 shows a typical measurement of the Raman signal for a HiPco SWCNT powder at room temperature, excited at $\lambda_{Exc} = 633$ nm. The observed peaks are explained as follows:

Radial breathing mode, "RBM"

Within the family of materials derived from graphite, the radial breathing mode, short "RBM", is unique to carbon nanotubes. The RBM, located between 100 and 400cm^{-1} , is a totally symmetric vibrational mode associated with a coherent vibration of carbon atoms in radial direction of the nanotube axis. It is especially important for the determination of the diameter of nanotubes through the linking of its frequency ω_{RBM} to the nanotube diameter d_t via

$$\omega_{RBM}[cm^{-1}] = \frac{A}{d_t[nm]} + B, \quad A = 234cm^{-1}nm, \ B = 10cm^{-1}$$
(2.3)

Therefore, if the incident or scattered light is in resonance with an excitonic transition of a nanotube according to equation 2.2, one can derive the diameter distribution of a sample consisting of different chiralities by varying the laser energy and investigate on the RBM. The value A in equation 2.3 can be determined by ab initio calculations and was found to be $234cm^{-1}$ [172]. The constant factor B depends on environmental influences. The value of $10cm^{-1}$ accounts

for intertube interactions in SWCNT bundles [173, 174]. The exact values are matter of a long lasting discussion and several different combinations of A and B have been proposed (e.g. A $= 217.8 cm^{-1}$ nm and B $= 15.7 cm^{-1}$ reported by Jorio et al. [175] or A $= 204 cm^{-1}$ nm and B $= 27 cm^{-1}$ by Meyer et al. [176]) but all these values are slightly sample and environment dependent. In this thesis i used the values given in Equation 2.3 as they best fit the kinds of samples used [37].

Tangential "G" mode

The graphite-like band (thus "G-Band") in carbon nanotubes is derived from the G-Band in graphite and is linked to an in-plane tangential vibration resulting in a stretching of the bond between the two carbon atoms in the graphene unit cell. It is observed around 1590cm^{-1} and is the most prominent feature seen in Raman measurements of carbon nanotubes. When the bond lengths and angles of graphene (or the nanotube) are modified by strain or external perturbations, the hexagonal symmetry is broken. Therefore, the G-Band is highly sensitive to strain but also curvature effects which are inherent to nanotubes due to the 1D quantum confinement. They give rise to up to six allowed G-Band phonons [177], although only two of them are usually dominating the spectrum, the G⁺ for in-plane vibrations along the tube axis (around 1590 cm^{-1}) and the diameter dependent G⁻ for in-plane vibrations along the circumferential direction (around 1570 cm^{-1}). The latter also shows an asymmetric (Fano-like) lineshape due to the interference with conduction electrons and is very sensitive on the tube type and doping [178, 179]. In Figure 2.12 the position of the G^+ and the G^- is plotted for 62 different nanotube species, performed by Jorio et al. [178]. It can be seen that while the position of G^+ exhibits almost no dependence on the tube type and diameter, the case is different for G^- : the frequencies not only shift to lower values by increasing the tube diameter but also a split between semiconducting and metallic nanotubes occur.



Figure 2.12: Dependence of the shape and position of the G^+ and G^- line on the nanotube type and diameter [178]: While the G^+ shows almost no chirality dependence, the position of the $G^$ band is heavily influenced by the metallicity and the diameter of the tube.

Other nanotube modes: D, M, iTOLA and 2D line

Although appearing as very low signals for the measurements on the samples used in this thesis and not being investigated quantitatively, a few thoughts shall be dedicated to other observed modes. The "D"-Mode of carbon nanotubes is located around 1300cm^{-1} which is also seen for other graphitic materials. In contrast to the RBM and G-Mode, the D-Mode originates from a second-order Raman process and becomes Raman-active by the presence of defects, impurities or strong sidewall functionalization. Therefore, it is often used to investigate on the quality of a given sample by calculating the ratio of the intensities of the D-Mode and the G-Band, as it is done here. The M-Mode around 1750cm^{-1} is an overtone of the oTO-Mode and the iTOLA around 1950cm^{-1} is a combination mode of the iTO and LA mode [167]. M and iTOLA are important to remember as to not confuse them with the carbon chain mode rising between both, which will be adressed in the last section of this chapter.

The 2D line is a very prominent feature observed for carbon nanotubes and is found at a frequency double to that of the D mode. Similarly, the 2D line also originates from a second-order Raman process but it is not linked to the presence of a defect and instead another phonon is involved. The peak is usually split due to different resonance conditions for the incoming and the scattered photon. Since Shi et al. observed that the 2D line shows only very small changes for DWCNT filled differently with linear carbon chains, this feature was not investigated for this thesis.

2.4.2 Raman spectroscopy of double-walled carbon nanotubes

The Raman signal of double-walled carbon nanotubes contains very interesting information on their nature. As mentioned in chapter 1, the inter-wall distance in DWCNT can vary from tube to tube, allowing a given inner tube species to be resident in different outer tube hosts. This can be seen by the splitting of RBM-lines at low temperatures so that tube-tube interactions are minimized [37, 38], illustrated in Figure 2.13a. The shielding of the inner tube from environmental effects through the outer tube has been identified by a vanishing factor B and narrowing of the same mode while measuring ω_{RBM} for inner tubes of DWCNT [181]. Also, by electrochemical doping Kalbac et al. found that while the outer tube is very sensitive to doping effects, the inner tube only slowly followed this behaviour [182]. By studying the coupling of ω_{RBM} for inner and outer tubes, Liu et al. observed that the weak van der Waals interaction between the tubes indeed is dependent on the inter-wall distance as well as the unit-area force constant is following the same trend as layers of graphite [39]. On the same subject, Pfeiffer et al. showed through investigation in the shift of the G-Band that the interaction between tubes is stronger in bundled SWCNT than the interaction between inner and outer tubes [38].

Concerning the electronic properties, DWCNT can have four different configurations with both tubes being semiconducting, metallic, or different. By studying metallicity separated tubes, Villalpando-Páez et al. discovered that these configurations have different effects on the Raman spectra as seen by different positions of the G-Band [180]. For example, as illustrated in Figure 2.13b, a shoulder of the G-Band appears at 1520cm^{-1} . This is attributed by the authors to environmental changes of the inner metallic tube as it is shielded from external perturbations. Simon et al. have investigated DWCNT structures grown by inserting C_{60}/C_{70} molecules into SWCNT with the filling material not being composed of conventional ¹²C but of different amounts of ¹³C [31]. In this way they could observe a strong splitting of the G-Line since the larger mass of the atoms making up the inner tube leads to a downshift of the observed frequency.



Figure 2.13: Raman spectra of DWCNT: (a) Raman signal of the RBM from DWCNT excited by different lasers in high resolution (hr). The top spectrum was recorded at 90K, the rest at 20K [37]. (b) Measurement of the G-Line of a sample with inner metallic and outer semiconducting tube [180]. Here an extra peak around 1520cm^{-1} is observed which is attributed to the G⁻ line of the thin inner tube shielded by the outer tube. (c) D-, (left) and G-mode (right) response of inner tubes from isotope engineered DWCNT [31]. Arrows and filled circles indicate inner and outer tubes respectively. The outer tube is made of conventional ¹²C whereas the inner tube consists of different amounts of ¹³C. Due to the larger mass of the latter the frequencies are downshifted.

2.4.3 Linear carbon chains investigated by Raman spectroscopy

In Raman measurements, only carbon chains of the polyyne type $(-C \equiv C_{-})_n$ can be seen since the cumulene type $(=C=C=)_n$ only has acoustic phonon branches and no optical phonon branches [184]. In any case, the polyyne type is expected to be far more abundant due to a higher stability than the cumulene type [183]. The alternating bond length of the polyynes (as triple and single bonds have different lengths, 1.2 and 1.3pm, respectively) gives rise to a bandgap following from the Peierls theorem [185], so exciting the chains at this energy again leads to an enhancement of the signal in Raman measurements. This bandgap as well as the measured Raman shift depend on the chain length, i.e. the number of carbon atoms within the chain which has been evaluated theoretically [183, 186] as well as experimental evidence for this behaviour was obtained [104, 187]. For long chains, Fantini et al. found that the values for the bandgap saturates at about 2.2 eV (around 564nm). Shi et al. used Raman mapping to evaluate the resonance condition of long linear carbon chains which is shown in Figure 2.14a [13].

By using several different lasers and measuring the intensity of the signal originating from the chains it was found that the resonance window is quite broad (than 50meV). Figure 2.14b shows several different approaches to calculate the Raman frequency as a function of the carbon chain length (2m is here the total number of atoms in the chain) [183]. The use of a linear/exponential



Figure 2.14: (a) Raman map of a DWCNT filled with linear carbon chains. By using different lasers, the resonance condition for the carbon chains of different lengths can be evaluated. The resonance window is broad, indicated e.g. by the red color for the strongest chain signal in the plot. (b) Different methods to calculate the Raman shift of the carbon chain signal as function of the chain length (2m is the total number of chain atoms). The linear/experimental approach fits best for reported values [183]

hybrid force field scaling scheme for describing the exponential behaviour of the carbon-carbon stretching seems most suitable for explaining different experimental findings, e.g. [98, 187, 188]. Wakabayashi et al. also found that the Raman shift of polyynes with the same size is depending on the environment [187]. For long carbon chains inside double-walled carbon nanotubes however, making exact predictions for each tube type is quite complicated since the size of the unit cell of the tubes involved is already big as one can expect from equation 1.6, so the number of carbon atoms to calculate with gets very large.

Figure 2.15 shows a typical result of a Raman measurement from DWCNT filled with linear carbon chains. The first obvious difference to the Raman signal of HiPco SWCNT from Figure 2.11 is the appearance of an additional mode at around 1855cm^{-1} resulting from the presence of carbon chains. The second difference can be seen for the RBM since inner and outer tubes contribute to the overall signal and the diameter distribution of the sample is big, leading to an overlap of both contributions. As a result, the peaks in the RBM are not sharp but smeared out.



Figure 2.15: Example of a typical Raman measurement of a DWCNT powder at room temperature after an annealing treatment, here $1460 \,^{\circ}$ C, excited with a 568nm laser: The radial breathing modes ("RBM") of both inner and outer tubes are seen. The D-Mode, an indication for the defect density of the sample, is quite low, showing the high quality of the sample. The "L"-Line around $1855 \,\mathrm{cm}^{-1}$ results from the presence of long linear carbon chains inside the inner tube of the DWCNT and its intensity compared to the G-Band can roughly be seen as a "filling factor" of the DWCNT with such chains. M and iTOLA are overtone modes not investigated in this thesis.

Chapter 3

Sample preparation & experimental setups

The following section represents partly the experimental section of the paper published in CAR-BON: "Purification, separation and extraction of inner tubes from double-walled carbon nanotubes by tailoring density gradient ultracentrifugation using optical probes" [147].

3.1 Synthesis of double-walled carbon nanotubes filled with linear carbon chains

3.1.1 Growth of pristine double-walled carbon nanotubes

For the growth of double-walled carbon nanotubes, the well established method of high vacuum chemical vapour decomposition of alcohol [49] (in the literature referred to as HVA-CVD or short CVD) was used, as shown in Fig 3.1. The catalyst used is similar to the one used by Endo et al. that yields in a very high content of DWCNT [61] but adapted for HVA-CVD [13]. First, a catalyst was placed in the center of the hot zone of a tube furnace (quartz) which was subsequently evacuated. The catalyst was a mixture of 97% (mass fraction) magnesium oxide (MgO) and 3% ammonium iron(III) citrate (C₆H₈O₇ nFe nH₃N). Establishing a high vacuum in the sample chamber before introducing the carbon source was very important: it has been shown by Grüneis et al. that a vacuum less than $< 10^{-5}$ mBar is essential for the growth of high quality DWCNT [189]. In the present case this pre-synthesis vacuum was always $< 10^{-6}$ mBar. When this pressure is reached, the catalyst is heated to 875 °C. Then the carbon source, ethanol (C_2H_5OH), is fed into the furnace to react with the catalyst and a rotary pump aids to establish a constant flow of ethanol which is kept for one hour.

The resulting material, which has typically a black appearance resembling charcoal, then has to be cleaned from all carbonaceous byproducts and remaining catalyst material to receive a good starting material. For this purification, the DWCNT samples were first exposed to hydrochloric acid to remove remaining catalysts with subsequent filtration of the carbonaceous material. This was followed by annealing in air flow at 400 °C for 2 hours to remove (burn) amorphous carbon and to remove possible SWCNT byproducts, another air treatment was applied. As shown by thermogravimetric analysis performed by Muramatsu et al., DWCNT have a higher oxidative



Figure 3.1: (a) Sketch of the setup for the synthesis of DWCNT: First, a crucible containing the catalyst is placed in the hot zone of the furnace, evacuated and then heated to 875 °C. Then the valve to the UHV pump is closed, the valve to the carbon source opened and the valve to the rotary pump opened, so a constant flow of ethanol to the catalyst is established. (b) Fotograph of the setup.

stability of up to 200 °C higher than SWCNT which is owed to their coaxial structure as well as to high cristallinity of the bundles [190]. In this work, an annealing temperature of 500 °C for 2 hours in air was used to remove SWCNT. The effectiveness of the latter step to remove SWCNT has been shown by Li-Pook-Than et al., where the intensity of the integrated Raman signal for SWNT is much less than 1% [60]. Figure 3.2 portrays the typical appearance of the sample in solid form before/after annealing and in liquid form after sonication and centrifugation.





Figure 3.2: Appearance of the samples in solid form (left) and liquid form after applying Procedure A (see section 3.3) to the sample (right).

3.1.2 Growing long linear carbon chains inside double-walled carbon nanotubes

The growth method of long linear carbon chains inside DWCNT in this thesis is fundamentally different than those used in other works [98, 191], as it did not involve opening and filling with another precursor. Instead, they are formed by high temperature annealing of the DWCNT samples after the synthesis process described above, utilizing non used carbon atoms from the synthesis for the formation of carbon chains. It has been proposed that carbon chains inside DWCNT are abundant as "bridges" between coalesced DWCNT [192], however, since the Raman signal of LCC can be detected for samples annealed for temperatures as low as 900 °C [13], it is highly unlikely that such a process is taking place and the LCC are really positioned inside the inner tube of a DWCNT parallel to the tube axis. More details on the growth process of the chains can be found in a recently published work of our group [13] but a key result is that the length and the growth yield of the LCC are strongly connected to the post-synthesis annealing temperature.



Figure 3.3: Furnace for high temperature annealing. The connections are similar to the furnace for synthesis, except that no ethanol is connected and the tube is made of Al_2O_3 and SiC.

Here, the samples were annealed in a tube furnace (Figure 3.3) at different temperatures in high vacuum (always $< 10^{-6}$ mbar), ranging from 1370 °C to 1530 °C for 45 minutes. This procedure for the growth of LCC inside DWCNT is identical to what has been reported by our group earlier [13]. After annealing the samples at their respective temperatures, they were placed on a copper block in a cryostat to measure their Raman response. Since the intensity of the chain signal in comparison to the G-Line of the nanotubes is temperature dependent [13] the samples were placed in a cryostat to provide a constant room temperature of 295K and a low laser power of 200μ W was used to avoid sample heating.

3.2 Suspensions of pristine and filled double-walled carbon nanotubes

In the introduction we have seen that carbon nanotubes can be produced by different techniques. In any case, if the method of choice did not involve patterned growth of isolated CNT like controlled deposition of catalyst particles on a substrate, then the nanotubes are bundled after synthesis. Within a bundle, the optical response of a specific nanotube can considerably be altered due to the presence of other nanotube species as it has been shown in section 2 for optical absorption and photoluminescence measurements. Consequently, proper isolation of single nanotubes is fundamental for observing the intrinsic optical properties of carbon nanotubes. An efficient way of isolating nanotubes is by dispersing them in a solution with the help of surfactants. This has been introduced by O'Connell et al. in the pioneering work where they first reported photoluminescence from SWCNT [123]. The dispersion process usually involves sonication of nanotubes in an aquaeous solution containing a surfactant and subsequent ultracentrifugation to remove any remaining impurities and bundles. The review of Wenseleers et al. gives an overview of the effectiveness of various surfactants [91]. Additionally, sorting techniques like gel chromatography or density gradient ultracentrifugation can be applied to achieve various results like semiconductor-metal sorting [74], chirality sorting [67] or sorting of carbon nanotubes with respect to their wall numbers [75]. However, strong sonication has the drawback of cutting nanotubes i.e. making them shorter, which also alters the optical properties as it has been shown by Heller et al. that the photoluminescence quantum yield is lower for shorter nanotubes [154].

Exactly these variations of the solubilization parameters hamper the investigation of DWCNT PL, as it is mentioned in section 2.2.2. To resolve this problem, several different solubilization techniques have been applied to pristine DWCNT samples from the same batch [147] with the outcome of each procedure shown in Figure 3.4:

Procedure A: The DWCNT sample was individualized via ultrasonication in a 2% w/v sodium deoxycholate (DOC) solution, using a steel tip with a diameter of 1/4 inch, 60W of power, for 4 hours. The sample was subsequently centrifugated at 10.000 x g for 30 minutes to remove metallic particles, with a speed low enough to ensure inner tube containment. After that, the supernatant (50%) rich with isolated DWCNT was collected for further investigation.

Procedure B: The DWCNT sample was individualized via ultrasonication similar as in Procedure A, but afterwards a first purification treatment by centrifugating at 220.000 x g for 2h was applied to remove non-nanotube impurities followed by the main DGU treatment in a gradient medium containing varying concentrations of OptiPrep solution (60% Iodixanol in H₂O, Sigma Aldrich) in a 2% w/v sodium dodecyl sulfate (SDS) solution: 40%, 35%, 32,5%, 30% and 27% iodixanol content for 9 hours and 240.000 x g. This is a slightly modified procedure from the method used by Yanagi et al. [76].

Procedure C: The DWCNT sample was individualized via ultrasonication in a 2% w/v sodium deoxycholate (DOC) solution, using a steel tip with a diameter of 1/2 inch, 17W of power, for 5 hours, followed by the same first purification by centrifugation as well as DGU treatment as in Procedure B.

Procedure D: Another part of the same sample batch sonicated in Procedure A was centrifugated at $1.000.000 \times \text{g}$ for 30 minutes; this is the identical procedure as for the HiPco SWCNT sample for SWCNT control used in this work and as in [10].

After separation of the layers (be it the supernatant (50%) from Procedure A and D or the



Procedure C



Procedure B



Procedure D

Figure 3.4: Outcome of different solubilization techniques for DWCNT described in the text above. Procedure A and D appear very similar, as centrifugation without a gradient most of the time only removes residual impurities and bundles. The DGU techniques applied in Procedure B and C give different outcomes depending on the sonication power prior to centriguation: high sonication power (B) results in two different layers with the top layer containing seperated inner and outer tubes and the bottom layer containing bundles. Applying low sonication gives two very different layers. Here, the top layer contains only small inner tubes, whereas the thick layer contains big inner tubes, outer tubes, not seperated DWCNT and bundles.

individual layers from B and C), Optical Absorption Spectroscopy (OAS) was performed. For checking the abundance of inner tube species in the pristine sample, photoluminescence spectroscopy was performed using a tuneable Dye-Laser coupled into a Nanolog spectrometer.

For analyzing the effect of different post-synthesis heat treatments on the Raman and PL response of DWCNT, Procedure A has been applied to all samples. To measure optical absorption and photoluminescence, the extracted solutions were put in a quartz cuvette.

3.3 Experimental setup for absorption measurements

The measurements of the optical density were always performed immediately after ultracentrifugation and right before the photoluminescence measurements. They were carried out with a Bruker VERTEX 80v Fourier transform spectrometer in transmission geometry, as illustrated in Figure 3.5. A cuvette containing a nanotube solution was placed in the center of the sample



Figure 3.5: (a) Setup for absorption measurements in transmission geometry. The sample is placed in the focused spot of the sample chamber (light grey). (b) Photograph of the spectrometer.

chamber (light grey) where it is in the focused position of the beam. As a lightsource, a glowbar lamp (red dot) for the visible/near-infrared range was used, the beamsplitter (green bars) was made of CaF_2 and the transmitted light is received either by a Si-detector for visible light (illuminated blue box in Figure 3.5a) or a mercury-cadmium-telluride (MCT) detector (left blue box in Figure 3.5a) for infrared light. The resolution was set to $2cm^{-1}$ and the visible/near-infrared range was scanned 100 times; this was sufficient for good reproduceability.

3.4 Experimental setup for photoluminescence measurements

For the PL measurements in this thesis, a NanoLog spectrometer (Horiba Jobin Yvon) was used. Basically, it consists of several components like an excitation source (Xe lamp), sample chamber and detectors for visible and near-infrared signals; since the measured nanotubes all emit in the near-infrared range and the PL of double-walled carbon nanotubes excited by a Xe lamp is too weak, the detector for signals in the visible range and the lamp were obsolete and external sources, i.e. laser sources, were used. The setup is illustrated in Figure 3.6:

A sample containing a solution of dispersed DWCNT (details on sample preparation in section 3) is placed in the spectrometer. At first, a pump laser (COHERENT, Verdi 5G, Nd:YAG, $\lambda = 532$ nm) with a maximum light power of 5.35W is used to excite two sorts of passive systems: Either a tuneable dye laser equipped with Rhodamin 6G for measurements between 565 and 605nm or DCM (4-(dicyanomethylene)-2-methyl-6-(4-dimethylaminostyryl)-4H-pyran) for measurements between 640 and 680nm, or a Titanum sapphire laser (Ti:Sa) for measurements with wavelengths $\lambda > 695$ nm. The used laser is guided to the sample to cause PL of the nanotubes.



Figure 3.6: (a) Sketch of the experimental procedure for the measurements of the photoluminescence signal. At first light from the pump laser (Nd:YAG) excites either a tuneable dye laser or a tuneable titanum sapphire laser (Ti:Sa) (For the latter measurements, the mirrors before and after the dye laser is removed). The beam is then guided into the spectrometer to the sample. The part of the near infrared PL signal (dashed red line) which passes through a low pass filter is then guided to a grating controlling the resolution, from which the signal is guided into an InGaAs detector. (b) Fotograph of the spectrometer with the sample chamber marked by the blue wall on the lower left. During measurements, the whole system is closed except directly above the sample which is excited by an external laser.

The part of the PL signal that passes through the low passfilter ($\lambda > 850$ nm) to exclude the laser line is then guided through the spectrometer via several mirrors to a grating that enables to control the resolution. An InGaAs detector is used as a sensor. In theory, wavelengths between 850 and 1700nm can be detected, however, since the nanotubes are dispersed in a solution mostly containing H₂O, the upper detection limit roughly is 1350nm. The diameter range for the species that potentially can be measured is therefore limited to an interval of d_t ≈ 0.6 - 1.1nm.

Excitation intensities and integration times for the measurements were chosen to account for two points: Detector saturation and compensation of intensity fluctuations. The dye solution was not perfectly homogeneous and showed little fluctuations during the measurements. Therefore, the integration time was always set to at least several seconds to minimize this error. Normalization to integration time and laser intensity was straightforward as the PL signal is scaling directly proportional to those two values. The laser power was always < 100mW. This intensity was low enough to avoid problems like nonlinear PL behaviour in the intense excitation regime caused by exciton-exciton annihilation that would lead to saturation effects in the PL intensity [193] or a significant broadening in the PL linewidth caused by an increase of exciton dephasing [139]; both of these effects were not observed. Also, by using a low power heating of the sample was avoided, since a difference in temperature also results in PL intensity differences [120], however, the PL intensity stayed constant for all measurements.

3.5 Experimental setup for Raman measurements

For the Raman measurements in this thesis, a multi-frequency Raman microscopy system (Horiba LabRAM HR) in backscattering geometry was used as shown in Figure 3.7 (top). In this system, an external laser (Coherent Innova 70C) with a wavelength of 568nm is coupled into the spectrometer via several mirrors and filters and focused on the sample with a microscope equipped with a 50x objective. A moveable mirror enables one to place a camera in the beampath of the backscattered light, allowing proper focusing of the incident laser beam on the sample. The Raman shift induced by the sample is then recorded with a CCD detector. The wavelength of 568nm was chosen since it is within the resonance window of the carbon chains.



Figure 3.7: Top: Schematic of the experimental setup for Raman measurements. The sample is actually placed inside the cryostat which has an optical window. The beam of an external laser (black line) is guided first through the spectrometer and several filters, so that the background is reduced greatly, and then is focused onto the sample with a 50x objective. The backscattered light (red line) is then guided back to a CCD detector. Bottom: Fotograph of the setup.
The samples themselves were placed in a cryostat on top of a copper block. This step is essential since the signal of the carbon chains is temperature dependent [13] so for comparing the Raman response of differently annealed samples the temperature has be the same for all samples and was chosen to be room temperature, 295K. The laser power was always 200μ W; although this power was much lower than what is commonly used in Raman measurements, the peak intensity reached values up to 150 counts per second. Combined with the thermal equilibrium of the sample, the signal intensity was stable and showed very little fluctuations (less than 1%).

Chapter 4

Results & discussion

4.1 Purification, separation and extraction of inner tubes from double-walled carbon nanotubes by tailoring density gradient ultracentrifugation using optical probes

The following section represents the result section of the paper published in CARBON: "Purification, separation and extraction of inner tubes from double-walled carbon nanotubes by tailoring density gradient ultracentrifugation using optical probes" [147].

4.1.1 Comparison of the optical absorption spectrum to single-walled carbon nanotubes

Before analyzing the samples after the DGU treatment, we compare the absorption spectra of the DWCNT sample not treated by DGU and using a low centrifugation speed (Procedure A) with the HiPco-sample that mainly contains SWCNT (for ease of comparison, the spectra were normalized to their optical density at 900nm): In Figure 4.1 we can see that the DWCNT absorption shows only weak features of the excitonic transitions between corresponding van Hove singularities in the density of states of inner tubes with diameters between 0.6 and 1nm. The reason for this lies within the DWCNT structure: For DWCNT, the space between inner and outer tubes is given by the van der Waals radius which can vary depending on the synthesis procedure [194]. DWCNT produced by similar CVD processes with comparable diameter distributions as in this work (e.g. [195, 196]) showed values in between 0.33 and 0.41nm, this means that the outer tube diameters in our samples are between 1.3 and 1.8nm. Early works assigned the absorption signal in the interval between 900 to 1200nm to an overlap of the inner tube E_{11} and outer tube E_{22} transition for such a diameter distribution [182, 197]. In the work of Iakoubovskii et al. [153], where a similar diameter distribution is used like in this work, the outer walls of DWCNT have been exposed to ozone etching to decompose the absorption spectra of DWCNT to their inner and outer shell contributions. After applying this method it can be seen that the E_{11} transition wavelengths of the inner tubes are in the same intervall (between 900 to 1200nm) as the E_{22} transition wavelengths of the outer tubes. Therefore we can safely assume that the small size of the peaks in the absorption spectrum of our samples is caused by the same mentioned overlap of inner tube and outer tube contributions.



Figure 4.1: Absorption spectra of the pristine DWCNT sample not treated by DGU and using a low centrifugation speed (Procedure A) and the HiPco SWCNT control. Spectra normalized to their optical density at 900nm, with the green graph multiplied by 2 for better differentiation.

4.1.2 Abundance of semiconducting inner tube species

For checking the abundance of different species in the DWCNT sample, photoluminescence spectroscopy was performed. Figure 4.2 shows the line scans of the DWCNT sample from Procedure A at two different excitation wavelengths, namely 569nm to excite inner tubes with smaller diameter and 660nm for bigger diameter inner tubes. The PL response shows that the line scans cover all non-zigzag semiconducting nanotube species with a diameter between 0.65nm and 1nm as also seen by Bachilo et al. [124] (PL emission of zigzag tubes could not be resolved which is most likely due to their lower PL quantum yield compared to semiconducting species with bigger chiral angles [126, 198, 199]). We also measured the Raman signal of this solution that gave us the same results as Kim et al. obtained while investigating on dispersed DWCNT [159] and additionally, the sample from Procedure A showed a much lower PL intensity when compared to the SWCNT reference sample (not shown). Combined with the result from the optical absorption measurement this highlights that the mild centrifugation from Procedure A is not affecting the diameter-distribution of inner and outer tubes within the sample and we can see no possible extraction of inner tubes.



Figure 4.2: PL Line scans at two different excitation wavelengths for the DWCNT sample from Procedure A. Spectra normalized to their optical density at 900nm.

4.1.3 Selective extraction of inner tubes by density gradient ultracentrifugation

With this background we can analyze the DGU experiments: As it can be seen in Figure 4.3a, b, the liquid columns resulting after applying the same DGU procedure to identical samples look very different from each other. This difference becomes even more remarkable when analyzing their optical absorption spectra (Figure 4.3c). The green curve shows the absorption spectrum of the sample prepared by Procedure B. The peaks correspond to the well known E_{22} and E_{11} transition energies of various nanotubes that can be assigned to the different species with the widely accepted assignement by Bachilo et al. [124]. Basically all (semiconducting) species with a diameter in the same range as the inner tubes seen in Raman measurements from [13] can be seen; the strength and sharpness of these peaks resemble the SWCNT spectrum as in Figure 4.1, as well as the spectrum of separated DWCNT reported by Miyata et al. [29]. In this work, this behaviour was associated with the extraction of inner tubes of DWCNT due to the sample preparation by tip-sonication and applying DGU.

In stark contrast to the latter absorption measurement stands the result of the DGU step from Procedure C, where a lower sonication intensity was applied in the solubilization process than in Procedure A and B. As it can already be assumed from the violet layer seen in the bottom left picture in Figure 4.3b which is usually a sign of enrichment of only a fraction of nanotubes [74], the investigation of this layer by checking its absorption spectrum confirms



Figure 4.3: Outcome of the DGU process after different sample treatments for the pristine DWCNT samples by varying sonication parameters. A thicker area at the top with a thin layer containing all extracted inner tubes whilst the part at the bottom seems to be made out of the remaining outer tubes (a). A single, violet layer and a black, seemingly homogeneous distribution of the rest of the material become apparent. The violet layer contains nanotubes with a diameter ≤ 0.8 nm, whereas the other, bigger part contains outer tubes selected by their metallicity as well as remaining DWCNT (not shown) (b). Optical absorption spectra of the extracted layers from both procedures after applying the same DGU treatment (c). The shape and size of the peaks from both procedures look similar to the peaks from the SWCNT sample in Figure 4.1. The biggest difference however is that some of the bigger inner tubes (d_t > 0.8nm) are missing in Procedure C (marked red) although traces of the (10,2) tubes (d_t = 0.88nm) can be seen. The small hump at 800nm in the black curve is caused by the detector change during the measurement, whereas the non-marked peaks in the green curve are associated with other big inner tubes or small outer tubes. Spectra normalized to their optical density at 900nm, with the green graph being offset by a constant factor for better differentiation.

this assumption. Reminding the abundance of different inner tube species confirmed by PL measurements (Figure 4.2), several different species are not to be seen in this graph (or at least too less abundant to be noticed): (7,5) with a diameter $d_t = 0.83$ nm, (8,4) with $d_t = 0.84$ nm, and (7,6) with $d_t = 0.89$ nm. This gives rise to the question, where in the sample these tubes are: according to the PL measurement from Procedure A in Figure 4.2 and since all the procedures have been performed on samples from the same batch, these bigger tubes must be in a lower layer of the DGU column. Surprisingly, these tubes are not present in a less peculiar layer directly underneath the violet one as one would expect from the diameter distribution of the former (ranging from $d_t = 0.62$ nm for the (5,4) tubes to $d_t = 0.80$ nm for the (9,2) species) but they are abundant in the more distant thick black layer underneath. For example the (8,4) species with a very prominent E₁₁ peak at 1124nm in the green curve in Figure 4.3c but without a similar peak

in the black curve, can be found in PL measurements by exciting the top of the black layer with their E_{22} transition wavelength of 596nm, as it is seen in Figure 4.4. Interestingly, these tubes show also a much weaker luminescence intensity, indicating that these species are abundant as DWCNT which are expected to have a much lower PL quantum yield than SWCNT from the layers above (this point is examined in more detail later). On the other hand, smaller diameter inner tubes are barely to be noticed in this lower layer (e.g. the (6,4), (6,5) or (8,3)), which is a sign of extraction of these inner tubes from their host tubes and therefore having a lower buoyant density than the DWCNT in this layer, so that only very few of these species are left in this area. The latter can be caused by insufficient debundling and therefore protection from cutting through the sonication process.



Figure 4.4: Line scans of the PL signal from different layers of the sample treated under Procedure B, excited at 596nm, the E_{22} transition wavelength of 596nm of the (8,4) species. This 'missing' species can be seen, although being considerably weaker than other present species. This can be a hint that in the lower layers of the as-centrifugated sample the nanotubes are abundant as DWCNT, therefore showing PL of inner tubes. Another interesting part of this figure is, that the lower layers show only very weak features of smaller tubes like (6,5), (6,4) or (8,3). Spectra normalized to their optical density at 900nm.

This also applies to other species like the (9,4) (d_t = 0.91nm) and the (8,6) (d_t = 0.96nm) tubes with an E₂₂ transition wavelength near 725nm; this transition can also only be seen for Process B. The other layers from the DGU process that where not mentioned in both procedures contain smaller amounts of the species discussed earlier or bundles of nanotubes that are not showing luminescence. These findings support the argument of inner tube extraction due to the tip-sonication treatment, but it also implies a diameter-dependent threshold for the cutting and therefore opening of the DWCNT what greatly influences the outcome after the centrifugation treatment.

4.1.4 Analysis of the photoluminescence intensity difference from doublewalled to single-walled carbon nanotubes

An interesting part in the discussion on DWCNT PL is the emission intensity of the inner tubes. Factors range in the literature from being weaker in comparison to SWCNT by a factor of at least 10.000 [8], or about a factor of 700 weaker [148] up to almost equal signal strength [151]. Tsyboulski et al. [8] compare the emission of two different layers of a DGU column to determine the difference in the PL quantum yield of DWCNT compared to SWCNT. The SWCNT origin is assigned to be only from residual SWCNT that survived the oxidation process and not extracted inner tubes from the centrifugation process. Extraction of inner tubes though can either enrich the number of emitters in a DGU layer (by moving to top layers) or deplete it (seen from a lower layers perspective) so this process can severely alter the abundance of discrete species within different layers. Koyama et al. [148] take a different path by analyzing the PL relaxation times of DWCNT compared to SWCNT. For their calculations, they equalized the relaxation rates of radiative and non-radiative decay processes from SWCNT to their DWCNT counterparts. However, this has to be questioned since the environment for a SWCNT is rather different than for a DWCNT, and environmental effects were shown to be of vital importance for the determination of luminescence decay rates [6, 129].

As mentioned in Figure 4.4, the PL signals in the black curve with smaller emission wavelengths than the (7,5) species (i.e. with $d_t < 0.8$ nm) are barely distinguishable against the background although being already amplified by a factor of 50. The very faint signals of the (8,3) (d_t = 0.78nm) and the (6,5) (d_t = 0.76nm) species can be understood as signals from tubes that have not been extracted and/or isolated completely. However, in our case, we chose a very mild form of purification for the pristine DWCNT sample to preserve the original DWCNT structure in Procedure A. For the normalization of the optical density that is crucial for a valid comparison between different samples as it gives an estimate on the number of emitters in the sample, we took the value of the optical density at 900nm. To finally compare the various PL intensities, we took the intensity of the (6,5) species which has a excitation wavelength of 569nm. because it is one of the most prominent species within the samples as well as it is abundant in both of the marked layers from Procedure B and C as seen in Figure 4.3. The difference in the intensity of the (6,5) inner tube species within the pristine DWCNT to these layers from each DGU experiment is approximately a factor of 50, as seen in Figure 4.5. It is unambiguous that for the PL process in Procedure A far more nonradiative decay channels after E_{22} excitation are available than for Procedure B and C.

The possible physical processes involved in PL quenching and their eventual impact on the PL intensity are not yet fully understood. The work of Shen et al. [200] gives an overview of different mechanisms that could explain this effect. The overall electronic structure of a DWCNT resulting from the inner and outer tube contributions can be rather complicated and vary heavily for each DWCNT, since it depends on several different factors like inter-wall distance, curvature, coupling strength, commensurability, metallicity of the outer tube, etc.

However, in Figure 4.5 it is clearly seen that PL from Procedure A is severely quenched in comparison to PL from Procedure B and C, where DGU was applied. This is a strong indication for the extraction of inner tubes from their outer tube hosts in the DGU process, whereafter quenching mechanisms induced by the presence of the outer tubes are eliminated.

The follow-up question is, whether applying DGU is essential for the extraction process or if inner and outer tubes are already separated before the centrifugation process. It has been



Figure 4.5: Line scans of the PL signal from the different centrifugated samples with an excitation wavelength of 569nm, the E_{22} transition wavelength of the (6,5) species (Emission Wavelength ~ 985nm). Spectra normalized to their optical density at 900nm.

mentioned in previous works that sonication alone can lead to extraction of inner tubes from DWCNT due to simultaneous opening of the host nanotube and 'shaking' of the DWCNT, where the inner tube is extracted since the frictional force between inner and outer tube is insignificant small [29, 201]. In that case, centrifugation at high speeds without a gradient medium as in the DGU process should be sufficient to remove remaining DWCNT, bundles, etc. due to their highly different buoyancies, leaving a sample consisting only of SWCNT. These, in return, should show (at least) a similar PL intensity than the extracted tubes from the DGU process. However, this is not the case. Applying the same centrifugation technique from the HiPco SWCNT sample to the DWCNT sample (Procedure D) leads only to a minor amplification of the PL intensity when compared to the pristine DWCNT sample (Procedure A), as seen in Figure 4.6.

This can be explained by the lack of a selective gradient surrounding the opened DWCNT in the centrifugation process. The surrounding medium of Procedure A and D is a homogeneous DOC solution, so no density differences that could act as a pulling force to the inner tubes are present, thus leaving either individualized DWCNT in the sample and/or SWCNT that were extracted by chance. However the case is, the resulting PL intensity differs strongly from the DGU processed nanotubes, with at least an order of magnitude difference in the PL intensity of those procedures. These findings, along with the differences seen in the DGU procedures as well as the difference from using a gradient medium or not, suggest, that strong ultrasonication and density-gradient ultracentrifugation are two essential complementary steps in achieving inner



Figure 4.6: Line scans of the PL signal from the different centrifugated samples with an excitation wavelength of 569nm, comparing the PL intensity from samples being treated by DGU (Procedure B) or not (Procedure A and D). Spectra normalized to their optical density at 900nm.

tube extraction of DWCNT samples.

Concommitant to previous studies by Miyata et al. [29] we found strong indications for inner tube extraction from DWCNT caused by the aforementioned solubilization techniques. We additionally confine that this process is strongly dependant on the parameters for sonication and centrifugation as well as on the tube chirality and separation of inner and outer tube. Our results indicate that by applying a lower sonication power to the sample prior to the DGU process, bigger DWCNT, that also have bigger inner tubes, are not opened in this process and therefore its inner tubes are not susceptible to extraction in a subsequent application of DGU. This can be explained by a higher mechanical stability of bigger tubes due to their lower curvature compared to smaller tubes. These results in return confine a pathway on how to avoid inner tube extraction in order to study the intrinsic PL response of inner tubes of DWCNT. We found strong evidence for a final proof that inner tubes of DWCNT are capable of exhibiting PL.

4.2 Enhancing the photoluminescence quantum yield by controlled growth of long linear carbon chains inside doublewalled carbon nanotubes

The following section represents a summary and discussion of experiments performed on DWCNT filled with linear carbon chains with the publication of the results being in preparation.

These experiments can be separated in three parts as it is indicated by the sample preparation described in chapter 3: Raman measurements of the annealed samples in solid form in a cryostat, optical absorption spectroscopy performed directly after solubilization and eventually photoluminescence spectroscopy.

4.2.1 Raman spectroscopy of double-walled carbon nanotube samples annealed at different temperatures



Figure 4.7: RBM of DWCNT annealed after synthesis in high vacuum at different temperatures [13]: All spectra were normalized to the G-Line and an offset of 7.5% was added for clarity. Samples were excited with a 568.2nm laser. The dotted lines denote shifts in the peak positions of all annealed samples compared to pristine DWCNT.

Figure 4.7 shows the result of measuring the RBM for differently annealed DWCNT as investigated in our recent study [13]. The signals reveal a broad diameter distribution for inner and outer tubes, with the diameters of the tubes given by equation 2.3 introduced in section 2

$$\omega_{RBM}[cm^{-1}] = \frac{A}{d_t[nm]} + B, \quad A = 234cm^{-1}nm, \ B = 10cm^{-1}$$

Filling of DWCNT with linear carbon chains (LCC) is achieved by post-synthesis annealing at temperatures that can be as low as 900 $^{\circ}$ C. The shift in the peak positions for the annealed samples compared to the pristine sample indicates an interaction between the DWCNT and the LCC. At the lowest growth temperatures most peaks are downshifted but the positions "recover" by increasing the growth temperature and eventually show an upshift at 1500 °C. This can be related to the chain length distribution within the sample: at 900 °C only short chains are produced. Excess charges of LCC able to interact with the nanotube are located at the chain ends [11, 105, 106], introducing the mentioned frequency downshift of the RBM. Raising the thermal energy leads to the growth of the chains so that less chain ends are abundant in the sample and the peak positions shift back to their original values. At the highest growth temperatures all carbon atoms available for LCC synthesis are already incorporated into the latter. The upshift of the RBM frequency here can be explained in a way that few short chains might already be present in the pristine sample, inducing a smaller downshift than the LCC inside the 1500 °C sample. The overall temperature dependence of the RBM is a first hint for a mechanical coupling between carbon chains and the nanotube sidewall which is consistent with pump-probe experiments using our samples that are currently investigating this correlation [202]. It is further supported by the correlation for the resonance condition of the RBM and the LCC [13].

The focus of this part of the thesis lies on the linear carbon chains inside the inner tubes of the DWCNT. An excitation energy of 2.18eV (568nm) allows to detect different chain lengths as it is close to the bandgap of long [13, 203] and short LCC [104]. Therefore, this laser was used to analyze the different contributions of the various chain lengths to the total LCC signal (More discussion on the resonance window of LCC at the end of this section). The Raman response of the G-Band and the LCC is plotted in Figure 4.8 with all signals being normalized to the intensity of the G-Line. Interestingly, the shape of the latter is only altered considerably at growth temperatures higher than $1460 \,^{\circ}\text{C}$ as two extra peaks (denoted by the roman numbers I and III) appear as shoulders of the main peak (II) that slightly diminish at even higher growth temperatures. A possible explanation of this phenomenon is a local change of the nanotube hybridization due to an increased interaction between long LCC and the nanotube sidewall [13]. These measurements were performed in a thermalized cryostat ensuring a constant (room) temperature. This is of special importance as the chain signal is strongly temperature dependent and the laser used for Raman measurements (power $200\mu W$) induces sample heating [13]. When such effects can be excluded, the shape and size of the carbon chain signal depends solely on the annealing temperature.

The frequency of the observed Raman shift is strongly connected to the chain length as long chains have been shown to exhibit smaller shifts than short chains [187, 188, 204]. These results were obtained by inserting polyynes of known length (between 8 and 16 carbon atoms) inside SWCNT or DWCNT and the frequencies were in a range of $\approx 1950 \text{cm}^{-1}$ to 2200cm^{-1} . For very long LCC Raman shifts around 1830cm^{-1} and 1850cm^{-1} were found by several groups although in most cases no explicit chain length was assigned to this frequency (e.g. [98, 103, 205, 206]) which indicates that the frequency saturates in this range. Consequently, the transformation of the carbon chain lineshape can be explained by different chain length contributions within the samples: at 1370 °C the main peak "leans" to the right i.e. to higher frequencies, indicating



Figure 4.8: G-Band and carbon chain signal of double-walled carbon nanotubes annealed in high vacuum at different temperatures. All spectra were normalized to the intensity of the G band.

that this sample consists of relatively many "short" chains compared to the other samples. This aspect changes by increasing the growth temperature to a more symmetric lineshape for the samples annealed at 1400 °C and 1430 °C and at even higher temperatures a small shoulder appears at $\approx 1830 \text{cm}^{-1}$.

To evaluate the contributions of the different chain lengths to the overall signal a lineshape analysis was performed. This can be executed in different ways and is illustrated in Figure 4.9 for the sample annealed at 1480 °C. For the following discussion the values of 1845cm^{-1} and 1855cm^{-1} were chosen to qualitatively distinguish between long (red), average long (green) and short chains (blue). The first method (Figure 4.9a, "Model 1") corresponds to the procedure of Fantini et al. [203] who fitted their spectra with a set of Lorentzians that had a shared linewidth of $\approx 10 \text{cm}^{-1}$. For the present sample this leads to four independent peaks. The fit (black line) reveals several deviations from the original signal as it does not pass through the measured positions (center of the circles) on several points along the graph; the fitted curve is flatter around 1830cm^{-1} but steeper between 1840cm^{-1} and 1845cm^{-1} than the observed datapoints and for the signal around 1865cm^{-1} the fit is above the measured values. Furthermore, the chain signal shows much more fine structure at temperatures below 100K so that the graph can not be reproduced by such a low number of peaks [13].

The major drawback of this method is that there is no physical model backing it up. As mentioned above, differently long LCC exhibit different Raman shifts [187, 188, 183] which means that by using this fitting procedure only four different chain lengths are present in the sample. Within the diameter distribution of inner tubes for our samples, ranging from 0.65nm

to 1nm determined by measurements of the RBM as well as optical absorption [147], there are more than 20 different tube diameters present supposed to produce these four different LCC lengths. This is not a realistic assumption for the whole system as there is no obvious limiting factor for such specific numbers. Therefore, this method was left disregarded for the analysis of the samples in this thesis.

In the same way a fit with a continuous and quasi-infinite number of peaks ("Model 2") is not realistic although it technically fits the measured curve as illustrated in Figure 4.9b. First, the number of carbon atoms obviously has to be an integer and second it has to be even so that the chain is terminated with the thermally more stable triple bond. Consequently, the LCC signal must originate from discrete LCC length contributions.



Figure 4.9: Fitting procedures for the LCC Raman response of the sample annealed at 1500 °C, qualitative limits for the definition of long (red), average long (green) and short chains (blue) were set to 1845cm^{-1} and 1855cm^{-1} . (a) Model 1: Method introduced by Fantini et al. [203] with linewidths of $\approx 10 \text{cm}^{-1}$ which results in four independent peaks. (b) Model 2: Fit with a continuous chain length distribution i.e. infinite number of possible frequencies. (c) Model 3: Fit with discrete peaks sharing a linewidth $\approx 3 \text{cm}^{-1}$.

The model that was used in this work to fit the obtained signals can be described as follows: The size of the Raman shift observed for LCC depends mainly on the carbon chain length. Environmental effects can alter the position of a single chain length since a charge transfer can induce an additional shift [183] but is only treated as a weak influence. The encapsulation of a LCC with specific length inside inner tubes with different diameters can lead to small differences in the peak position due to the different confinement of the nanotubes. This is based on a similar effect observed for the splitting of the RBM from inner tubes being resident inside different outer tubes [38]. The Raman response was fit by a set of Voigtians that correspond to a Gaussian convolution of Lorentzian curves, reflecting a statistical distribution of inner tube diameters within the sample ("Model 3", Figure 4.9c). The coherence lifetime of each contribution was assumed to be equal for different chain lengths, so the Voigt curves had a shared line width (\approx 3cm^{-1} which is close to the spectral resolution of 2cm^{-1} set in our experiments). By doing so the signal could be fitted very well with 34 independent peaks (Exact values and positions of the peaks can be found in the appendix).

This procedure was performed for all annealed samples. The size change of the different peaks compared to the total LCC signal then reflects a variation of the chain length distribution depending on the growth temperature. In Figure 4.10 the integrated area coverage of the contributions from the different chain lengths to the overall signal as a function of the temperature is plotted.

To interpret these results the following model is proposed: At low temperatures $(1370 \,^{\circ}\text{C})$ the length distribution of LCC is more random as in some tubes of the sample the concentration of carbon atoms usable for chain formation was higher in the beginning by chance, facilitating the process. Increasing the temperature to $1400 \,^{\circ}\text{C}$ enables the growth of short and average long chains. At even higher temperatures long chains can be formed which shows a maximum of the contribution to the LCC signal at $1460 \,^{\circ}\text{C}$. This temperature appears to be the highest possible temperature for the growth of long chains as surpassing this temperature leads to a reduction of the long chain contribution. It indicates the decomposition of the latter so the number of short and average long chains increases at $1480 \,^{\circ}\text{C}$. Here an optimum absolute number of LCC must be present within the sample in terms of resonance behaviour so the signal reaches a high intensity (3 times the intensity of the G-Band) as shown earlier in Figure 4.8. By further raising the growth temperature the decomposition of long chains still might be able to form average long chains so that this contribution increases.

Now we have to validate the approach of Model 3 by testing side effects of the Raman response which might lead to a modification of the LCC signal. One obvious factor is the alteration in the resonance Raman condition due to the change in the energy gap transitions of the LCC as function of the chain length [186]. In order to check this factor we performed multi frequency Raman measurements with a tuneable dye-laser (Rhodamine 6G) [13]. The Raman response of a DWCNT sample annealed at 1480 °C excited with lasers of different excitation energies is plotted as a Raman map in Figure 4.11. The signal of all energies was normalized to the intensity of the G-Line ($\equiv 1$ in the coloured plot) which has an (almost) constant shape for the whole excitation window and the main peak is located as expected for nanotubes at $\approx 1590 \text{cm}^{-1}$. The signal of the carbon chains themselves can be seen on the high frequency side of the Raman map. The difference in the intensity of the LCC for the sample annealed at 1480 °C seen here (≈ 1.4) compared to the value observed in Figure 4.8 (≈ 1.4) can be attributed to the experimental procedure. The dye laser had a constant output power before the sample of 2mW which causes local heating as the sample was not placed in a thermalized cryostat for



Figure 4.10: Integrated area of the chain signal as a function of the LCC growth temperature, using Model 3. The error of these values is small, lower than 2% of the given percentage.

these measurements. This leads to a decrease of the intensity since the Raman intensity of LCC is temperature dependent [13]. The three dotted white boxes denoted by the integers 1,2 and 3 mark different contributions to the overall chain response and vertical line scans right of the Raman map show the intensity profiles of these contributions along the central axis of the boxes. These profiles were created to investigate the resonance behaviour of differently long LCC (as the length of the chains is reflected by the Raman shift). The first vertical line is attributed to long chains since it has the lowest Raman shift. The signal is fairly constant for almost all used excitation energies with a small maximum at 2.08eV (596nm) indicating that the resonance window of these chains is very broad. Box number 2 is related to "average long" LCC showing a strong maximum at an energy ≈ 2.18 eV and box number 3 represents the "short" chains within the sample. For the latter, the resonance window could not be resolved fully due to the limited range of the laser system. The progression of the curve foreshadows that the maximum of this type of LCC can be found at an excitation energy slightly larger than 2.2eV. These values are close to the ones observed by resonance Raman profile measurements of long chains by Fantini et al. who found a resonance maximum at 2.2eV [203] but also for short chains, namely $C_{10}H_2$ inside DWCNT, observed by Moura et al. [104]. This off-resonance for the short chains may lead to an underestimation of the absolute number of short chains within the sample, however, as the 568nm laser was used for all samples this error is constant and therefore does not change the ratio of this contribution between different samples.



Figure 4.11: Raman map of a DWCNT sample annealed at 1480 °C, all single spectra normalized to the G-Line at $\approx 1590 \text{cm}^{-1}$ with its intensity in the colour bar set to 1. The signal of the carbon chains with the main peak $\approx 1850 \text{cm}^{-1}$ can be separated in 3 parts, long, average long and short chains as discussed earlier; quantitative assignment of the chain lengths will be discussed later in the text. Vertical intensity profiles along the center of the white, dotted boxes of these contributions plotted right to the map. The white horizontal bar (black in the profiles) marks the energy of the laser used for the line shape analysis of the chain signal for the differently annealed samples, corresponding to a wavelength of 568nm.

The chain length distribution within the samples is of great importance for analyzing the effect of the LCC on the photoluminescence behaviour for the differently annealed samples later on in this chapter. The excess charges are located at the chain ends [11, 105, 106] and this effect becomes stronger with increasing chain length [12]. On the other hand, some inner tube species are better suited for the growth of long chains than other chiralities because of their diameter, so the chain lengths can be different for tubes of unequal size. Therefore, a variation of the PL signal depending on the inner tube diameter might occur.

As a last point in the analysis of the Raman response from the LCC an estimate on the actual chain length is performed. The work of Yang et al. [183] gives a theoretical approach to evaluate the frequency behaviour for the Raman shift of differently long LCC and is plotted with the black curve in Figure 4.12. They calculated the Raman active optical frequencies of polyynes with first-principles methods and used a hybrid linear/exponential scaling scheme for simulating the behaviour of the carbon-carbon bond stretching force constant couplings. The frequency saturation for long chains is found to occur at 1870cm⁻¹ which is close to the above mentioned values. Still, it is only on the edge of the highest observed Raman shift for the samples used in this thesis marked by the dotted black lines and also the experimentally evaluated frequencies of short polyynes inside SWCNT could not be reproduced. This can be attributed to the fact that

environmental effects were not included in the used model. Such effects have to be considered since the potential energy of the otherwise very reactive LCC is lowered remarkably by the insertion into a nanotube [101]. Wakabayashi et al. have shown that the Raman shift of the $C_{10}H_2$ inserted into a SWCNT is $62cm^{-1}$ lower than the frequency observed for the same chain in a solution of hexane [187]. To model the frequency observed for chains inside DWCNT in this thesis, this difference of $62cm^{-1}$ was used as a first attempt to incorporate environmental effects in the model of Yang et al. and is illustrated by the green graph in Figure 4.12 which is downshifted as a whole compared to the black curve.



Figure 4.12: Model calculations for the Raman shift of LCC as function of the chain length by Yang et al. (black curve) [183]. The same model fit is either shifted energetically downwards by 51cm^{-1} (blue curve) so that the lowest observed frequency in Raman measurements in this thesis matches the longest chain length seen in HR-TEM measurements (red dashed line) [13], or by 62cm^{-1} which is the difference in the Raman shift of $C_{10}H_2$ molecules inside SWCNT and hexane observed by Wakabayashi et al. [187]. Added to this model are experimentally evaluated Raman shifts for polyynes of known size inside SWCNT by Wakabayashi et al. [187], Malard et al. [188], Moura et al. [104] and Zhao et al. [98].

In this way, the theoretical prediction is closer to the values observed for different polyynes inside SWCNT [187, 188] and fits well for the values reported for $C_{10}H_2$ molecules inside DWCNT [98, 104]. It can also be used to roughly estimate the number of carbon atoms linked together for the LCC signal observed for the samples used in this work and is 30 for the highest and 66 for the lowest frequency. Admittedly, these values can only be seen as a minimum boundary since chain lengths including at least 150 atoms have been observed in HR-TEM images for similar samples from our group [13]. To account for this deviation, another model was established as the blue curve in Figure 4.12 is downshifted from the black curve only by 51cm^{-1} . This value was taken so that the fit from Yang et al. matches the lowest observed Raman frequency of carbon chains observed in this thesis and HR-TEM measurement. In this way, the highest observed Raman frequency corresponds to a chain length of 32 atoms. The difference in the assigned chain length between the two models giving the green and the blue graph unambiguously demonstrates that environmental effects such as encapsulation of LCC in carbon nanotubes are not negligible for the correct length assignment. Although the assigned chain lengths for the highest Raman frequency are quite similar (32 and 30), a strong dissonance is revealed for the lowest frequency (150 and 66). The divergence between these values might arise from the interaction of the LCC with the nanotube; Cahangirov et al. predicted in a theoretical study that the excess charges of the chains which are located at the end of the LCC grow as the chain becomes longer [12]. This could lead to an upshift of the Raman frequency counterbalancing the downshift due to an elongation of the chains. A theoretical model that accounts for environmental effects is currently in preparation.

4.2.2 Optical absorption spectroscopy of filled double-walled carbon nanotubes in solution



Figure 4.13: (a) Comparison of the absorption spectra from DWCNT (blue) and SWCNT (grey) in solution [147]. (b) Spectra of suspended pristine (black) and DWCNT samples filled with linear carbon chains grown at different temperatures. Spectra were normalized at the minimum between the E_{11} and E_{22} at 900nm to the same optical density.

After the Raman measurements all samples were solubilized to elucidate on their optical properties. The parameters of the procedure on how homogeneous DWCNT suspensions are received are of uttermost importance for the absorption and the photoluminescence of DWCNT. Strong sonication and subsequent application of density gradient ultracentrifugation (DGU) leads to the extraction of inner tubes [29, 147]. There are also strong hints that carbon chains can be extracted if DGU is applied and that this process is diameter dependent [207] which is currently under investigation. Consequently, for evaluating absorption and luminescence behaviour of DWCNT filled with linear carbon chains it is crucial to prohibit the separation of outer tubes, inner tubes and LCC. In order to exclude these unwanted effects all samples were solubilized by tip sonication in an aqueous solution of 2% w/v sodium deoxycholate and purified by centrifugation without a gradient medium and 10.000 x g for 30 minutes. This corresponds to Procedure A described in chapter 3 which has been shown in our study that it does not lead to the extraction of inner tubes [147].

Before analyzing the effect of filling DWCNT with LCC on the optical properties, the absorption spectrum of pristine DWCNT has to be recapitulated. As reported features of the excitonic transitions between corresponding van Hove singularities of DWCNT are strongly attenuated in comparison to SWCNT (e.g. [8, 29, 147, 208]), illustrated in Figure 4.13a. This is attributed to tube-tube interactions and the overlap between inner and outer tube contribution to the absorption spectrum. The DWCNT samples used for the growth of linear carbon chains in this thesis are made by an identical synthesis procedure and therefore the same assignment can be used.

In Figure 4.13b the absorption of DWCNT annealed at different temperatures is plotted after normalization to the minimum optical density between E_{11} and E_{22} at 900nm (same procedure



Figure 4.14: (a) Absorption spectra of SWCNT filled with ferrocene taken at different stages of the filling process (after [10]). The E_{11} signal of some tubes is enhanced which is marked by the grey area. (b) Absorption spectra of all samples used after normalization and background subtraction. The indices i and o represent contributions of inner and outer tubes. (c) Comparison of the absorption spectra from pristine DWCNT and the samples annealed at 1400 °C and 1480 °C. Similar as for the ferrocene example the E_{11} of several species (marked grey) is enhanced by the presence of LCC. (d) Chain length distribution observed in Raman measurements discussed in the previous section.

as applied in [147]). The spectra of the latter exhibit more pronounced peaks than the pristine sample as these samples are filled with linear carbon chains. Incorporation of e.g. ferrocene in the hollow space of SWCNT has been shown to alter the optical properties of their host tubes [10]: illustrated in Figure 4.14a is the development of the optical response of HiPco SWCNT for different stages in the filling process. Ferrocene enhances the optical response of nanotubes depending on the tube-diameter and this is marked grey in Figure 4.14a.

To analyze the absorption spectra of the annealed DWCNT they were first normalized at the minimum between the E_{11} and E_{22} at 900nm to the same optical density before background subtraction of the high energy contribution was performed as discussed in section 2.3.1. The result of these procedures can be seen in Figure 4.14b. The size and shape of the E_{11} peaks of the inner tubes change for all filled DWCNT compared to the pristine sample. For example the signal of the (7,5) species is much more pronounced, also the (8,3) and (6,5). The strongest influence of the LCC is observed for the sample annealed at 1400 °C. This illustrates that the incorporated linear carbon chains affect the optical properties of DWCNT. Figure 4.14c places more emphasis on this change: Here, the focus lies on the absorption spectra of the pristine sample, the samples annealed at 1400 °C and 1480 °C. The latter is of special interest since this sample exhibited the strongest intensity of the LCC signal in Raman measurements as discussed in the previous section. The E_{11} peaks are slightly more pronounced than the pristine sample as marked by the grey areas but they are weaker compared to the DWCNT filled with carbon chains grown at 1400 °C. This is a first hint that the chain length distribution plays an important role for the effect of the LCC on the optical properties of DWCNT (shown in Figure 4.14d). While the DWCNT annealed at 1480 °C contain more long chains, the LCC grown at 1400 °C are more of short and average length. This indicates that short carbon chains play an important role for the intensity increase of the E_{11} peaks in contrast to their longer counterparts. Another interesting feature is the peak around 1120nm that represents a superposition of the E_{11} excitonic transition of the (8,4), (7,6) and (9,4) species. The shape of this peak is rather unsymmetric for the pristine sample but changes its appearance for the annealed samples. The underlying reason for this alteration might be a diameter selective influence of the LCC on the inner tube's optical properties.

The intensity increase observed in optical absorption measurements for peaks of excitonic transitions can be understood as a result from a charge transfer between LCC and inner tube. For SWCNT it has been shown that doping (e.g. by the surfactant) leads to a decrease of the intensity of absorption features as it depletes the number of electrons in the valence band and induces a shift of the Fermilevel [10, 209, 210]. Filling with ferrocene on the other hand compensates for this doping, increasing the E_{11} absorption intensity. The same process can be postulated for DWCNT filled with LCC: Excitonic transitions of inner tubes are strongly attenuated compared to SWCNT (Figure 4.13a) due to doping by the outer tubes. The LCC induce an opposite charge transfer to the inner tube, compensating the outer tube influence and therefore increasing the E_{11} intensity. However, a detailed analysis of the correlation between the absorption spectra and the chain length distribution for all observed species filled with chains grown at several different temperatures is complicated by the overlap of inner and outer tube contribution. To further investigate on this issue, photoluminescence spectroscopy was performed on the same solubilized samples. Since the PL response of the inner tubes also strongly depends on their absorption cross section [127, 211] an enhancement of the PL emission pathways can be expected.

4.2.3 Photoluminescence spectroscopy of double-walled carbon nanotubes filled with linear carbon chains

Photoluminescence spectroscopy has the advantage over absorption spectroscopy that specific chiralities can be addressed directly [197]. By exciting the nanotubes with light of a wavelength corresponding to their E_{22} transition energy they subsequently exhibit maximum emission at a wavelength corresponding to their E_{11} transition energy. In this way samples subjected to different procedures can be compared. A PL map of a pristine DWCNT sample is shown in Figure 4.15:



Figure 4.15: PL map of pristine DWCNT. The black circles mark the area of the strongest intensity for a given inner tube denoted by its (n,m) values. For wavelengths above 680nm the intensity was multiplied by 5 due to the low PL emission of these chiralites.

The resonance maxima of 9 different semiconducting nanotube species could be evaluated and the position of each chirality is given in Table 4.1. These values are close to reported resonance wavelengths of suspended SWCNT obtained by several groups (e.g. [10, 171, 197]) and did not vary significantly (within the spectrometer accuracy of 0.5nm) for all samples. The intensity observed in a PL measurement depends on the magnitude of the PL process being quenched by external factors. As shown in section 4.1 and reference [147], the PL efficiency of

Chirality	(6,4)	(6,5)	(8,3)	(7,5)	(8,4)	(10,2)	(7,6)	(9,4)	(8,6)
Diameter [nm]	0.69	0.76	0.78	0.83	0.84	0.88	0.89	0.91	0.96
\mathbf{E}_{22} resonance [nm]	587	569	670	647	595	742	652	727	724

Table 4.1: Observed E_{22} resonance wavelengths of inner tube species within the range of the used setup. The accuracy of the spectrometer is 0.5nm.

inner tubes of DWCNT compared to SWCNT is very low which is illustrated in Figure 4.16. The difference of the PL intensity for the (6,5) species was found to be up to a factor of 50 lower for DWCNT. PL of inner tubes from DWCNT is strongly affected by tube-tube interactions between inner and outer tube that increase the number of nonradiative pathways for exciton energy relaxation. This factor in return can severly be altered by the sample preparation for solubilizing the nanotubes. In the same report we found that by applying density gradient ultracentrifugation after sonication to the nanotube suspensions, inner tubes can be extracted from their outer tube hosts, increasing their PL quantum yield dramatically [147]. Therefore, to elucidate on the effect of linear carbon chains being incorporated in DWCNT on the PL properties of the latter, the technique corresponding to Procedure A in the experimental section was chosen to exclude an extraction process (tip sonication in an aqueous solution of 2% w/v sodium deoxycholate and purification by centrifugation without a gradient medium and 10.000 x g for 30 minutes).



Figure 4.16: Comparison of the PL intensity for the (6,5) tubes as SWCNT (blue) and inner tube of a DWCNT (black) with the latter showing much lower PL intensity. Adapted from [147].

For an evaluation of the luminescence behaviour of DWCNT filled with linear carbon chains each species for each sample was measured with an excitation wavelength corresponding to its as mentioned E_{22} resonance. The Figures 4.17a-c show three examples of the numerous PL spectra taken for pristine DWCNT and the samples annealed at 1400 °C and 1480 °C representing filled DWCNT. These growth temperatures for the LCC were chosen in this context as the 1400 °C annealed sample showed the strongest change in the absorption spectra as discussed in the previous section and the 1480 °C annealed sample exhibited the strongest intensity of LCC in Raman measurements. The first line scans in Figure 4.17a investigate the change in the PL signal of (6,5) tubes with a diameter $d_t = 0.76$ nm. The intensity of this chirality is amplified greatly for the chain filled samples compared to pristine inner tubes. From the intensity of



Figure 4.17: Photoluminescence line scans of different species. Spectra were normalized at the minimum between the E_{11} and E_{22} at 900nm to the same optical density observed in absorption measurements as well as to the same laser input power and integration time of the PL signal. The intensities are further normalized to the intensity of the selected species being in resonance for pristine DWCNT so that $I_{Pristine} \equiv 1$. (n,m) assignment performed on the work of Bachilo et al. [124]. PL line scan at (a) 569nm, the resonance of (6,5) tubes. (b) 670nm, the resonance of (8,3) tubes and (c) 742nm, the resonance of (10,2) tubes.

the sidepeaks, i.e. tubes that are not in resonance with the incident laser wavelength it is already foreshadowed that for different species other growth temperatures for the carbon chains lead to the strongest PL intensity. This becomes apparent when other species are measured at their E₂₂ resonances. For e.g. the (8,3) inner tubes with $d_t = 0.78$ nm the sample annealed at 1400 °C gives the highest intensity and the same observation is done for the (10,2) species with with $d_t = 0.88$ nm. Furthermore, the (8,3) filled with LCC grown at 1400 °C species exhibits the strongest PL signal for inner tubes of DWCNT investigated in this thesis which indicates a diameter-dependent optimum of nanotube-chain interaction for PL amplification. In order to quantitatively analyze the PL response a line shape analysis (example illustrated in Figure 4.18a) for all spectra was performed to evaluate the correct PL signal of the species being in resonance since other species might give overlapping contributions (e.g. the (6,5) next to the (8,3)). The results obtained in this analysis are depicted in Figure 4.18b, 4.19a and 4.20 (Error bars were not included, as the maximum error was always within \pm 0.1 of the amplification value).



Figure 4.18: (a) Fitting procedure for all samples illustrated on the example of the (8,3) species annealed at 1400 °C. (b) Fitted intensity of each investigated species as function of the LCC growth temperature and chirality.

Measuring the 9 different species observed in the PL map (Figure 4.15) for all samples at their respective E_{22} resonance wavelength and comparing their intensity to the pristine sample gives two types of correlations: First, the PL amplification as function of the tube diameter is shown in Figure 4.19a for three representative samples. The amplification reaches a maximum for the (8,3) species with a diameter of 0.78nm for all samples annealed at temperatures $\leq 1480 \,^{\circ}\text{C}$ (here only 1400 °C, red curve, and 1480 °C, green curve, is shown for clarity), for the 1500 °C (blue) and 1530 °C sample (not shown) the (6,5) species exhibits a maximum in the amplification (Plots of the PL from DWCNT filled with LCC grown at other temperatures are shown in the Appendix). The appearance of a diameter-dependent optimum in the PL amplification is similar to the PL enhancement of SWCNT filled with ferrocene as observed by Liu et al. [10] (black curve). There the amplification of the PL intensity was attributed to a local charge transfer between ferrocene molecule and the nanotube sidewall which is depending on the tube diameter and can only be observed for SWCNT with a diameter larger than 0.9nm due to the size of ferrocene. In the present case of LCC inside DWCNT the effect might be similar in nature as the excess charges on the end of a LCC interact with the inner tube [11] leading to an optimum of the charge transfer at a specific tube diameter. The position of the optimum diameter can be linked to the ability of different inner tube species to form LCC which is connected to the ability of nanotubes to actually incorporate carbon atoms. The minimum nanotube diameter for doing so can be estimated from the van der Waals (vdW) radii of the carbon atoms of both the nanotube wall and the chains in the center (sketched in Figure 4.19b, top). The typical vdW radius of carbon is 0.17nm if no charge transfer is involved. The minimum diameter for insertion of carbon atoms into a carbon nanotube then would be $4 \ge 0.17$ nm = 0.68 nm. This is only the



Figure 4.19: (a) Amplification of DWCNT filled with carbon chains as function of the inner tube diameter. Growth temperatures: Red = 1400 °C, green = 1480 °C and purple = 1500 °C). The appearance of a diameter-dependent maximum is similar to the observation of PL amplification found for SWCNT filled with ferrocene, black curve [10]. (b) Top: Minimum distances between the carbon chain atoms (black dot) and the inner tube wall given by the van der Waals radius r_{vdW} (dashed lines and black arrow) of carbon. Bottom: Minimum interlayer distance between concentric layers in DWCNT.

case if no other interactions are considered; analogue to the case of varying interwall distances between inner and outer tubes of DWCNT (2 x vdW radius, illustrated in Figure 4.19b, bottom) that have been reported to be up to 0.42nm [35], the ideal diameter for encapsulating carbon atoms in nanotubes can be larger than 0.68nm. The (6,4) species with $d_t = 0.69nm$ is very close to the minimum required diameter and therefore probably only contains a low number of LCC that can interact with the nanotube to increase the PL intensity. For chains grown below 1500 °C the case is similar for (6,5) inner tubes, as the PL signal is only marginally amplified. The diameter of (8,3) being $d_t = 0.78nm$ is unambiguously the closest to the ideal diameter regarding the gain in amplification compared to the (6,5) tubes. For larger diameter inner tubes the interaction between LCC and nanotube weakens and is caused by the larger distance between carbon chains and the nanotube sidewall similar to the drop of PL enhancement of ferrocene filled SWCNT [10].

The shift of the PL amplification maximum to lower diameters at temperatures ≥ 1500 °C on the other hand can be related to the formation process and thermal stability of linear carbon chains. The PL amplification as function of the growth temperature is plotted in Figure 4.20. There the curves can be seperated in three different groups according to their diameter and temperature dependence: "Small" inner tubes like the (6,4) and (6,5) tubes, whose diameters of 0.69nm and 0.76nm are close to the smallest possible diameter for containing LCC as mentioned above; "medium"-sized inner tubes with diameters ranging from 0.78nm to 0.89nm and "large"



Figure 4.20: Amplification of the PL intensity of DWCNT as function of the annealing temperature. For clarity, the species are seperated in three groups according to their diameter. The right panel shows sketches of DWCNT with different diameters and a single carbon atom including their van der Waals radii (dashed grey line for the nanotube, size of the black dot for the carbon atom). As the diameter is increased the latter can either move freely along the nanotube axis or even receives an additional degree of freedom for the movement inside large diameter tubes. In the bottom graph the result of the Raman line shape obtained earlier is shown for the discussion in the text.

inner tubes with diameters > 0.9nm. In the lower two graphs the result of the Raman line shape analysis on the chain length distribution obtained in the previous section is plotted; important to note for this context is that the chain signal observed by Raman spectroscopy originates from the whole sample, i.e. LCC from different species are detected simultaneously. Based on the observations from Raman, optical absorption and photoluminescence spectroscopy, a model for the carbon chain formation process is given with the PL enhancement depending on the number of chain ends within a sample, as this factor already played an important role in absorption spectroscopy in the previous section (in the right panel sketches are drawn to illustrate the diameter dependent carbon atom diffusion inside DWCNT with the van der Waals radius of the nanotubes marked as dashed grey lines and the carbon atom with this radius included as a big black dot):

The (6,4) species ($d_t = 0.69nm$) are just on the edge of the diameter limit for incorporating carbon atoms, therefore only small amounts of chains appear to be able to reside inside these tubes causing a weak amplification of the PL signal. Also, since the amplification is almost constant for all temperatures, it is likely that an energy barrier preventing long range diffusion exists (illustrated by the curled arrows). Tubes with (6,5) chirality ($d_t = 0.76nm$) appear to show the same constant behaviour at low growth temperatures but when exceeding 1460 °C, the PL is increased higher. This might be caused by the larger inner tube diameter compared to the (6,4), lowering the aforementioned energy barrier that is then overcome at higher thermal energies, so the formation of average long chains is facilitated. Their number increases at an even higher growth temperature of 1530 °C, so the PL decreases again as the shortest chains form more and more average long chains, lowering the number of chain ends.

The medium sized tubes $(0.78 \text{nm} \leq d_t \leq 0.89 \text{nm})$ show a completely different progression of the PL amplification than the small tubes $(d_t \leq 0.76 \text{nm})$. For these tubes, the carbon atoms are able to move "freely" along the nanotube axis (depicted by the long straight arrows) since the inner tube diameter is already much bigger than the minimum required diameter of 0.68 nm as discussed earlier. Interestingly, they exhibit the same temperature dependence like the short chain contribution observed in Raman measurements which indicates that the abundance of this chain type is the most important factor for the PL enhancement. In the beginning a first local maximum is reached at 1400 °C. Then the PL amplification decreases concommitant to the formation of long LCC at the expense of short and average long chains. At 1480 °C, long chains start breaking up, leading to a second local maximum as the number of chain ends is increased. At even higher temperatures, long chains continue breaking up but short chains continue to grow longer, resulting in a lower total PL signal. The overall decrease in PL from 0.78 nm to 0.89 nm can be explained by the larger diameter of the tubes lowering the interaction between carbon chains and nanotube sidewall similar as with ferrocene inside SWCNT [10].

For large inner tubes ($d_t \ge 0.91$ nm), the amplification is already very weak. The first maximum is only reached at 1430 °C which can be caused by the large diameter of these tubes: the movement is not restricted to a one-dimensional path anymore but small radial movements are also possible (sketched by the short arrows perpedicular to the tube axis). This decreases their diffusion length along the nanotube axis displayed by the shorter arrows in the sketch compared to the picture above and eventually impedes long chain formation. After this mark the progression again follows the Raman response of the short chains. In the next section the physical background of the PL amplification caused by the interaction between LCC and nanotube will be discussed.

4.2.4 Discussion on the physical process behind the luminescence signal and enhancement

The unambiguous correlation between carbon chain length and amplification of the PL signal of the same samples as shown before leads to the question of the physical process that causes the amplification. At first, we have to consider the PL quantum yield of non-filled DWCNT. For pristine samples, the strongest PL quenching occurs from the outer tubes as pointed out in section 4.1. Structural factors like metallicity of the outer tube and in some cases small wall-to-wall distances are attributed to cause the overall low PL quantum yield of inner tubes from DWCNT samples [200]. Although the outer wall shields the inner tubes from external effects like functionalization, changes in the outer wall structure (e.g. defects) can locally alter the interaction between inner and outer tube, giving additional quenching sites to the intrinsic inner tube quenching sites. In our experiments we applied completely reproducible conditions in order to exclude varying environmental conditions for the inner tubes of the different samples. This allowed us to achieve a highly stable PL response, enabling us to elucidate the relative PL quantum yield with an error below 5% on average. Now we can turn to a detailed analysis of the PL enhancement.

In the literature several methods of influencing the recombination of excitons have been presented, showing that the reduction of non-radiative recombination channels leads to an increase of the PL quantum yield. All of these methods have in common that they are accompanied by a change of additional parameters like charge transfer complexes (e.g. ferrocene inside nanotubes [10]) as well as covalent (oxygen or diazonium salts) and noncovalent functionalization (encapsulation of H₂O or C₆₀). For instance, the filling of SWCNT with ferrocene has been shown to increase their PL response [10]. The amplification was attributed to a local charge transfer from the ferrocene molecule to the nanotube sidewall, cancelling out external perturbations like doping from the surfactant molecule. This was further supported by an increase in the absorption features of the E_{11} excitonic transitions which indicates a "re"-filling of the electron states. A similar observation could also be made for the chain-filled samples investigated, however, an increase of the E_{11} absorption could not be seen for all species that also showed a strong increase in PL. Therefore, other processes must also be involved for some of the tubes.

Covalent functionalization by oxygen-doping of SWCNT also leads to a strong enhancement of the PL signal [9, 82]. The oxygen induces a strong local, covalent rehybridization of the nanotube sidewall that traps mobile excitons so they can not reach sites that reduce radiative exciton recombination. The emission wavelength is severely red-shifted in both reports, at least ≈ 120 nm. Similar observations were made by Piao et al. [146], where a controlled introduction of defects by diazonium salt functionalization led to a red-shift of almost 200nm. The local, covalent changes in the hybridization of the nanotube sidewall were attributed to enable "harvesting" from dark excitonic states, meaning that the number of allowed optical transitions was increased.

Noncovalent functionalization by filling of C_{60} inside SWCNT modifies the optical band gap depending on the nanotube chirality [144]. The emission can shift either to the red or to the blue with the magnitude of these changes varying between 20 to 150nm and is attributed to a change in the hybridization between the nanotube states and the C_{60} molecular orbitals. Water-filling also induces noncovalently a red-shift which is more than 10nm [130]. The latter shift is caused by dielectric screening effects reducing the exciton binding energy. Both of these filling materials were not reported to change the PL quantum yield. Compared to these values, the shifts in the emission wavelength observed for the present samples were on the one hand considerably smaller, with only two species showing a shift larger than the detection limit of our setup that is 0.5nm. On the other hand, the emission shifted solely to the blue. The only species showing a noteworthy change in the emission wavelength is the (6,5). The blue-shift of \approx 6nm compared to the pristine sample is almost the same for all annealed samples and is illustrated in Figure 4.21. This shift could be caused by the small diameter of the (6,5) (d_t = 0.76nm) close to the minimum diameter of encapsulating carbon chains, inducing a noncovalent hybridization between LCC and nanotube. For the (6,4) species with d_t = 0.69nm a blue-shift of \approx 1nm was seen for all LCC filled samples. The degree of filling in this kind of tubes is already very low so the exciton energy is influenced only marginally. The small amplitude of the shift in the emission wavelength for both species is consistent with reference [10] and excludes a strong covalent hybridization between LCC and the inner tubes. A weak change in the van der Waals interaction due to the confinement in small inner tubes can be the underlying reason for this blue-shift of the (6,4) and (6,5) tubes.

As a last point, it is not known if the carbon chains alter the exciton fine structure of the inner tubes. As mentioned in section 2, the bright excitonic state is located energetically just above a dark state. Brightening of the dark state due to magnetic effects can be excluded since the magnetic flux has to be strong enough (using magnetic fields tens of Tesla strong) so the Aharanov-Bohm splitting exceeds the mixing between the direct exciton states due to short-range Coulomb interaction [119].



Figure 4.21: Shift in the emission wavelength for inner tubes filled with LCC. A shift of ≈ 6 nm was seen for all samples filled with LCC but only for the (6,5) species. The (6,4) also exhibit a minor blue-shift of ≈ 1 nm. For all other investigated species, no shift bigger than the detection limit of 0.5 nm was observed.

Ruling out differences in the environment outside of the inner tube, strong covalent hybridization and strong magnetic fields, two possible mechanisms might be involved in the enhancement



Figure 4.22: (a) Schematic of mobile excitons being prevented to interact with quenching sites, therefore enhancing the PL quantum yield. If the sites of local charge transfer act as "hot spots" for enhanced radiative exciton recombination or simply as barriers so that quenching sites can not be reached by the excitons, is not known. (b) Sketch of the reduction of nonradiative pathways. The *-sign for conduction and valence bands denotes that these energy values are reduced by the exciton binding energies. In the left picture, the exciton created by absorption of light from an inner tube transfers its energy to the tube, prohibiting inner tube luminescence. In the right picture, such a relaxation is prevented which enables the inner tube to exhibit photoluminescence.

of the PL quantum yield observed for the inner tubes of DWCNT filled with LCC, illustrated in both pictures of Figure 4.22:

(1) The chain ends establish a charge transfer to the inner tube [11] that cancels out the influence of the outer tube similar as ferrocene inside SWCNT cancels out external perturbations [10]. Therefore sites with enhanced radiative exciton recombination probability are created (sketched by the yellow circles). This approach is supported by the result of optical absorption measurements of the annealed samples shown in section 4.2.2: doping of carbon nanotubes leads to the filling/depletion of electronic states [209, 210] which decreases the intensity of absorption features. Counterbalancing this doping then results in a recovery of these properties. Such an increase in absorption intensity was observed for some selected tubes like the (7,5) or (8,4) but not for other species. A strong increase for the (8,3) as in PL was not found, so, as mentioned above, a charge transfer can not be the only process responsible for the PL intensity enhancement.

(2) Another process could involve the localization of mobile excitons (orange circle) "trapped" between potential walls created by the carbon chain ends (in this case, the yellow circles represent such potential walls). These obstacles prevent the excitons from interacting with quenching sites, similar as suggested for the PL enhancement of SWCNT by oxygen doping [9, 82] but without strong covalent hybridization of the nanotube sidewall that would invoke a considerable red-shift. In this way, scattering between bright and dark excitonic states facilitated by local defects or other deviations from ideality can be prevented. This approach is supported by the diameter and temperature dependence of the PL amplification: For those tubes large enough to be sufficiently above the minimum diameter required for carbon chain encapsulation, i.e. all species with $d_t \geq 0.78$ nm, the progression of the PL amplification is closely related to the abundance of short LCC. These types of chains contain more chain ends (where excess charges are located [105, 106]) so there are more sites interacting with the nanotube leading to higher PL. This interaction decreases with growing inner tube diameter as the distance between chain and tube is increased.

Summarizing, our results provide a sound way to finally proof that PL from inner tubes of DWCNT is weak but is existing. External perturbations by the outer tube is lowering their PL quantum yield but it does not completely suppress PL. These findings demonstrate a pathway to tailor the optical properties of inner tubes and it may be possible to further enhance the PL response of DWCNT either by optimizing the growth yield of linear carbon chains or other dopants. The strong correlation between chain length distribution and PL amplification can also aid in the development of theoretical models that are able to improve the understanding of interactions between filler material and host tube but also on the mechanism of tube-tube interactions in DWCNT reducing PL.

Chapter 5 Conclusions and outlook

In this thesis, double-walled carbon nanotubes were synthesized by high vacuum chemical vapour decomposition of ethanol and subsequently treated by various sorts of procedures to modify their structure. The first part of the result section is dedicated to the still ongoing debate whether DWCNT are capable of exhibiting photoluminescence. For elucidating this question, optical absorption and photoluminescence spectroscopy were performed on pristine DWCNT samples. Although having been purified by the same DGU technique, the samples treated with different sonication intensities show clearly unsimilar absorption spectra due to the difference in the sonication procedure. While all the inner tube species that have been seen in the PL measurement were also abundant after applying DGU when being sonicated under a stronger input power, some tubes $(d_t > 0.8nm)$ can not be seen if a lower input power has been used. This can be attributed to the well known fact that nanotubes can be cut in the sonication process and smaller tubes are more susceptible to damage than bigger tubes, implying a diameter-dependent threshold for the cutting (i.e. opening) of the DWCNT. This effect is the basic requirement of the extraction process in the subsequent DGU procedure, as it can be seen by the development of the abundance of different nanotube species in the optical absorption spectra after applying the same DGU technique to samples treated by different sonication intensities. Tiny fractions of bigger diameter inner tubes like the (10,2) ($d_t = 0.88$ nm) can be observed which can be explained by possible defect-assisted cutting of bigger tubes. Furthermore, the difference in the PL intensity of the extracted tubes compared to the pristine DWCNT sample was found to be a factor of 50 stronger; this is associated to the outer tube shielding of the DWCNT lowering the PL quantum yield of the inner tube. In the final graph it has been shown that the factor of the purification technique (DGU or no DGU) is not negligible since the resulting PL intensities vary by at least one order of magnitude. For the investigation on inner tube extraction, the details of the solubilization technique with respect to sonication intensity and centrifugation parameters as well as nanotube parameters such as tube type and chirality are of vital importance. Our results show strong indications that inner tube extraction can be avoided and the resulting PL signal originates from the inner tubes of DWCNT.

The second part of the results section is focusing on linear carbon chains inside DWCNT and how they affect the optical properties of the latter. The same kind of DWCNT samples as used for the extraction experiments where subjected to high temperature annealing treatments at different temperatures in high vacuum after synthesis and the removal of catalyst particles and SWCNT. This procedure leads to the growth of carbon chains inside the inner tubes of DWCNT with different yield by varying the temperature since the size and shape of the chainrelated Raman band changes. By performing a line shape analysis of the Raman response from the differently annealed samples it was found the ratio between long, average and short chains is strongly dependent on the applied temperature. The highest amount of the longest chains was observed for the sample annealed at 1460 °C, being in agreement with a previous report of our group. At higher temperatures the chains become shorter again, implying that they are less stable above this mark. Average long chains on the other hand can still be grown at higher temperatures as their number continues to increase. After these measurements the samples where solubilized with tip-sonication and a ultracentrifugation technique that did not extract inner tubes like mentioned before. The optical absorption spectra of chain-filled DWCNT showed a selective increase of the E_{11} feature of the (7,5) and (8,4) species which was similar for all samples but almost no changes were seen for other species. This can be attributed to the still heavily attenuated absorption features of the DWCNT compared to SWCNT due to tube-tube interactions and the overlap of inner and outer tube contributions. Photoluminescence spectroscopy in a broad range of excitation wavelengths was subsequently performed. The PL intensity is amplified greatly for various chiralities and shows a diameter dependence reminiscent of PL amplification SWCNT filled with ferrocene, though it is observed at smaller diameters due to the smaller extension of the chains. The maximum is found for the (8,3) species ($d_t = 0.78$ nm) for the sample annealed at 1400 °C exhibiting 6 times brighter luminescence than the pristine sample. Analyzing the temperature dependence of the PL amplification for nine different species reveals different progressions according to the inner tube diameter and can be correlated to the chain length distribution evaluated by Raman spectroscopy. Small tubes ($d_t \leq 0.76$ nm) have a diameter close to the smallest possible inner tube diameter for the insertion of carbon atoms (\approx 0.68 nm). The PL of (6.4) is almost constant despite changes in the chain length distribution for the overall sample; this indicates that chain formation in this type of tubes is hampered by an energy barrier due to the inner tube confinement. The case is almost the same for the slightly larger (6,5) tubes though at temperatures exceeding 1460 °C, LCC formation is facilitated so the PL amplification deviates from the constant case. For medium sized tubes (0.78nm $\leq d_t \leq$ 0.89nm) the amplification was the strongest which implies that tubes with this diameter do not hold diameter dependent obstacles for LCC formation. The strong correlation between the temperature dependence of the PL with the progression observed for short carbon chains hints that this chain type is most important for the influence of LCC on the PL of inner tubes. This might be related to the higher number of chain ends for a given number of carbon atoms when they are abundant as short carbon chains instead of long chains. Excess charges of LCC that can induce doping to the nanotube are located at these chain ends so the length distribution of LCC is crucial for the magnitude of the PL alteration. Large diameter inner tubes ($d_t > 0.9$ nm) appear similarly although the first amplification maximum is observed at a higher temperature compared to the medium sized tubes. The progression of the latter can be explained by the higher degree of freedom given for carbon atoms within nanotubes with non-ideal diameter, allowing radial movements, so the diffusion length along the tube axis is reduced which impedes long chain formation.

Combining the results of the inner tube extraction studies with the correlation between chain length distribution of LCC grown inside the inner tubes and the inner tube PL amplification, these studies serve as a final proof that inner tubes of double-walled carbon nanotubes are capable of exhibiting photoluminescence.
The work described in this thesis contributes to the field of tailoring the optical properties of double-walled carbon nanotubes either by extracting inner tubes or by filling DWCNT with linear carbon chains. An open question is how chain-filled DWCNT respond to the application of DGU to the nanotube suspension. First results indicate that inner tubes are extracted but that some of the LCC remain inside these extracted tubes, depending on the tube diameter. It might be possible to improve the DGU process in a way that SWCNT with optimum diameters (e.g. the (8,3) species with $d_t = 0.78$ nm) filled with long linear carbon chains can be obtained. This could lead to SWCNT with enhanced optical properties compaired to pristine SWCNT. Also, other properties like electrical transport could be studied in more detail since the effect of different external perturbations of the chains' properties due to different environments (varying tube types) would be minimized. Another topic is the underlying physical process of the PL amplification and the mechanical coupling of the chains to the nanotube. Both of these two questions are currently under investigation.

Bibliography

- Maultzsch J., Pomraenke R., Reich S., Chang E., Prezzi D., Ruini A., et al., *Exciton binding energies in carbon nanotubes from two-photon photoluminescence*, Physical Review B, 72 (24), 241402 (2005).
- [2] Wong E., Sheehan P., Lieber C., Nanobeam mechanics: Elasticity, strength, and toughness of nanorods and nanotubes, Science, 277 (5334), 1971–1975 (1997).
- [3] Chang C.C., Hsu I.K., Aykol M., Hung W.H., Chen C.C., Cronin S.B., A New Lower Limit for the Ultimate Breaking Strain of Carbon Nanotubes, ACS Nano, 4 (9), 5095–5100 (2010).
- [4] Welsher K., Liu Z., Sherlock S.P., Robinson J.T., Chen Z., Daranciang D., et al., A route to brightly fluorescent carbon nanotubes for near-infrared imaging in mice, Nature Nanotechnology, 4 (11), 773–780 (2009).
- [5] Cui K., Chiba T., Omiya S., Thurakitseree T., Zhao P., Fujii S., et al., Self-assembled microhoneycomb network of single-walled carbon nanotubes for solar cells, Journal OF Physical Chemistry Letters, 4 (15), 2571–2576 (2013).
- [6] Duque J.G., Pasquali M., Cognet L., Lounis B., Environmental and synthesis-dependent luminescence properties of individual single-walled carbon nanotubes, Acs Nano, 3 (8), 2153–2156 (2009).
- [7] Piao Y., Chen C.F., Green A.A., Kwon H., Hersam M.C., Lee C.S., et al., Optical and electrical properties of inner tubes in outer wall-selectively functionalized double-wall carbon nanotubes, Journal of Physical Chemistry Letters, 2 (13), 1577–1582 (2011).
- [8] Tsyboulski D.A., Hou Y., Fakhri N., Ghosh S., Zhang R., Bachilo S.M., et al., Do inner shells of double-walled carbon nanotubes fluoresce?, Nano Letters, 9 (9), 3282–3289 (2009).
- [9] Miyauchi Y., Iwamura M., Mouri S., Kawazoe T., Ohtsu M., Matsuda K., Brightening of excitons in carbon nanotubes on dimensionality modification, Nature Photonics, 7 (9), 715–719 (2013).
- [10] Liu X., Kuzmany H., Ayala P., Calvaresi M., Zerbetto F., Pichler T., Selective enhancement of photoluminescence in filled single-walled carbon nanotubes, Advanced Functional Materials, 22 (15), 3202–3208 (2012).
- [11] Fan X., Liu L., Lin J., Shen Z., Kuo J.L., Density functional theory study of finite carbon chains, ACS Nano, 3 (11), 3788–3794 (2009).

- [12] Cahangirov S., Topsakal M., Ciraci S., Long-range interactions in carbon atomic chains, Physical Review B, 82 (19), 195444 (2010).
- [13] Shi L., Rohringer P., Ayala P., Suenaga K., Kotakoski J., Meyer J., et al., to be submitted (2014).
- [14] Novoselov K., Geim A., Morozov S., Jiang D., Zhang Y., Dubonos S., et al., *Electric field effect in atomically thin carbon films*, Science, 306 (5696), 666–669 (2004).
- [15] Iijima S., Helical microtubules of graphitic carbon, Nature, 354 (6348), 56–58 (1991).
- [16] Zheng L., O'Connell M., Doorn S., Liao X., Zhao Y., Akhadov E., et al., Ultralong singlewall carbon nanotubes, Nature Materials, 3 (10), 673–676 (2004).
- [17] Zeng M.G., Shen L., Cai Y.Q., Sha Z.D., Feng Y.P., Perfect spin-filter and spin-value in carbon atomic chains, Applied Physics Letters, 96 (4), 042104 (2010).
- [18] Deng X., Zhang Z., Tang G., Fan Z., CH Y., Spin filtering and large magnetoresistance behaviors in carbon chain-zigzag graphene nanoribbon nanojunctions, Physics Letters A, 378, 1540–1547 (2014).
- [19] Mikhailovskij I.M., Sadanov E.V., Kotrechko S., Ksenofontov V.A., Mazilova T.I., Measurement of the inherent strength of carbon atomic chains, Physical Review B, 87 (4), 045410 (2013).
- [20] Harris P., Carbon Nanotube Science: Synthesis, Properties and Applications, Cambridge University Press (2009).
- [21] Jorio A., Dresselhaus M., Dresselhaus G. (Editors), Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications, Springer (2008).
- [22] Saito R., Dresselhaus G., Dresselhaus M., Physical properties of carbon nanotubes, Imperial College Press (1998).
- [23] Dresselhaus M., Dresselhaus G., Saito R., Physics of carbon nanotubes, Carbon, 33 (7), 883–891 (1995).
- [24] Bourlon B., Physique Interfeuillet dans les Nanotubes de Carbone Multifeuillets, Ph.D. thesis, Université Paris VI (2005).
- [25] Saito R., Fujita M., Dresselhaus G., Dresselhaus M., Electronic structure of graphene tubules based on C₆₀, Physical Review B, 46 (3), 1804–1811 (1992).
- [26] Vajtai R. (Editor), Springer Handbook of Nanomaterials, Springer (2013).
- [27] Hamada N., Sawada S., Oshiyama A., New One-Dimensional Conductors Graphitic Microtubules, Physical Review Letters, 68 (10), 1579–1581 (1992).
- [28] Kim Y., Muramatsu H., Hayashi T., Endo M., Terrones M., Dresselhaus M., Thermal stability and structural changes of double-walled carbon nanotubes by heat treatment, Chemical Physics Letters, 398 (1-3), 87–92 (2004).

- [29] Miyata Y., Suzuki M., Fujihara M., Asada Y., Kitaura R., Shinohara H., Solution-phase extraction of ultrathin inner shells from double-wall carbon nanotubes, Acs Nano, 4 (10), 5807–5812 (2010).
- [30] Zhang R., Ning Z., Zhang Y., Zheng Q., Chen Q., Xie H., et al., Superlubricity in centimetres-long double-walled carbon nanotubes under ambient conditions, Nature Nanotechnology, 8 (12), 912–916 (2013).
- [31] Simon F., Kramberger C., Pfeiffer R., Kuzmany H., Zolyomi V., Kurti J., et al., Isotope engineering of carbon nanotube systems, Physical Review Letters, 95 (1) (2005).
- [32] Muramatsu H., Hayashi T., Kim Y.A., Shimamoto D., Endo M., Meunier V., et al., Bright photoluminescence from the inner tubes of "peapod"-derived double-walled carbon nanotubes, Small, 5 (23), 2678–2682 (2009).
- [33] Damnjanovic M., Milosevic I., Vukovic T., Sredanovic R., Full symmetry, optical activity, and potentials of single-wall and multiwall nanotubes, Physical Review B, 60 (4), 2728– 2739 (1999).
- [34] Zólyomi V., Koltai J., Rusznyak A., Kuerti J., Gali A., Simon F., et al., Intershell interaction in double walled carbon nanotubes: Charge transfer and orbital mixing, Physical Review B, 77 (24) (2008).
- [35] Li Y., Wang K., Wei J., Gu Z., Wang Z., Luo J., et al., Tensile properties of long aligned double-walled carbon nanotube strands, Carbon, 43 (1), 31–35 (2005).
- [36] Liu K., Wang W., Xu Z., Bai X., Wang E., Yao Y., et al., Chirality-dependent transport properties of double-walled nanotubes measured in situ on their field-effect transistors, Journal of the American Chemical Society, 131 (1), 62–63 (2009).
- [37] Pfeiffer R., Kuzmany H., Kramberger C., Schaman C., Pichler T., Kataura H., et al., Unusual high degree of unperturbed environment in the interior of single-wall carbon nanotubes, Physical Review Letters, 90 (22) (2003).
- [38] Pfeiffer R., Kramberger C., Simon F., Kuzmany H., Popov V., Kataura H., Interaction between concentric tubes in DWCNTs, European Physical Journal B, 42 (3), 345–350 (2004).
- [39] Liu K., Hong X., Wu M., Xiao F., Wang W., Bai X., et al., Quantum-coupled radialbreathing oscillations in double-walled carbon nanotubes, Nature Communications, 4 (2013).
- [40] Ebbesen T., Ajayan P., Large-scale synthesis of carbon nanotubes, Nature, 358 (6383), 220–222 (1992).
- [41] Bethune D., Kiang C., Devries M., Gorman G., Savoy R., Vazquez J., et al., Cobaltcatalyzed growth of carbon nanotubes with single-atomic-layer walls, Nature, 363 (6430), 605–607 (1993).
- [42] Iijima S., Ichihashi T., Single-shell carbon nanotubes of 1-nm diameter, Nature, 363 (6430), 603–605 (1993).

- [43] Saito Y., Nishikubo K., Kawabata K., Matsumoto T., Carbon nanocapsules and singlelayered nanotubes produced with platinum-group metals (Ru, Rh, Pd, Os, Ir, Pt) by arc discharge, Journal of Applied Physics, 80 (5), 3062–3067 (1996).
- [44] Yakobson B., Smalley R., Fullerene nanotubes: $C_{1,000,000}$ and beyond, American Scientist, 85 (4), 324–337 (1997).
- [45] Guo T., Nikolaev P., Thess A., Colbert D., Smalley R., Catalytic growth of single-walled nanotubes by laser vaporization, Chemical Physics Letters, 243 (1-2), 49–54 (1995).
- [46] Thess A., Lee R., Nikolaev P., Dai H., Petit P., Robert J., et al., Crystalline ropes of metallic carbon nanotubes, Science, 273 (5274), 483–487 (1996).
- [47] Eklund P., Pradhan B., Kim U., Xiong Q., Fischer J., Friedman A., et al., Large-scale production of single-walled carbon nanotubes using ultrafast pulses from a free electron laser, Nano Letters, 2 (6), 561–566 (2002).
- [48] Rümmeli M., Borowiak-Palen E., Gemming T., Pichler T., Knupfer M., Kalbac M., et al., Novel catalysts, room temperature, and the importance of oxygen for the synthesis of singlewalled carbon nanotubes, Nano Letters, 5 (7), 1209–1215 (2005).
- [49] Maruyama S., Kojima R., Miyauchi Y., Chiashi S., Kohno M., Low-temperature synthesis of high-purity single-walled carbon nanotubes from alcohol, Chemical Physics Letters, 360 (3-4), 229–234 (2002).
- [50] Lefebvre J., Austing D.G., Bond J., Finnie P., Photoluminescence imaging of suspended single-walled carbon nanotubes, Nano Letters, 6 (8), 1603–1608 (2006).
- [51] Murakami Y., Chiashi S., Miyauchi Y., Hu M., Ogura M., Okubo T., et al., Growth of vertically aligned single-walled carbon nanotube films on quartz substrates and their optical anisotropy, Chemical Physics Letters, 385 (3-4), 298–303 (2004).
- [52] Nikolaev P., Bronikowski M., Bradley R., Rohmund F., Colbert D., Smith K., et al., Gasphase catalytic growth of single-walled carbon nanotubes from carbon monoxide, Chemical Physics Letters, 313 (1-2), 91–97 (1999).
- [53] Kitiyanan B., Alvarez W., Harwell J., Resasco D., Controlled production of single-wall carbon nanotubes by catalytic decomposition of CO on bimetallic Co-Mo catalysts, Chemical Physics Letters, 317 (3-5), 497–503 (2000).
- [54] Saito T., Ohshima S., Okazaki T., Ohmori S., Yumura M., Iijima S., Selective Diameter Control of Single-Walled Carbon Nanotubes in the Gas-Phase Synthesis, Journal of Nanoscience and Nanotechnology, 8 (11), 6153–6157 (2008).
- [55] Shiozawa H., Pichler T., Grueneis A., Pfeiffer R., Kuzmany H., Liu Z., et al., A catalytic reaction inside a single-walled carbon nanotube, Advanced Materials, 20 (8), 1443–1449 (2008).
- [56] Li Y., Mann D., Rolandi M., Kim W., Ural A., Hung S., et al., Preferential growth of semiconducting single-walled carbon nanotubes by a plasma enhanced CVD method, Nano Letters, 4 (2), 317–321 (2004).

- [57] Bachilo S., Balzano L., Herrera J., Pompeo F., Resasco D., Weisman R., Narrow (n,m)distribution of single-walled carbon nanotubes grown using a solid supported catalyst, Journal of the American Chemical Society, 125 (37), 11186–11187 (2003).
- [58] Moon J., An K., Lee Y., Park Y., Bae D., Park G., High-yield purification process of singlewalled carbon nanotubes, Journal of Physical Chemistry B, 105 (24), 5677–5681 (2001).
- [59] Borowiak-Palen E., Pichler T., Liu X., Knupfer M., Graff A., Jost O., et al., Reduced diameter distribution of single-wall carbon nanotubes by selective oxidation, Chemical Physics Letters, 363 (5-6), 567–572 (2002).
- [60] Li-Pook-Than A., Lefebvre J., Finnie P., Type- and species-selective air etching of singlewalled carbon nanotubes tracked with in situ Raman spectroscopy, ACS Nano, 7 (8), 6507– 6521 (2013).
- [61] Endo M., Muramatsu H., Hayashi T., Kim Y.A., Terrones M., Dresselhaus N.S., 'Buckypaper' from coaxial nanotubes, Nature, 433 (7025), 476–476 (2005).
- [62] Andrews R., Jacques D., Qian D., Dickey E., Purification and structural annealing of multiwalled carbon nanotubes at graphitization temperatures, Carbon, 39 (11), 1681–1687 (2001).
- [63] Tsang S., Chen Y., Harris P., Green M., A simple chemical method of opening and filling carbon nanotubes, Nature, 372 (6502), 159–162 (1994).
- [64] Kamarás K., Pekker A., Botka B., Hu H., Niyogi S., Itkis M.E., et al., The effect of nitric acid doping on the optical properties of carbon nanotube films, Physica Status Solidi B -Basic Solid State Physics, 247 (11-12), 2754–2757 (2010), 24th International Winterschool on Electronic Properties of Novel Materials - Molecular Nanostructures (IWEPNM 2010), Tirol, AUSTRIA, MAR 06-13, 2010.
- [65] Shelimov K., Esenaliev R., Rinzler A., Huffman C., Smalley R., Purification of single-wall carbon nanotubes by ultrasonically assisted filtration, Chemical Physics Letters, 282 (5-6), 429–434 (1998).
- [66] Niyogi S., Hu H., Hamon M., Bhowmik P., Zhao B., Rozenzhak S., et al., Chromatographic purification of soluble single-walled carbon nanotubes (s-SWNTs), Journal of the American Chemical Society, 123 (4), 733–734 (2001).
- [67] Ghosh S., Bachilo S.M., Weisman R.B., Advanced sorting of single-walled carbon nanotubes by nonlinear density-gradient ultracentrifugation, Nature Nanotechnology, 5 (6), 443–450 (2010).
- [68] Joselevich E., Carbon nanotube synthesis and organisation, Springer (2008).
- [69] Flavel B.S., Kappes M.M., Krupke R., Hennrich F., Separation of Single-Walled Carbon Nanotubes by 1-Dodecanol-Mediated Size-Exclusion Chromatography, ACS Nano, 7 (4), 3557–3564 (2013).
- [70] Krupke R., Hennrich F., von Lohneysen H., Kappes M., Separation of metallic from semiconducting single-walled carbon nanotubes, Science, 301 (5631), 344–347 (2003).

- [71] Liu H., Nishide D., Tanaka T., Kataura H., Large-scale single-chirality separation of singlewall carbon nanotubes by simple gel chromatography, Nature Communications, 2 (2011).
- [72] Zheng M., Jagota A., Semke E., Diner B., Mclean R., Lustig S., et al., DNA-assisted dispersion and separation of carbon nanotubes, Nature Materials, 2 (5), 338–342 (2003).
- [73] Zheng M., Jagota A., Strano M., Santos A., Barone P., Chou S., et al., Structure-based carbon nanotube sorting by sequence-dependent DNA assembly, Science, 302 (5650), 1545– 1548 (2003).
- [74] Arnold M.S., Green A.A., Hulvat J.F., Stupp S.I., Hersam M.C., Sorting carbon nanotubes by electronic structure using density differentiation, Nature Nanotechnology, 1 (1), 60–65 (2006).
- [75] Green A.A., Hersam M.C., Processing and properties of highly enriched double-wall carbon nanotubes, Nature Nanotechnology, 4 (1), 64–70 (2009).
- [76] Yanagi K., Udoguchi H., Sagitani S., Oshima Y., Takenobu T., Kataura H., et al., Transport mechanisms in metallic and semiconducting single-wall carbon nanotube networks, Acs Nano, 4 (7), 4027–4032 (2010).
- [77] Fagan J.A., Simpson J.R., Bauer B.J., Lacerda S.H.D.P., Becker M.L., Chun J., et al., Length-dependent optical effects in single-wall carbon nanotubes, Journal of the American Chemical Society, 129 (34), 10607–10612 (2007).
- [78] Ayala P., Arenal R., Loiseau A., Rubio A., Pichler T., The physical and chemical properties of heteronanotubes, Reviews of Modern Physics, 82 (2), 1843–1885 (2010).
- [79] Taylor R., Walton D., The chemistry of fullerenes, Nature, 363 (6431), 685–693 (1993).
- [80] Hirsch A., Functionalization of single-walled carbon nanotubes, Angewandte Chemie -International Edition, 41 (11), 1853–1859 (2002).
- [81] Susi T., Nitrogen-doped single-walled carbon nanotube thin films, Ph.D. thesis, Aalto University (2011).
- [82] Ghosh S., Bachilo S.M., Simonette R.A., Beckingham K.M., Weisman R.B., Oxygen doping modifies near-infrared band gaps in fluorescent single-walled carbon nanotubes, Science, 330 (6011), 1656–1659 (2010).
- [83] Avila Orta C., González-Morones P., Espinoza-González C., Martínez-Colunga J., Neira-Velázquez M., Sáenz-Galindo A., et al., Syntheses and Applications of Carbon Nanotubes and Their Composites, chapter Toward Greener Chemistry Methods for Preparation of Hybrid Polymer Materials Based on Carbon Nanotubes, 167–192, InTech (2013).
- [84] Chen J., Hamon M., Hu H., Chen Y., Rao A., Eklund P., et al., Solution properties of single-walled carbon nanotubes, Science, 282 (5386), 95–98 (1998).
- [85] Jeon I.Y., Chang D., Kumar N., Baek J.B., Functionalization of carbon nanotubes, carbon nanotubes - polymer nanocomposites, InTech, ISBN: 978-953-307-498-6, Available from: http://www.intechopen.com/books/carbon-nanotubespolymernanocomposites/functionalization-of-carbon-nanotubes (2011).

- [86] Ma P.C., Kim J.K., Tang B.Z., Functionalization of carbon nanotubes using a silane coupling agent, Carbon, 44 (15), 3232–3238 (2006).
- [87] Hamon M., Hui H., Bhowmik P., Itkis H., Haddon R., Ester-functionalized soluble singlewalled carbon nanotubes, Applied Physics A - Materials Science & Processing, 74 (3), 333–338 (2002).
- [88] Hamon M., Chen J., Hu H., Chen Y., Itkis M., Rao A., et al., Dissolution of single-walled carbon nanotubes, Advanced Materials, 11 (10), 834+ (1999).
- [89] Unger E., Graham A., Kreupl F., Liebau M., Hoenlein W., Electrochemical functionalization of multi-walled carbon nanotubes for solvation and purification, Current Applied Physics, 2 (2), 107–111 (2002).
- [90] Kim K., Bae D., Kim J., Park K., Lim S., Kim J., et al., Modification of electronic structures of a carbon nanotube by hydrogen functionalization, Advanced Materials, 14 (24), 1818–1821 (2002).
- [91] Wenseleers W., Vlasov I., Goovaerts E., Obraztsova E., Lobach A., Bouwen A., Efficient isolation and solubilization of pristine single-walled nanotubes in bile salt micelles, Advanced Functional Materials, 14 (11), 1105–1112 (2004).
- [92] Sloan J., Wright D., Woo H., Bailey S., Brown G., York A., et al., Capillarity and silver nanowire formation observed in single walled carbon nanotubes, Chemical Communications, (8), 699–700 (1999).
- [93] Jorge J., Flahaut E., Gonzalez-Jimenez F., Gonzalez G., Gonzalez J., Belandria E., et al., Preparation and characterization of alpha-Fe nanowires located inside double wall carbon nanotubes, Chemical Physics Letters, 457 (4-6), 347–351 (2008).
- [94] Kitaura R., Nakanishi R., Saito T., Yoshikawa H., Awaga K., Shinohara H., High-Yield Synthesis of Ultrathin Metal Nanowires in Carbon Nanotubes, Angewandte Chemie-International Edition, 48 (44), 8298–8302 (2009).
- [95] Pichler T., Kramberger C., Ayala P., Shiozawa H., Knupfer M., Ruemmeli M.H., et al., Bonding environment and electronic structure of Gd metallofullerene and Gd nanowire filled single-wall carbon nanotubes, Physica Status Solidi B - Basic Solid State Physics, 245 (10), 2038–2041 (2008).
- [96] Chikkannanavar S., Taubert A., Luzzi D., Filling single wall carbon nanotubes with metal chloride and metal nanowires and imaging with scanning transmission electron microscopy, in: Bernier, P and Ajayan, P and Iwasa, Y and Nikolaev, P (Editor), Making functional materials with nanotubes, volume 706 of Materials Research Society Symposium Proceedings, 205–210, Materials Research Society (2002).
- [97] Britz D., Khlobystov A., Wang J., O'Neil A., Poliakoff M., Ardavan A., et al., Selective host-guest interaction of single-walled carbon nanotubes with functionalised fullerenes, Chemical Communications, (2), 176–177 (2004).

- [98] Zhao C., Kitaura R., Hara H., Irle S., Shinohara H., Growth of linear carbon chains inside thin double-wall carbon nanotubes, Journal of Physical Chemistry C, 115 (27), 13166–13170 (2011).
- [99] Heimann R., Evsyukov S., Kavan L. (Editors), Carbyne and carbynoid structures, Kluwer Academic Press (1999).
- [100] Kavan L., *Electrochemical carbon*, Chemical Reviews, 97 (8), 3061–3082 (1997).
- [101] Kuwahara R., Kudo Y., Morisato T., Ohno K., Encapsulation of carbon chain molecules in single-walled carbon nanotubes, Journal of Physical Chemistry A, 115 (20), 5147–5156 (2011).
- [102] Kertesz M., Yang S., Energetics of linear carbon chains in one-dimensional restricted environment, Physical Chemistry Chemical Physics, 11 (2), 425–430 (2009).
- [103] Shi L., Sheng L., Yu L., An K., Ando Y., Zhao X., Ultra-thin double-walled carbon nanotubes: A novel nanocontainer for preparing atomic wires, Nano Research, 4 (8), 759–766 (2011).
- [104] Moura L.G., Fantini C., Righi A., Zhao C., Shinohara H., Pimenta M.A., Dielectric screening in polygnes encapsulated inside double-wall carbon nanotubes, Physical Review B, 83 (24), 245427 (2011).
- [105] Mölder U., Burk P., Koppel I., Quantum chemical calculations of geometries and gasphase deprotonation energies of linear polyyne chains, International Journal of Quantum Chemistry, 82 (2), 73–85 (2001).
- [106] Cataldo F. (Editor), Polyynes: Synthesis, Properties, and Applications, CRC Press/Taylor & Francis (2005).
- [107] Schindler A., Spiessberger S., Hergert S., Fruehauf N., Novak J.P., Yaniv Z., Suspensiondeposited carbon-nanotube networks for flexible active-matrix displays, Journal of the Society for Information Display, 16 (5), 651–658 (2008).
- [108] Martel R., Schmidt T., Shea H., Hertel T., Avouris P., Single- and multi-wall carbon nanotube field-effect transistors, Applied Physics Letters, 73 (17), 2447–2449 (1998).
- [109] Dabera G.D.M.R., Jayawardena K.D.G.I., Prabhath M.R.R., Yahya I., Tan Y.Y., Nismy N.A., et al., *Hybrid carbon nanotube networks as efficient hole extraction layers for organic photovoltaics*, ACS Nano, 7 (1), 556–565 (2013).
- [110] Dang X., Yi H., Ham M.H., Qi J., Yun D.S., Ladewski R., et al., Virus-templated selfassembled single-walled carbon nanotubes for highly efficient electron collection in photovoltaic devices, Nature Nanotechnology, 6 (6), 377–384 (2011).
- [111] Heller D., Jeng E., Yeung T., Martinez B., Moll A., Gastala J., et al., Optical detection of DNA conformational polymorphism on single-walled carbon nanotubes, Science, 311 (5760), 508–511 (2006).

- [112] Cherukuri P., Bachilo S., Litovsky S., Weisman R., Near-infrared fluorescence microscopy of single-walled carbon nanotubes in phagocytic cells, Journal of the American Chemical Society, 126 (48), 15638–15639 (2004).
- [113] Kam N., O'Connell M., Wisdom J., Dai H., Carbon nanotubes as multifunctional biological transporters and near-infrared agents for selective cancer cell destruction, Proceedings of the National Academy of Sciences of the United States of America, 102 (33), 11600–11605 (2005).
- [114] Lefebvre J., Maruyama S., Finnie P., Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications, chapter Photoluminescence: Science and Applications, 287–320, Springer (2008).
- [115] Miyauchi Y., Photoluminescence studies on exciton photophysics in carbon nanotubes, Journal of materials chemistry C, 1 (40), 6499–6521 (2013).
- [116] Dvorak M., Wei S.H., Wu Z., Origin of the variation of exciton binding energy in semiconductors, Physical Review Letters, 110 (1), 016402 (2013).
- [117] Miyauchi Y., Ajiki H., Maruyama S., Electron-hole asymmetry in single-walled carbon nanotubes probed by direct observation of transverse quasidark excitons, Physical Review B, 81 (12), 121415 (2010).
- [118] Chou S.G., Plentz F., Jiang J., Saito R., Nezich D., Ribeiro H.B., et al., Phonon-assisted excitonic recombination channels observed in DNA-wrapped carbon nanotubes using photoluminescence spectroscopy, Physical Review Letters, 94 (12), 127402 (2005).
- [119] Ando T., Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications, chapter Role of the Aharanov-Bohm Phase in the Optical Properties of Carbon Nanotubes, 229–250, Springer (2008).
- [120] Matsunaga R., Miyauchi Y., Matsuda K., Kanemitsu Y., Symmetry-induced nonequilibrium distributions of bright and dark exciton states in single carbon nanotubes, Physical Review B, 80 (11), 115436 (2009).
- [121] Perebeinos V., Tersoff J., Avouris P., Radiative lifetime of excitons in carbon nanotubes, Nano Letters, 5 (12), 2495–2499 (2005).
- [122] Miyauchi Y., Hirori H., Matsuda K., Kanemitsu Y., Radiative lifetimes and coherence lengths of one-dimensional excitons in single-walled carbon nanotubes, Physical Review B, 80 (8), 081410 (2009).
- [123] O'Connell M., Bachilo S., Huffman C., Moore V., Strano M., Haroz E., et al., Band gap fluorescence from individual single-walled carbon nanotubes, Science, 297 (5581), 593–596 (2002).
- [124] Bachilo S., Strano M., Kittrell C., Hauge R., Smalley R., Weisman R., Structure-assigned optical spectra of single-walled carbon nanotubes, Science, 298 (5602), 2361–2366 (2002).

- [125] Qian H., Georgi C., Anderson N., Green A.A., Hersam M.C., Novotny L., et al., Exciton transfer and propagation in carbon nanotubes studied by near-field optical microscopy, Physica Status Solidi B, 245 (10), 2243–2246 (2008).
- [126] Reich S., Thomsen C., Robertson J., Exciton resonances quench the photoluminescence of zigzag carbon nanotubes, Physical Review Letters, 95 (7), 077402 (2005).
- [127] Vialla F., Roquelet C., Langlois B., Delport G., Santos S.M., Deleporte E., et al., *Chirality Dependence of the Absorption Cross Section of Carbon Nanotubes*, Physical Review Letters, 111 (13) (2013).
- [128] Hirori H., Matsuda K., Kanemitsu Y., Exciton energy transfer between the inner and outer tubes in double-walled carbon nanotubes, Physical Review B, 78 (11), 113409 (2008).
- [129] Gokus T., Cognet L., Duque J.G., Pasquali M., Hartschuh A., Lounis B., Mono- and biexponential luminescence decays of individual single-walled carbon nanotubes, Journal of Physical Chemistry C, 114 (33), 14025–14028 (2010).
- [130] Cambre S., Santos S.M., Wenseleers W., Nugraha A.R.T., Saito R., Cognet L., et al., Luminescence properties of individual empty and water-filled single-walled carbon nanotubes, ACS Nano, 6 (3), 2649–2655 (2012).
- [131] Hagen A., Moos G., Talalaev V., Hertel T., Electronic structure and dynamics of optically excited single-wall carbon nanotubes, Applied Physics A - Materials Science & Processing, 78 (8), 1137–1145 (2004).
- [132] Jones M., Engtrakul C., Metzger W.K., Ellingson R.J., Nozik A.J., Heben M.J., et al., Analysis of photoluminescence from solubilized single-walled carbon nanotubes, Physical Review B, 71 (11), 115426 (2005).
- [133] Hartschuh A., Qian H., Meixner A., Anderson N., Novotny L., Nanoscale optical imaging of excitons in single-walled carbon nanotubes, Nano Letters, 5 (11), 2310–2313 (2005).
- [134] Crochet J., Clemens M., Hertel T., Quantum yield heterogeneities of aqueous single-wall carbon nanotube suspensions, Journal of the American Chemical Society, 129 (26), 8058– 8059 (2007).
- [135] Hertel T., Himmelein S., Ackermann T., Stich D., Crochet J., Diffusion limited photoluminescence quantum yields in 1-D semiconductors: Single-wall carbon nanotubes, ACS Nano, 4 (12), 7161–7168 (2010).
- [136] Tsyboulski D.A., Rocha J.D.R., Bachilo S.M., Cognet L., Weisman R.B., Structuredependent fluorescence efficiencies of individual single-walled cardon nanotubes, Nano Letters, 7 (10), 3080–3085 (2007).
- [137] Cognet L., Tsyboulski D.A., Rocha J.D.R., Doyle C.D., Tour J.M., Weisman R.B., Stepwise quenching of exciton fluorescence in carbon nanotubes by single-molecule reactions, Science, 316 (5830), 1465–1468 (2007).

- [138] Crochet J.J., Duque J.G., Werner J.H., Lounis B., Cognet L., Doorn S.K., Disorder limited exciton transport in colloidal single-wall carbon nanotubes, Nano Letters, 12 (10), 5091– 5096 (2012).
- [139] Inoue T., Matsuda K., Murakami Y., Maruyama S., Kanemitsu Y., Diameter dependence of exciton-phonon interaction in individual single-walled carbon nanotubes studied by microphotoluminescence spectroscopy, Physical Review B, 73 (23), 233401 (2006).
- [140] Tsyboulski D.A., Bakota E.L., Witus L.S., Rocha J.D.R., Hartgerink J.D., Weisman R.B., Self-assembling peptide coatings designed for highly luminescent suspension of singlewalled carbon nanotubes, Journal of the American Chemical Society, 130 (50), 17134–17140 (2008).
- [141] Matsuda K., Inoue T., Murakami Y., Maruyama S., Kanemitsu Y., Exciton dephasing and multiexciton recombinations in a single carbon nanotube, Physical Review B, 77 (3), 033406 (2008).
- [142] Bonaccorso F., Hasan T., Tan P.H., Sciascia C., Privitera G., Di Marco G., et al., Density gradient ultracentrifugation of nanotubes: Interplay of bundling and surfactants encapsulation, Journal of Physical Chemistry C, 114 (41), 17267–17285 (2010).
- [143] Rohlfing M., Redshift of excitons in carbon nanotubes caused by the environment polarizability, Physical Review Letters, 108 (8), 087402 (2012).
- [144] Okazaki T., Okubo S., Nakanishi T., Joung S.K., Saito T., Otani M., et al., Optical band gap modification of single-walled carbon nanotubes by encapsulated fullerenes, Journal of the American Chemical Society, 130 (12), 4122–4128 (2008).
- [145] Takagahara T., Hanamura E., Giant-oscillator-strength effect on excitonic optical nonlinearities due to localization, Physical Review Letters, 56 (23), 2533–2536 (1986).
- [146] Piao Y., Meany B., Powell L.R., Valley N., Kwon H., Schatz G.C., et al., Brightening of carbon nanotube photoluminescence through the incorporation of sp(3) defects, Nature Chemistry, 5 (10), 840–845 (2013).
- [147] Rohringer P., Shi L., Liu X., Yanagi K., Pichler T., Purification, separation and extraction of inner tubes from double-walled carbon nanotubes by tailoring density gradient ultracentrifugation using optical probes, Carbon, in press (2014).
- [148] Koyama T., Asada Y., Hikosaka N., Miyata Y., Shinohara H., Nakamura A., Ultrafast exciton energy transfer between nanoscale coaxial cylinders: Intertube transfer and luminescence quenching in double-walled carbon nanotubes, ACS Nano, 5 (7), 5881–5887 (2011).
- [149] Yang S., Parks A.N., Saba S.A., Ferguson P.L., Liu J., Photoluminescence from inner walls in double-walled carbon nanotubes: Some do, some do not, Nano Letters, 11 (10), 4405–4410 (2011).
- [150] Hertel T., Hagen A., Talalaev V., Arnold K., Hennrich F., Kappes M., et al., Spectroscopy of single- and double-wall carbon nanotubes in different environments, Nano Letters, 5 (3), 511–514 (2005).

- [151] Jung Y.C., Muramatsu H., Fujisawa K., Kim J.H., Hayashi T., Kim Y.A., et al., Optically and biologically active mussel protein-coated double-walled carbon nanotubes, Small, 7 (23), 3292–3297 (2011).
- [152] Hayashi T., Shimamoto D., Kim Y.A., Muramatsu H., Okino F., Touhara H., et al., Selective optical property modification of double-walled carbon nanotubes by fluorination, ACS Nano, 2 (3), 485–488 (2008).
- [153] Iakoubovskii K., Minami N., Ueno T., Kazaoui S., Kataura H., Optical characterization of double-wall carbon nanotubes: Evidence for inner tube shielding, Journal of physical chemistry C, 112 (30), 11194–11198 (2008).
- [154] Heller D.A., Mayrhofer R.M., Baik S., Grinkova Y.V., Usrey M.L., Strano M.S., Concomitant length and diameter separation of single-walled carbon nanotubes, Journal of the American Chemical Society, 126 (44), 14567–14573 (2004).
- [155] Fagan J.A., Becker M.L., Chun J., Nie P., Bauer B.J., Simpson J.R., et al., Centrifugal length separation of carbon nanotubes, Langmuir, 24 (24), 13880–13889 (2008).
- [156] Zhang J., Miyata Y., Kitaura R., Shinohara H., Preferential synthesis and isolation of (6,5) single-wall nanotubes from one-dimensional C₆₀ coalescence, Nanoscale, 3 (10), 4190–4194 (2011).
- [157] Kishi N., Kikuchi S., Ramesh P., Sugai T., Watanabe Y., Shinohara H., Enhanced photoluminescence from very thin double-wall carbon nanotubes synthesized by the zeolite-ccvd method, Journal of Physical Chemistry B, 110 (49), 24816–24821 (2006).
- [158] Shimamoto D., Muramatsu H., Hayashi T., Kim Y.A., Endo M., Park J.S., et al., Strong and stable photoluminescence from the semiconducting inner tubes within double walled carbon nanotubes, Applied Physics Letters, 94 (8), 083106 (2009).
- [159] Kim J.H., Kataoka M., Shimamoto D., Muramatsu H., Jung Y.C., Hayashi T., et al., Raman and fluorescence spectroscopic studies of a DNA-dispersed double-walled carbon nanotube solution, ACS Nano, 4 (2), 1060–1066 (2010).
- [160] Kataura H., Kumazawa Y., Maniwa Y., Umezu I., Suzuki S., Ohtsuka Y., et al., Optical properties of single-wall carbon nanotubes, Synthetic Metals, 103 (1-3), 2555–2558 (1999).
- [161] Murakami Y., Einarsson E., Edamura T., Maruyama S., Polarization dependence of the optical absorption of single-walled carbon nanotubes, Physical Review Letters, 94 (8) (2005).
- [162] Liu X., Electronic structure and excited states of pristine and intercalated single-wall carbon nanotubes, Ph.D. thesis, Technische Universität Dresden (2003).
- [163] Miyata Y., Yanagi K., Maniwa Y., Kataura H., Optical evaluation of the metal-tosemiconductor ratio of single-wall carbon nanotubes, Journal of Physical Chemistry C, 112 (34), 13187–13191 (2008).
- [164] Miyauchi Y., Chiashi S., Murakami Y., Hayashida Y., Maruyama S., Fluorescence spectroscopy of single-walled carbon nanotubes synthesized from alcohol, Chemical Physics Letters, 387 (1-3), 198–203 (2004).

- [165] Anis B., Haubner K., Boerrnert F., Dunsch L., Ruemmeli M.H., Kuntscher C.A., Stabilization of carbon nanotubes by filling with inner tubes: An optical spectroscopy study on double-walled carbon nanotubes under hydrostatic pressure, Physical Review B, 86 (15) (2012).
- [166] Backes C., Mundloch U., Ebel A., Hauke F., Hirsch A., Dispersion of HiPco (R) and CoMoCAT (R) Single-Walled Nanotubes (SWNTs) by Water Soluble Pyrene Derivatives-Depletion of Small Diameter SWNTs, Chemistry-A European Journal, 16 (11), 3314–3317 (2010).
- [167] Dresselhaus M., Dresselhaus G., Saito R., Jorio A., Raman spectroscopy of carbon nanotubes, Physics Reports - Review Section of Physics Letters, 409 (2), 47–99 (2005).
- [168] Thomsen C., Reich S., Raman scattering in carbon nanotubes, in: M. Cardona, R. Merlin (Editors), Light scattering in solid IX, volume 108 of Topics in applied physics, 115–234, Springer (2007).
- [169] Jorio A., Pimenta M., Souza A., Saito R., Dresselhaus G., Dresselhaus M., Characterizing carbon nanotube samples with resonance Raman scattering, New Journal of Physics, 5 (2003).
- [170] Martin R., Falicov L., Introductory concepts, in: C. M (Editor), Light scattering in solids I, volume 8 of Topics in applied physics, chapter 3, 70, Springer (1983).
- [171] Fantini C., Jorio A., Souza M., Strano M., Dresselhaus M., Pimenta M., Optical transition energies for carbon nanotubes from resonant Raman spectroscopy: Environment and temperature effects, Physical Review Letters, 93 (14), 147406 (2004).
- [172] Kurti J., Kresse G., Kuzmany H., First-principles calculations of the radial breathing mode of single-wall carbon nanotubes, Physical Review B, 58 (14), R8869–R8872 (1998).
- [173] Kuzmany H., Plank W., Hulman M., Kramberger C., Gruneis A., Pichler T., et al., Determination of SWCNT diameters from the Raman response of the radial breathing mode, European Physical Journal B, 22 (3), 307–320 (2001).
- [174] Henrard L., Hernandez E., Bernier P., Rubio A., van der Waals interaction in nanotube bundles: Consequences on vibrational modes, Physical Review B, 60 (12), R8521–R8524 (1999).
- [175] Jorio A., Araujo P.T., Doorn S.K., Maruyama S., Chacham H., Pimenta M.A., *The Kataura plot over broad energy and diameter ranges*, Physica Status Solidi B - Basic Solid State Physics, 243 (13), 3117–3121 (2006), 20th International Winterschool/Euroconference on Electronic Properties of Novel Materials, Kirchberg, AUSTRIA, MAR 04-11, 2006.
- [176] Meyer J., Paillet M., Michel T., Moreac A., Neumann A., Duesberg G., et al., Raman modes of index-identified freestanding single-walled carbon nanotubes, Physical Review Letters, 95 (21) (2005).
- [177] Dresselhaus M., Eklund P., Phonons in carbon nanotubes, Advances in Physics, 49 (6), 705–814 (2000).

- [178] Jorio A., Souza A., Dresselhaus G., Dresselhaus M., Swan A., Unlu M., et al., G-band resonant Raman study of 62 isolated single-wall carbon nanotubes, Physical Review B, 65 (15) (2002).
- [179] Saito R., Fantini C., Jiang J., Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications, chapter Excitonic States and Resonance Raman Spectroscopy of Single-Walled Carbon Nanotubes, 251–286, Springer (2008).
- [180] Villalpando-Páez F., Son H., Nezich D., Hsieh Y.P., Kong J., Kim Y.A., et al., Raman spectroscopy study of isolated double-walled carbon nanotubes with different metallic and semiconducting configurations, Nano Letters, 8 (11), 3879–3886 (2008).
- [181] Villalpando-Páez F., Raman spectroscopy of double walled carbon nanotubes with different metallic and semiconducting configurations, Ph.D. thesis, Massachusetts Institute of Technology (2010).
- [182] Kalbac M., Kavan L., Zukalova M., Dunsch L., In-situ vis-near-infrared and raman spectroelectrochemistry of double-walled carbon naotubes, Advanced Functional Materials, 15 (3), 418–426 (2005).
- [183] Yang S., Kertesz M., Zolyomi V., Kurti J., Application of a novel linear/exponential hybrid force field scaling scheme to the longitudinal Raman active mode of polyyne, Journal of Physical Chemistry A, 111 (12), 2434–2441 (2007).
- [184] Ashcroft N., Mermin N. (Editors), Solid state physics, Saunders College (1976).
- [185] Peierls R. (Editor), Quantum theory of solids, Oxford University Press (1955).
- [186] Yang S., Kertesz M., Bond length alternation and energy band gap of polyyne, Journal of Physical Chemistry A, 110 (31), 9771–9774 (2006).
- [187] Wakabayashi T., Murakami T., Nagayama H., Nishide D., Kataura H., Achiba Y., et al., Raman spectral features of longer polyynes HC(2n)H (n=4-8) in SWNTs, European Physical Journal D, 52 (1-3), 79–82 (2009).
- [188] Malard L.M., Nishide D., Dias L.G., Capaz R.B., Gomes A.P., Jorio A., et al., Resonance Raman study of polyynes encapsulated in single-wall carbon nanotubes, Physical Review B, 76 (23), 233412 (2007).
- [189] Grueneis A., Ruemmeli M.H., Kramberger C., Barreiro A., Pichler T., Pfeiffer R., et al., High quality double wall carbon nanotubes with a defined diameter distribution by chemical vapor deposition from alcohol, Carbon, 44 (15), 3177–3182 (2006).
- [190] Muramatsu H., Hayashi T., Kim Y.A., Shimamoto D., Kim Y.J., Tantrakarn K., et al., Pore structure and oxidation stability of double-walled carbon nanotube-derived bucky paper, Chemical Physics Letters, 414 (4-6), 444–448 (2005).
- [191] Zhang J., Feng Y., Ishiwata H., Miyata Y., Kitaura R., Dahl J.E.P., et al., Synthesis and transformation of linear adamantane assemblies inside carbon nanotubes, ACS Nano, 6 (10), 8674–8683 (2012).

- [192] Endo M., Kim Y.A., Hayashi T., Muramatsu H., Terrones M., Saito R., et al., Nanotube coalescence-inducing mode: A novel vibrational mode in carbon systems, Small, 2 (8-9), 1031–1036 (2006).
- [193] Murakami Y., Kono J., Nonlinear photoluminescence excitation spectroscopy of carbon nanotubes: Exploring the upper density limit of one-dimensional excitons, Physical Review Letters, 102 (3), 037401 (2009).
- [194] Pfeiffer R., Pichler T., Kim Y.A., Kuzmany H., Carbon Nanotubes: Advanced Topics in the Synthesis, Structure, Properties and Applications, chapter Double-wall carbon nanotubes, 495–530, Springer (2008).
- [195] Ren W., Li F., Chen J., Bai S., Cheng H., Morphology, diameter distribution and Raman scattering measurements of double-walled carbon nanotubes synthesized by catalytic decomposition of methane, Chemical Physics Letters, 359 (3-4), 196–202 (2002).
- [196] Wei J.Q., Jiang B., Zhang X.F., Zhu H.W., Wu D.H., Raman study on double-walled carbon nanotubes, Chemical Physics Letters, 376 (5-6), 753-757 (2003).
- [197] Weisman R.B., Bachilo S.M., Dependence of optical transition energies on structure for single-walled carbon nanotubes in aqueous suspension: An empirical kataura plot, Nano Letters, 3 (9), 1235–1238 (2003).
- [198] Oyama Y., Saito R., Sato K., Jiang J., Samsonidze G.G., Gruneis A., et al., Photoluminescence intensity of single-wall carbon nanotubes, Carbon, 44 (5), 873–879 (2006).
- [199] Jorio A., Fantini C., Pimenta M.A., Heller D.A., Strano M.S., Dresselhaus M.S., et al., Carbon nanotube population analysis from raman and photoluminescence intensities, Applied Physics Letters, 88 (2), 023109 (2006).
- [200] Shen C., Brozena A.H., Wang Y., Double-walled carbon nanotubes: Challenges and opportunities, Nanoscale, 3 (2), 503–518 (2011).
- [201] Kolmogorov A.N., Crespi V.H., Smoothest bearings: Interlayer sliding in multiwalled carbon nanotubes, Physical Review Letters, 85 (22), 4727–4730 (2000).
- [202] Cerullo G., Maiuri M., Hauer J., unpublished results.
- [203] Fantini C., Cruz E., Jorio A., Terrones M., Terrones H., Van Lier G., et al., Resonance Raman study of linear carbon chains formed by the heat treatment of double-wall carbon nanotubes, Physical Review B, 73 (19), 193408 (2006).
- [204] Moura L.G., Malard L.M., Carneiro M.A., Venezuela P., Capaz R.B., Nishide D., et al., Charge transfer and screening effects in polyynes encapsulated inside single-wall carbon nanotubes, Physical Review B, 80 (16) (2009).
- [205] Zhao X., Ando Y., Liu Y., Jinno M., Suzuki T., Carbon nanowire made of a long linear carbon chain inserted inside a multiwalled carbon nanotube, Physical Review Letters, 90 (18), 187401/1-4 (2003).

- [206] Jinno M., Ando Y., Bandow S., Fan J., Yudasaka M., Iijima S., Raman scattering study for heat-treated carbon nanotubes: The origin of ≈ 1855cm⁻¹ Raman band, Chemical Physics Letters, 418 (1-3), 109–114 (2006).
- [207] Rohringer P., unpublished results.
- [208] Huh J.Y., Walker A.R.F., Ro H.W., Obrzut J., Mansfield E., Geiss R., et al., Separation and characterization of double-wall carbon nanotube subpopulations, Journal of Physical Chemistry C, 114 (26), 11343–11351 (2010).
- [209] Kazaoui S., Minami N., Jacquemin R., Kataura H., Achiba Y., Amphoteric doping of single-wall carbon-nanotube thin films as probed by optical absorption spectroscopy, Physical Review B, 60 (19), 13339–13342 (1999).
- [210] Jacquemin R., Kazaoui S., Yu D., Hassanien A., Minami N., Kataura H., et al., Doping mechanism in single-wall carbon nanotubes studied by optical absorption, Synthetic Metals, 115 (1-3), 283–287 (2000).
- [211] Crochet J.J., Duque J.G., Werner J.H., Doorn S.K., Photoluminescence imaging of electronic-impurity-induced exciton quenching in single-walled carbon nanotubes, Nature Nanotechnology, 7 (2), 126–132 (2012).

Appendix

Data of the sample annealed at $1480 \,^{\circ}$ C measured by Raman spectroscopy with a 568nm laser and fitted with the method of Fantini et al. [203].



Peak	Type	Amplitude [arb.u.]	Position $[\rm cm^{-1}]$	FWHM $[cm^{-1}]$
В	Constant Bg	152.159480		
1	Lorentz Amp	206.212696	1830.61320	10.0478229
2	Lorentz Amp	812.164053	1842.67553	10.0478229
3	Lorentz Amp	2251.07069	1851.04245	10.0478229
4	Lorentz Amp	470.689902	1856.54573	10.0478229

Data of the sample annealed at 1480 °C measured by Raman spectroscopy with a 568nm laser and fitted with 34 Voigtians. For the other samples the peak positions were similar, only the amplitude varied.



Peak	Type	Amplitude [arb.u.]	Center $[\rm cm^{-1}]$	$FWHM \ [cm^{-1}]$	FW Base
В	Constant Bg	237.687967			
1	Voigt Amp	31.1018035	1823.49456	3.15336583	10.5112193
2	Voigt Amp	41.2542786	1825.43417	3.15336583	10.5112193
3	Voigt Amp	71.0756561	1827.18115	3.15336583	10.5112193
4	Voigt Amp	62.0640663	1828.21811	3.15336583	10.5112193
5	Voigt Amp	113.695343	1829.61251	3.15336583	10.5112193
6	Voigt Amp	113.827458	1831.23872	3.15336583	10.5112193
7	Voigt Amp	95.3373615	1832.88063	3.15336583	10.5112193
8	Voigt Amp	106.965625	1834.16533	3.15336583	10.5112193
9	Voigt Amp	190.731608	1835.90587	3.15336583	10.5112193
10	Voigt Amp	206.148449	1837.58284	3.15336583	10.5112193
11	Voigt Amp	242.718097	1839.11234	3.15336583	10.5112193
12	Voigt Amp	284.582956	1840.44978	3.15336583	10.5112193
13	Voigt Amp	377.492154	1841.84799	3.15336583	10.5112193
14	Voigt Amp	455.596220	1843.17444	3.15336583	10.5112193
15	Voigt Amp	577.088115	1844.69336	3.15336583	10.5112193
16	Voigt Amp	457.786397	1846.24639	3.15336583	10.5112193
17	Voigt Amp	530.945553	1847.48058	3.15336583	10.5112193
18	Voigt Amp	773.623935	1848.98328	3.15336583	10.5112193

19	Voigt Amp	850.335922	1850.26186	3.15336583	10.5112193
20	Voigt Amp	1087.23914	1851.60645	3.15336582	10.5112193
21	Voigt Amp	873.797931	1853.19859	3.15336583	10.5112193
22	Voigt Amp	578.276583	1854.70572	3.15336583	10.5112193
23	Voigt Amp	491.154569	1856.14053	3.15336583	10.5112193
24	Voigt Amp	395.852090	1857.53289	3.15336583	10.5112193
25	Voigt Amp	269.145067	1858.88644	3.15336583	10.5112193
26	Voigt Amp	190.629960	1860.18227	3.15336583	10.5112193
27	Voigt Amp	159.181976	1861.77515	3.15336583	10.5112193
28	Voigt Amp	107.546592	1863.84306	3.15336583	10.5112193
29	Voigt Amp	49.4015732	1865.72469	3.15336583	10.5112193
30	Voigt Amp	31.5319602	1866.62263	3.15336583	10.5112193
31	Voigt Amp	38.4008884	1868.23650	3.15336583	10.5112193
32	Voigt Amp	36.6533515	1870.34644	3.15336583	10.5112193
33	Voigt Amp	11.7894760	1872.77509	3.15336583	10.5112193
34	Voigt Amp	13.6359359	1875.11085	3.15336583	10.5112193



Amplification of the PL Intensity compared to the pristine sample for DWCNT filled with linear carbon chains grown at different temperatures as function of the inner tube diameter.

Curriculum Vitae - Philip Rohringer

Nationality: Austrian Place/Date of birth: Wien, Austria, 1985/02/03 Address: Koppstraße 95a/1/7, 1160 Wien, Austria E-Mail: <u>philip.rohringer@univie.ac.at</u> Phone: +43 660 4950032

Education

PHD in Physics Faculty of Physics/University of Vienna Electronic Properties of Materials

Faculty of Physics/University of Vienna Electronic Properties of Materials

Mag. rer. nat. in Physics

03/2011-Present

11/2008-01/2011

University of Vienna, Vienna, Austria03/2011-PresentFaculty of Physics/Electronic Properties of MaterialsOptical experiments on double-walled carbon nanotubes filled with carbon chains.

Thesis: "Annealing of ion-beam induced lattice defects in YBa₂Cu₃O₇"

Responsible for photoluminescence and optical absorption spectroscopy equipment

Tokyo Metropolitan University, Tokyo, Japan02/2013Department of Physics/Nanoscience Research IISeperation of double-walled carbon nanotube species and extraction of inner tubes.

Teaching Experience

Research Activities

University Lecturer	03/2011-02/2014
Faculty of Physics/University of Vienna Exercises to "Solid State Physics I & II" Exercises to "Experimental Physics 4"	
Tutor	10/2009-02/2011
Faculty of Physics/University of Vienna	
Experimental lab course in physics for nutritional scientists	

Skills & Abilities

Technical Skills

Nanotube synthesis (CVD), separation (DGU) and sample preparation techniques (suspensions and thin films) Photoluminescence spectroscopy Optical absorption spectroscopy Multi-frequency Raman spectroscopy Extensive experience with UHV systems Closed cycle cryostat systems for transport and optical measurements

Computer Skills

Origin, Peak Fit, Labview, Testpoint, basic programming skills in C++, Python, HTML

Languages

German: Native language English: Excellent (spoken and written) French: Basic (written)