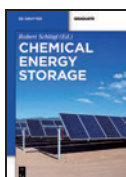


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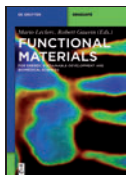
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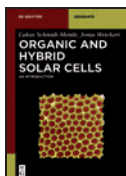


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Next Generation Composites for Sustainable
Energy Applications

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Dominik Eder and Robert Schlögl

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Preface

Today's world is facing major challenges that directly affect our modern life. The demand for energy is expected to double by the year 2050. As a consequence of increased energy utilization the need is growing to protect our environment from the adverse effects of pollution and the destruction of natural habitats. To ensure sufficient supply of clean water and air and to nourish the growing population without conflicts and poverty are additional global challenges. In this arena, the transformation of the fossil energy system into a sustainable operation and the technical increase of energy efficiency are key objectives of chemical sciences with their ability to create novel fuels, materials and processes of molecular transformations. Using the energy of sunlight to split water into hydrogen as a clean energy source and storing energy in batteries and supercapacitors are two popular examples of energy science. Both challenges critically involve the availability of novel carbon materials. Carbon is the most versatile chemical element for designing molecules and materials. It enables us to address a wide range of functional characteristics by varying the assembly of only one type of atoms interacting with each other in essentially only two binding modes, i.e. sp^2/sp^3 hybridization.

The unlimited number of combinations of the two basic bonding motives allows the realization of molecular and supra-molecular properties limited only by our imagination. Hetero-atomic additions to the carbon backbone give additional chemical and structural diversity that needs exploitation in interface-controlled material science applications. The interplay between combining building blocks of carbon and decorating the products with hetero-elements forms the basis of a knowledge-based carbon material science. A critical strategy of material design is to combine carbon with other materials with diverging properties into spatial arrangements that create synergistic functions. Such materials, known as composites, were developed for carbon-based systems with the maturation of polymer science and are implemented today in numerous products ranging from materials for packaging, dental and medical use, energy production and storage, to structural materials for lightweight applications.

Nanocarbon composites are multiphase materials, in which a nanostructured *filler* (i.e. particles, whiskers, fibers, nanotubes or lamellae) is dispersed in an organic (i.e. polymer) or inorganic (i.e. carbon, ceramic or metal) *matrix*. In the last few years, carbon in the form of nanotubes (CNTs) in addition to nanostructured fibers or as graphene has attracted wide interest as a filler for nanocomposites. Typical application profiles are a high electrical conductivity in transparent conducting polymers or a remarkable fracture toughness reinforcing ceramics such as hydroxyapatite for bone replacement. Nanocomposites have a considerable impact on large-scale industrial applications of lightweight structural materials in aerospace and e-mobility, of electrically conducting plastics for electronic applications or as packaging materials with reduced gas permeability for foodstuff and air-sensitive goods.

Nanocarbon hybrids are a new class of composite materials in which the carbon nanostructures are compounded with thin layers of metals, semiconductors, inorganic glasses or ceramics. The carbon component gives ready access for gases and fluids to a large fraction of the inner surface area of the inorganic compound. In addition, a large interface between two materials with different bulk properties allows for the design of materials with interface-dominated properties. Their special appeal arises from charge and energy transfer through this interface, giving rise to transport properties different from the linear combination of the respective bulk properties. Although still at an early stage of research, such hybrid materials have demonstrated potential in applications concerning energy conversion and environmental protection. These include improved sensitivities in bio/chemical sensors, increased energy densities in batteries and larger capacities in supercapacitors, higher currents in field emission devices, more efficient charge separation and thus superior activities in photocatalysts and improved efficiencies in photovoltaics.

This book is dedicated exclusively to the family of nanocarbon hybrids covering a multidisciplinary research field that combines materials chemistry and physics with nanotechnology and applied energy sciences. It provides both introductory material on fundamental principles as well as reviews of the current research. Therefore, this book should be helpful for Master and PhD students wishing to become familiar with a modern field of knowledge-driven material science as well as for senior researchers and industrial staff scientists who explore the frontiers of knowledge.

The **first part of this book** introduces the concept of nanocarbons as building blocks. It establishes a scientific foundation for their subsequent use in hybrids and composites. *Chapter 1* provides a concise introduction into the world of carbon nanotubes (CNTs), explaining their unique structural characteristics, synthesis routes and key characterization techniques. It summarizes the profile of exceptional properties of CNT. *Chapter 2* concentrates on the synthesis and characterization of graphene-based materials, including single-layer and few-layer graphene as well as graphene oxide and its chemically/thermally reduced counterpart. The chapter further demonstrates that the dispersion of nanocarbons remains a key challenge for their implementation into hybrids. Chapters 3 and 4 are dedicated to the post-synthesis processing of nanocarbons. In particular, *Chapter 3* focuses on the chemical functionalization of CNTs, providing examples for a whole range of covalent and noncovalent functionalization routes. *Chapter 4* offers a comprehensive review on doping and filling of CNTs and the effect of defects on the hybridization of CNTs with polymers.

The **second part of this book**, comprising Chapters 5 to 10, is dedicated to the synthesis of nanocarbon hybrids and composites. *Chapter 5* begins by identifying the general synthesis routes towards nanocarbon hybrids, which can be categorized into *ex situ* (i.e. “building block”) and *in situ* approaches, and comparing their advantages and disadvantages on the basis of some of the most intriguing recent results. In general, the *ex situ* route is a two-step process in which the inorganic compound is synthesized first, taking advantage of the existing wealth of knowledge in synthesizing nano-

materials (*i.e.* structure-property relationship). In a second step, the inorganic compound is linked to the nanocarbon surface via covalent, noncovalent or electrostatic interactions. In the *in situ* approach the inorganic or polymeric compound is grown on the (modified) nanocarbon surface from molecular precursors via (electro)chemical, vapor-based or physical deposition techniques, exploiting the stabilizing effects of nanocarbon as templates and as local heat sinks.

The examples discussed in *Chapter 5* cover a wide range of synthetic aspects, yet concentrate on hybrids involving CNTs, while *Chapter 6* summarizes recent developments on the hybridization of graphene-based materials. *Chapter 7* on the other hand introduces sustainable carbon materials made from hydrothermal carbonization (HTC) as promising candidates for hybrid materials. *Chapter 8* then combines nanocarbons with polymers and documents that engineering the interfaces is a challenge that is equally important in the synthesis of nanocarbon hybrids and of carbon composites. The book section is concluded by *Chapters 9 and 10*, which are dedicated to specific examples of hybrids. Chapter 9 describes hybrids whose components are all carbon based, such as CNTs hybridized with graphene, while Chapter 10 discusses the incorporation of graphene oxide into metal-organic framework structures (MOFs).

The **third part of the book** highlights the potential of nanocarbon hybrids for various important applications, particularly concerning environmental and sustainable energy applications. These include electrode materials in batteries and electrochemical capacitors (*Chapters 11 and 12*), sensors and emitters in field emission devices (*Chapter 13*), electrocatalysts in fuel cells (*Chapter 14*), supports for heterogeneous catalysts (*Chapter 15*), next-generation photocatalysts (*Chapter 16*), as well as active compounds in electrochromic and photovoltaic applications (*Chapters 17 and 18*). All these chapters discuss the benefits of nanocarbon hybrids in the respective application, identify major challenges and critically review the present state of research with the most intriguing recent developments. Finally, *Chapter 19* elaborates on the importance of defects and edge atoms in graphene-based hybrid materials.

This book illustrates that nanocarbon hybrid materials are an exciting new class of multi-purpose composites with great potential to become the next-generation energy materials. The synergistic effects in nanocarbon hybrids are manifold and it is clear that a detailed fundamental understanding of their origins will be essential to exploit the options given by combining classes of materials with diverging properties.

We foremost express our deepest thanks to our colleagues who spent considerable time and effort in writing the chapters in this book. We hope that this book will be useful to those interested in the subject of nanocarbon hybrids from many different perspectives and that it will establish a sound foundation for future research. We further would like to thank Julia Lauterbach and Karin Sora of De Gruyter Publishers for their tireless support and guidance. It is a particular pleasure to acknowledge the students of the Münster group for their invaluable help in proof-reading.

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Part I: **Nanocarbon building blocks**

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1 A short introduction on carbon nanotubes

1.1 Introduction

Carbon nanotubes (CNTs) constitute a nanostructured carbon material that consists of rolled up layers of sp^2 hybridized carbon atoms forming a honeycomb lattice. After diamond, graphite and fullerenes, the one-dimensional tubular structure of CNTs is considered the 4th allotrope of carbon (graphene is the 5th).

For a long time the discovery of CNTs was attributed to the S. Iijima, who investigated soot formation during the production of fullerenes via arc discharge and observed the presence of “microfibrils” made of concentric carbon layers. Later he identified these microfibrils as possessing a honeycomb structure and being capped with fullerenes [1]. However, although this seminal paper in *Nature* in 1991 undoubtedly initiated a research field that has become tremendously popular, it was not the first publication on CNTs. In fact, electron micrographs of CNTs and carbon fibers have been published throughout the decades since as early as the 1950s, usually while being studied as by-products, impurities or catalyst poison in heterogeneous catalysis [2, 3]. It is now widely accepted that the first report on CNTs was published in 1952 by Radushkevich and Lukyanovich [4], who investigated the hydrogenation of CO over Fe catalysts under reaction conditions today deemed as suitable for CNT production. They documented the formation of “unusual carbon structures” by transmission electron microscopy (TEM). In contrast to these multi-walled CNTs (MWCNTs), the first report on single-walled carbon nanotubes (SWCNTs) was published in 1993 by Kiang *et al.* [5] and Iijima *et al.* [6] simultaneously (in the same issue of *Nature* on consecutive pages).

The remarkable interest in CNTs arose mainly because of their unique properties (see Section 1.3) that commend them for a wide range of applications involving both *science fiction*, *i.e.* space elevator [7], bullet-proof shirts [8], artificial muscles [9], and *real life applications*, *i.e.* field emission sources [10], Li-ion batteries [11], electrochemical storage devices [12], molecular sensors [13], hydrogen storage [14] and enhancing plant growth [15]. The incorporation of CNTs into organic or ceramic matrices (*i.e.* nanocomposites) and coating them with functional materials (*i.e.* hybrids) has increased their applicability and so stimulated further interest.

This chapter provides a concise summary of the most important concepts and characteristics of CNTs including structural aspects (*i.e.* chirality, defects, doping), properties (*i.e.* mechanical, electronic, thermal), synthesis and characterization techniques and post-processing strategies (*i.e.* purification, separation, functionalization), and is thus intended as an introduction for newcomers.

1.2 Structural aspects

1.2.1 Chirality

The structure of CNTs can be understood as sheets of graphene (*i.e.* monolayers of sp^2 hybridized carbon, see Chapter 2) rolled-up into concentric cylinders. This results in the saturation of part of the dangling bonds of graphene and thus in a decrease of potential energy, which counterbalances strain energy induced by curvature and thus stabilizes the CNTs. Further stabilization can be achieved by saturating the dangling bonds at the tips of the tubes so that in most cases CNTs are terminated by fullerene caps. Consequently, the smallest stable fullerene, *i.e.* C₆₀, which is ~ 0.7 nm in diameter, thus determines the diameter of the smallest CNT. The fullerene caps can be opened by chemical and heat treatment, as described in Section 1.5.

CNTs may consist of just one layer (*i.e.* single-walled carbon nanotubes, SWCNTs), two layers (DWCNTs) or many layers (MWCNTs) and per definition exhibit diameters in the range of $0.7 < d < 2$ nm, $1 < d < 3$ nm, and $1.4 < d < 150$ nm, respectively. The length of CNTs depends on the synthesis technique used (Section 1.1.4) and can vary from a few microns to a current world record of a few cm [16]. This amounts to aspect ratios (*i.e.* length/diameter) of up to 10^7 , which are considerably larger than those of high-performance polyethylene (PE, Dyneema). The aspect ratio is a crucial parameter, since it affects, for example, the electrical and mechanical properties of CNT-containing nanocomposites.

The structure of SWCNTs is characterized by the concept of chirality, which essentially describes the way the graphene layer is wrapped and is represented by a pair of indices (n, m) . The integers n and m denote the number of unit vectors (a_1, a_2) along the two directions in the hexagonal crystal lattice of graphene that result in the chiral vector C_n (Fig. 1.1):

$$C_n = na_1 + ma_2.$$

If $m = 0$, the nanotubes are called “zigzag” nanotubes, if $n = m$, the nanotubes are defined as “armchair” nanotubes, and all other orientations are called “chiral”. The deviation of C_n from a_1 is expressed by the inclination angle θ and ranges from 0° (“armchair”) to 30° (“zigzag”) [17].

The lattice vector and thus (n, m) can be also used to calculate the tube diameter following

$$d = \frac{a\sqrt{m^2 + mn + n^2}}{\pi}$$

where $a = 1.42 \times \sqrt{3} \text{ \AA} = 0.246 \text{ nm}$ corresponds to the lattice constant in the graphite sheet (C-C distance for sp^2 hybridized carbon: $1.42 \text{ \AA}$).

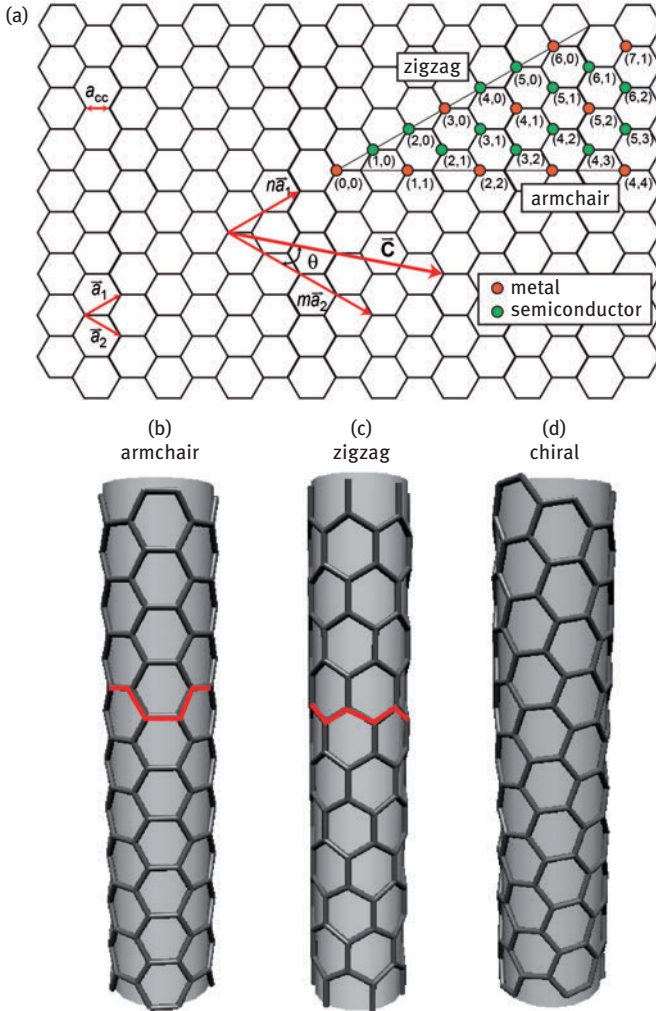


Fig. 1.1: (a) Schematic of unrolled SWCNT showing chiral vector $\vec{C}_n$ and the effect of m and n on the electronic properties of SWCNTs. (b, c, d) The direction of the chiral vector affects the appearance of the nanotube showing (b) (4,4) armchair, (c) (6,0) zigzag and (d) (5,3) exemplary chiral shape. With kind permission from [18].

1.2.2 Defects

Depending on the synthesis procedure (see Section 1.4) and purification methods (Section 1.6.1), the structure of synthesized carbon nanotubes may include a range of defects (see Chapter 4).

“Topological defects” describe the presence of rings other than hexagons, *i.e.* pentagons (n_5) and heptagons (n_7), which result in “kinks” and “elbows” in the usu-

ally planar hexagonal carbon layer. Strictly speaking, the fullerene caps are also topological defects as pentagons are essential for a spherical carbon structure. Pentagons and heptagons further accumulate near other defect sites in CNTs [19]. However, no ring sizes other than pentagons and heptagons have yet been observed [20]. Common occurrences of topological defects are pentagon-heptagon pairs directly connected to each other, which are also called Stone–Wales defects. This particular defect structure is more energetically favorable than other combinations [21]. $n_5 - n_7$ pairs can also be the center for intramolecular and intermolecular junctions, connecting two parts of one CNT with different helicity or two different CNTs [22]. The density of Stone–Wales defects is typically small due to the high activation barrier for the bond rotation (*i.e.* few eV). Stone–Wales defects further affect the absorption and charge transfer characteristics and increase strain energy, which leads to enhanced reactivity (*i.e.* for nucleophilic attack). A related group of defects are dislocations and vacancies. Vacancies can be induced by electron irradiation (*e.g.* by electron microscopy) and are also centers of enhanced chemical reactivity. On the other hand, vacancies can be annihilated in the presence of neighboring pentagon-heptagon pairs via an atomic exchange mechanism [23].

Although a honeycomb lattice theoretically consists of sp^2 atoms, the carbon's ability to represent intermediate states of hybridization leads to another kind of defect to counterbalance the strain energy induced by high curvature. This so-called **rehybridization** results in a higher π -character of the C–C bonds [24]. Furthermore, local sp^3 hybridization can be induced through chemical treatment, such as after thermal elimination of functional groups.

In general, most of these defects considerably affect the electronic, mechanical and chemical properties of CNTs [25]. For instance, the presence of just one carbon vacancy in the outer (*i.e.* load-bearing) carbon layer reduces the CNT's tensile strength by 30 % [26]. Defects are also scattering centers that limit the ballistic transport of electrons. However, structural defects on the outer surface of CNTs can also be beneficial when it comes to hybridizing them with metal oxides or other materials. Defects can serve as reaction centers for functionalization and as nucleation sites for crystal growth, influencing both crystallization (*i.e.* crystal structure, crystal defects) and growth (*i.e.* size, morphology) of the coating material [27–29].

1.2.3 Doping

Another set of defects is created through the introduction of heteroatoms into CNTs, providing an attractive tool for adjusting their electronic characteristics. Heteroatoms can be incorporated in different ways. An early approach [30] was **intercalation** between the walls of MWCNTs. This can be achieved *ex situ* [31–33], *i.e.* processing ready-made MWCNTs (*e.g.* annealing in ammonia), or *in situ*, *i.e.* during CNT synthesis [30].

In the latter case the experimental procedure depends on the synthesis method employed (see Section 1.5).

Alternatively, carbon atoms in the CNT lattice can be substituted for light elements such as nitrogen or boron (“**on-wall doping**”) [34], which again can be achieved *ex situ* or *in situ* (i.e. using nitrogen-containing carbon precursors in a CVD process). *Ex situ* substitutional doping requires the removal of a carbon atom and is thus energetically challenging.

The idea of nitrogen doping of carbon materials has been investigated since the 1960s [35]. In graphitic materials like CNTs, nitrogen can be bonded in two ways [36]: In the graphite-like bonding, only one carbon atom is replaced by a nitrogen atom, being covalently bonded to the three neighboring carbon atoms. The other possibility is the additional existence of a stabilizing defect next to the nitrogen atom, called pyridine type N.

In general, differences in chemical bonding and electron configuration between carbon atoms and dopants mandate the deviation from the geometric and electronic equilibrium structure of the aromatic layers in CNTs. As a consequence, topological defects such as Stone–Wales defects are formed with increased probability [37].

In addition, differences in electron density between carbon and the dopant result in considerably altered electronic properties, because the dopant can either act as an electron donor (e.g. nitrogen) or acceptor (e.g. boron). In the case of graphite-like doping, these electrons are injected into the π system of the graphitic structure, which leads to the desired n-type doping [38]. Pyridine-type N doping may produce n- or p-type behavior, depending on the doping level and the number of carbon vacancies [36].

1.3 Properties of CNTs

CNTs have received tremendous interest from both fundamental and applied research due to their unique physical properties [39]. These properties stem from their aromatic nature as well as the quasi 1D tubular geometry that renders many properties anisotropic. Table 1.1 summarizes the most important properties of CNTs.

1.3.1 Mechanical properties

CNTs are among the world’s strongest materials. The mechanical characteristics of CNTs stand out due to their very high stiffness and tensile strength. The Young’s modulus, i.e. a measure of stiffness and thus of how much a given material deforms upon application of mechanical stress, is about 1 TPa, which is comparable to in-plane graphite [40].

Tensile strength is the maximum mechanical stress that can be applied to a material without breaking it. Values have been calculated that reach up to 800 GPa for SWCNTs [41, 42]. Experimental data are typically significantly lower. Measuring the mechanical properties of individual CNTs constitutes a considerable challenge. The most reliable yet tedious approach is to identify an individual tube on a substrate and connect each end to an AFM tip. Still, the data are often not comparable due to the presence of a random number of structural defects (*i.e.* vacancies), which dramatically affect the strength of the CNT. Pugno *et al.* calculated that the presence of just one defect in the outer wall can reduce the tensile strength of a CNT by one third [7]. Therefore, the experimental data for single MWCNTs range from 15 to 270 GPa [43, 44]. In spite of these large differences, CNTs have the highest tensile strength of all known materials and even the “weakest” of the investigated CNTs are ~ 30 times stronger than steel [43].

1.3.2 Electronic properties

The electronic properties of CNTs are of particular importance for hybrid materials and strongly depend on the structure of the CNTs. Theoretical [45–48] and experimental results [49] reveal that SWCNTs are either metallic or semiconducting depending on diameter and chirality, while MWCNTs are generally metallic (due to band alignment upon interlayer interactions).

Flat single-layer graphene is a zero band-gap semiconductor [50], in which every direction for electron transport is possible. However, when the graphene sheet is rolled up to form a SWCNT, the number of allowed states is limited by quantum confinement in the radial direction [17], *i.e.* the movement of electrons is confined by the periodic boundary condition [51]:

$$C \cdot k = 2\pi q$$

in which C is the circumference of the CNT, k is the wave vector and q is an integer. As mentioned above, the orientation of the wave vector k depends on the (n, m) chirality on the tube. In the case of $|n - m| = 3q$, k passes through a Kpoint in the Brillouin Zone and the CNT is metallic, while for $|n - m| \neq 3q$, no Kpoint will be passed by k and the band structure is characterized by a finite band gap, *i.e.* the CNT is semiconducting (Fig. 1.2). The band gap decreases with increasing diameter of the CNT. However, very small CNTs might show exceptional behavior due to curvature effects [52] which result in a deviation from this classification.

In principle, metallic CNTs are ballistic conductors (*i.e.* electrons move without scattering), which means that the resistance is independent of the nanotube length. In MWCNTs, the conductance is defined by the outermost layer [53]. In general, the ballistic nature of CNTs is affected by the presence of structural defects [54]. Still, experimental values for electric current density are exceptionally high, *i.e.* up to $4 \cdot$

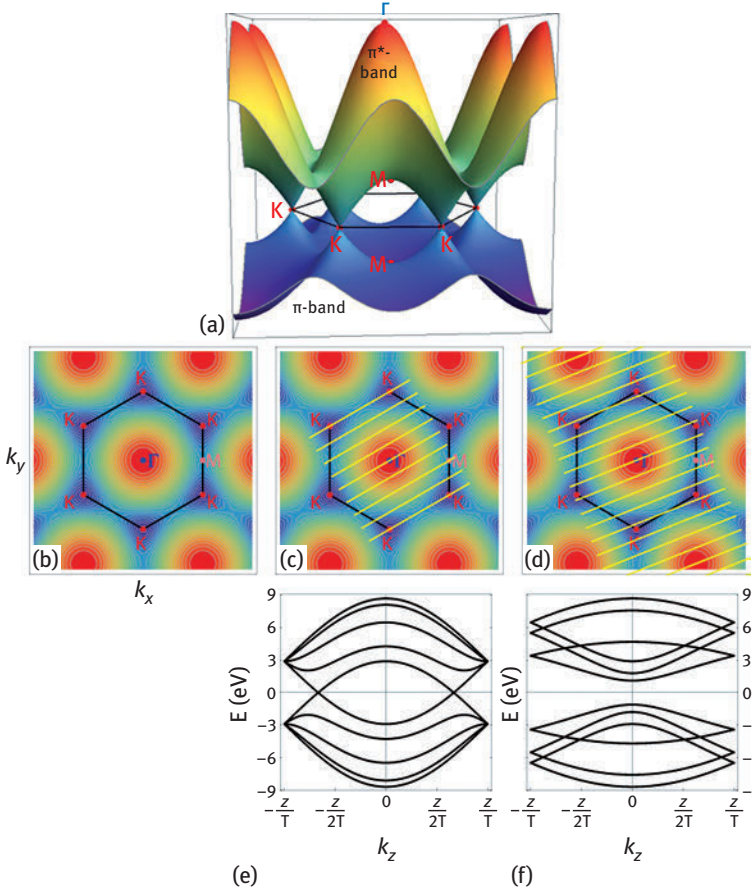


Fig. 1.2: (a), (b), (c), and (d) show the corresponding wave vectors (yellow lines) and K-points (red dots) for structures in reciprocal space, as calculated by the tight binding method, belonging to (a) and (b) graphene, (c) metallic (4,4) SWCNT, (d) semiconducting (5,3) SWCNT, respectively. The blue dots represent energy maxima and the pink points represent saddle (M) points. (e) and (f) represent electronic band structures: (e) shows a (4,4) metallic nanotube where wave vectors cross a K-point and (f) shows a (5,3) semiconducting nanotube where no wave vectors cross a K-point. With kind permission from [18].

10^9 A/cm^2 , which is more than 1000 times greater than in metals such as copper or aluminum [55] and is only outmatched by graphene [56].

1.3.3 Thermal properties

The thermal conductivity of individual SWCNTs was calculated to be as large as $6600 \text{ Wm}^{-1}\text{K}^{-1}$ in axial direction, but only $1.52 \text{ Wm}^{-1}\text{K}^{-1}$ perpendicular to its axis

[57]. Although the experimental values are significantly lower (e.g. $3500 \text{ Wm}^{-1}\text{K}^{-1}$ [58]), thermal conductivity is still roughly ten times that of copper, which is generally considered a material with good thermal conduction.

CNTs also possess a high thermal stability when treated in inert atmosphere (e.g. 2800°C). In air, however, SWCNTs and MWCNTs will oxidize, albeit at comparatively high temperatures ranging between ~ 650 and 750°C , respectively [59]. The presence of defects can to some extent affect the oxidation of CNTs, slightly reducing the oxidation temperature. Furthermore, the oxidation temperature of CNTs can be reduced considerably by the presence of metal oxide particles on the surface of CNTs (such as in nanocarbon-inorganic hybrids), in some cases down to 320°C [60]. This catalytic activity of metal oxides correlates with their reducibility, *i.e.* the feasibility to create an oxygen vacancy, which suggests that the catalytic oxidation of CNTs proceeds via lattice oxygen at the metal oxide-CNT interface, presumably according to the Mars–van Krevelen mechanism.

Tab. 1.1: Properties of CNTs, from [39] with kind permission from ACS Publications.

Property	SWCNTs	MWCNTs	Graphite
Specific gravity	0.8 g/cm^3	$< 1.8 \text{ g/cm}^3$	2.26 g/cm^3
Young's modulus	$\sim 1.4 \text{ TPa}$	$\sim 0.3\text{--}1 \text{ TPa}$	1 TPa (in plane)
Strength	$50\text{--}500 \text{ GPa}$	$15\text{--}60 \text{ GPa}$	
Resistivity	$5\text{--}50 \mu\Omega \text{ cm}$		$50 \mu\Omega \text{ cm}$ (in plane)
Thermal conductivity	$3000 \text{ Wm}^{-1}\text{K}^{-1}$		$3000 \text{ Wm}^{-1}\text{K}^{-1}$ (in plane) $6 \text{ Wm}^{-1}\text{K}^{-1}$ (in plane)
Thermal expansion	Negligible		$-1 \times 10^{-6}\text{K}^{-1}$ (in plane) $29 \times 10^{-6}\text{K}^{-1}$ (c-axis)
Thermal stability	$600\text{--}800^\circ\text{C}$ in air 2800°C in vacuum		

1.4 Characterization

This section provides brief insights on some of the most important characterization techniques used for CNTs and other nanocarbons in addition to microscopy-related (*i.e.* SEM, TEM, AFM, STM) and diffraction (*i.e.* X-ray, electron) techniques.

Raman spectroscopy is one of the most powerful techniques for the characterization of nanocarbons. It is also a convenient technique because it involves almost no sample preparation and leaves the material unharmed. There are four characteristic bands for CNTs: The band at $\sim 200 \text{ cm}^{-1}$ is called radial breathing mode (RBM). It depends on the curvature and can be used to calculate the diameter of SWCNTs [61]. The relatively broad D-band at 1340 cm^{-1} is assigned to sp^2 -related defects and disorder in the graphitic structure of the material. The tangential C–C stretching mode is located at $\sim 1560 \text{ cm}^{-1}$ (G-band). The second order mode of the D-band can be observed (G' -band,

also known as 2D-band) at $2450\text{--}2650\text{ cm}^{-1}$ [62]. The quantity of defects is often evaluated by comparing the I_D/I_G ratio of the D- and G-bands [63]. Information on the chirality of SWCNTs can be obtained by correlating the RBM and the anti-Stokes Raman lines [63].

Information obtained: Diameter of SWCNTs, defects/crystallinity of CNTs, number of layers (if few).

Photoluminescence spectroscopy is used to analyze the electronic properties of semiconducting CNTs [64]. The emission wavelength is particularly sensitive to the tube diameter [65] and chemical defects [66]. However, a more dedicated sample preparation is required in order to eliminate van der Waals and charge transfer interactions between bundled CNTs. This can be done via ultrasonication or treatment of the bundles with surfactants that separate individual CNTs and suppress interactions between them [67].

Information obtained: Chirality of semiconducting SWCNTs (and thus diameter), band gap, bundling.

X-ray photoelectron spectroscopy (XPS) and infrared spectroscopy (FTIR) are used to gather information about the surface properties of CNTs, including functionalization, doping and structural modifications. In a study on SWCNTs, the C1s consisted of signals for sp^2 (2843.0 eV), sp^3 (285.0 eV) and oxygen bonded carbon (288.5 eV). Compared to highly-ordered pyrolytic graphite (HOPG) [68], the C1s peak of CNTs is significantly broadened because of defects and C-H bonds on the surface.

Computational simulations [68] suggest the possibility of identifying 7–8 **infrared**-active vibrational modes that depend on the chiral structure of CNTs. This was supported by experimental infrared spectroscopy [69] of SWCNTs, where features around 1598 and 874 cm^{-1} were found that could be linked to the calculated results.

Information obtained: sp^2/sp^3 level (i.e. defect), functional groups, dopants, chirality.

1.5 Synthesis

The topic of different synthesis techniques is well covered in several text books [70, 71] and review articles [72–74]. Thus, only a very brief introduction on the most important approaches is given here.

1.5.1 Laser ablation

Among the first techniques, applied primarily for SWCNTs, is the vaporization of a mixture of graphite target through ablation using a pulsed [75] or continuous [76] laser. In order to obtain SWCNTs, the graphite target needs to be modified with a metal catalyst (e.g. Co, Ni), the process needs to be carried out in an inert atmosphere (argon/nitrogen) and under reduced pressure (e.g. 650 mbar) and can be optimized by increasing the temperature to about 1200 °C [77]. Interestingly, helium is not used because its low molecular weight results in too high a cooling rate, which negatively affects nanotube formation [78].

Scott and co-workers [79] proposed a mechanism for CNT formation that involves the initial formation of a carbon cloud consisting of short carbon entities (C_1 – C_3) and vaporized catalyst. Upon cooling, the condensation of the catalyst hinders the aggregation of carbon blocks into larger clusters, while supporting the anisotropic addition of carbon units into SWCNTs instead. The deposited SWCNTs are then collected from the cooled chamber walls after the synthesis.

In general, this synthesis approach features a good control over the diameter by adjusting the pressure in the reaction chamber and produces SWCNTs with few structural defects. Disadvantages are the high cost and poor scalability of this method due to the usage of a laser.

1.5.2 Arc discharge

Ablation of graphite through arc discharge constitutes another method that has become popular due to its simplicity. It involves applying an electric field (DC) between two graphite rods in an argon-filled reaction chamber. This stimulates an arc discharge between the graphite electrodes that creates very high local temperatures (~ 4000 °C). As a result, carbon is vaporized from the anode and re-deposited on the cathode, forming MWCNTs [80]. During the process, the anode is moved in order to provide a constant distance between the electrodes (*i.e.* distance of 1 cm). Although this technique is primarily used to produce MWCNTs, SWCNTs can also be obtained in high yields using a catalyst on the cathode or anode (e.g. Co [5] or Ni-Y [81]).

The advantages of this method include the simple experimental setup as well as the possibility to produce CNTs in relatively large quantities. However, it typically produces relatively short CNTs with a wide range of diameters as well as low purity, often producing fullerenes, graphite sheets or amorphous carbon as side products [82].

1.5.3 Molten salt route / electrolytic process

One synthesis approach that does not rely on CNT formation from the gas phase is molten salt synthesis. The reactor consists of a vertically oriented quartz tube that contains two graphite electrodes (*i.e.* anode is also the crucible) and is filled with ionic salts (*e.g.* LiCl or LiBr). An external furnace keeps the temperature at around 600 °C, which leads to the melting of the salt. Upon applying an electric field the ions penetrate and exfoliate the graphite cathode, producing graphene-type sheets that wrap up into CNTs on the cathode surface. Subsequently, the reactor is allowed to cool down, washed with water, and nanocarbon materials are extracted with toluene [83]. This process typically yields 20–30 % MWCNTs of low purity.

This process is very simple and requires low temperatures. However, the MWCNTs predominantly contain a large number of structural defects as well as amorphous carbon impurities. Furthermore, a significant part of the salt remains encapsulated within the CNTs.

1.5.4 Chemical vapor deposition (CVD)

Chemical vapor deposition (CVD) is versatile and currently the most popular method for the synthesis of SWCNTs and MWCNTs as well as other nanocarbons. CVD requires (1) a carbon source (*e.g.* methane, acetylene, toluene, ethanol etc.), (2) a catalyst (*e.g.* Fe, Co, Ni and various alloys), and (3) a suitable energy source (*e.g.* heat, plasma, laser). In the simplest case, *i.e.* the thermal CVD process, the carbon source is injected into a tube reactor along with an inert or reducing feed gas and decomposed at temperatures between 550–1200 °C. The resulting small carbon units then diffuse into the catalyst nanoparticles, which were either pre-deposited on a suitable substrate (*e.g.* silica, alumina) or continuously injected along with the carbon source (*e.g.* ferrocene-toluene solutions [84]). The key requirement for a suitable catalyst is a low solubility of carbon in the metal [71]. When the carbon concentration reaches saturation, carbon atoms segregate to the surface and precipitate in the thermodynamically favored hexagonal structure, still attached to the metal surface via 3d- π interactions [85]. According to the *yarmulke* mechanism [86], the driving force for this precipitation is the compensation of the high surface energy of the catalyst nanoparticles by the very low surface energy of this graphene-type sheet. These layers can act as nucleation sites for the growth of CNTs, which grow as long as carbon atoms are provided via diffusion through the bulk catalyst. In most cases the metal catalyst is pre-deposited onto a substrate such as silica or alumina. Depending on the strength of interaction between the catalyst particles and the support, the CNTs grow either via a base-growth model (*i.e.* metal particles remain attached to the substrate) or a tip-growth mechanism (*i.e.* the particles are lifted off the surface upon CNT growth and remain encapsulated near the CNTs' tips). In general, MWCNTs require the growth of multiple layers on the catalyst

particle and favor larger catalyst particles. In contrast, SWCNTs are primarily produced on small catalyst particles, where the formation of additional layers is energetically restricted by their curvature [87]. The *yarmulke* mechanism further implies that all layers grow simultaneously.

The pre-deposition of catalyst particles enables the growth of vertically aligned CNTs [88] on substrates with positional control of the growth, such as is required for electrical devices for example [89]. In the modification of “continuously feeding the catalyst”, variation of reaction time provides excellent control of the CNT length. Finally, it enables the continuous production of hierarchical nanocarbon assemblies, such as CNT fibers [84], which are macroscopic materials that harness the nanoscopic properties of CNTs and offer great potential for applications (*i.e.* rope, cables, and components in textiles...). In contrast, the CNTs often contain more defects than those produced *e.g.* via laser ablation, while part of the metal catalyst generally remains within the CNT sample, typically encapsulated within the interior walls, and may require post-synthesis purification (see next section). Still, the CVD process is a versatile and scalable technique that renders it the preferred method both for scientific as well as commercial production of high quality CNTs in large yields [90].

1.6 Post-synthesis treatments

1.6.1 Purification

Depending on the synthesis technique, CNTs may contain various impurities, including fullerenes and irregular carbon structures on the surface (*i.e.* amorphous) as well as residual salts and metal catalysts often encapsulated within a carbon shell.

Metal catalyst particles that are not encapsulated or covered by a carbon shell can easily be removed by washing the CNTs in mineral acids such as HCl. If the metal particles are covered by an “amorphous” carbon shell, this acid treatment can be assisted by microwave heating [91]. In contrast, metal particles that are encapsulated within closed CNTs require harsher conditions, such as ultrasonication/heating under reflux in strongly oxidizing acids (*e.g.* $\text{HNO}_3/\text{H}_2\text{SO}_4$), which first open the tubes and then dissolve the metal residues. It further renders the CNTs hydrophilic by incorporating oxygen functionalities, such as carboxylic, epoxy and hydroxyl groups (see Section 1.6.3). This property enables better dispersion in aqueous solutions as well as subsequent hybridization with inorganic compounds into composites and especially hybrid materials. However, apart from being a tedious and nasty chemical process, oxidative acid treatment does not provide sufficient control over the type, number and location of such functional groups (and thus the inorganic coating).

A more gentle approach would be the oxidative treatment in humid air at elevated temperatures [92]. This method selectively removes the amorphous carbon, while keeping the corrosion of the carbon surface to a minimum. The degree of pu-

rification/functionalization is determined by the vapor pressure of water as well as the temperature. In the latter case, the applied temperature must remain well below that of CNT oxidation (*i.e.* 600–700 °C), which strongly depends on the presence of catalytic impurities. For example, the presence of reducible metal oxides attached to the CNT's surface can reduce the oxidation temperature down to values as low as 330 °C [60].

A more sensitive approach to purification is the usage of non-oxidizing heat treatments [39, 93]. The amorphous carbon coating can be easily removed via annealing at ~ 1000 °C in flowing inert atmosphere. The tips of CNTs can be opened and much of the metal residues removed upon raising the temperature to about 1600 °C, depending on the melting point of the metal particles. At even higher temperatures (2000 °C, Ar), graphitization of the CNTs may even lead to an annealing of structural defects [39].

Tab. 1.2: Summary of typical purification techniques for CNTs. ^a Treatment can remove metal catalyst residues. ^b Carbon residues (*e.g.* amorphous or organic aromatic debris). ^c Purification introduces covalently bonded functional groups. ^d Only if not covered with carbon or encapsulated within CNT. ^e Only amorphous carbon around metal particles. From [39] with kind permission from ACS Publications.

	Metals ^a	Carbon ^b	Functional ^c	Comments
Heating in air/O ₂		X	X	opens tips
Heating in wet O ₂		X		
HCl _{conc}	X ^d			assisted with microwave or magnetic field
HNO ₃ /H ₂ SO ₄	X	X	X	open tips, shortens CNTs
Microwave		X ^e		aided by acids (<i>e.g.</i> , HCl)
Ar @ 2000 °C	X	X		anneals crystal structure

1.6.2 Separation of metallic and semiconducting CNTs

As mentioned above, the electronic properties of SWCNTs depend on their chirality and may be semiconducting or metallic. There is still no satisfying way to produce just one sort of SWCNTs, which would require the exact control of catalyst particle size at elevated temperature. Hence, the separation of semiconducting from metallic SWCNTs is of paramount importance for their application in, for example, electric devices, field emission and photovoltaics etc.

Common separation methods can be divided into chemical and physical routes. **Chemical approaches** rely on the interaction of the surface of different CNT types with surfactant molecules. Early work has shown that octadecylamine [94] and agarose gel [95] adsorb preferably on semiconducting SWCNTs, while diazonium reagents [96] and DNA [97, 98] show preference with metallic tubes. The assemblies with adsorbed molecular species are considerably larger and heavier than the indi-

vidual CNTs and can subsequently be separated via standard separation methods like ion exchange, chromatography or microfiltration. With these techniques CNTs can be separated depending on length [99], diameter [97] and chirality [100].

The **physical approach** uses alternating current (ac-) dielectrophoresis to separate metallic and semiconducting SWCNTs in a single step without the need for chemical modifications [101]. The difference in dielectric constant between the two types of SWCNTs results in an opposite movement along an electric field gradient between two electrodes. This leads to the deposition of metallic nanotubes on the microelectrode array, while semiconducting CNTs remain in the solution and are flushed out of the system. Drawbacks of this separation technique are the formation of mixed bundles of CNTs due to insufficient dispersion and difficulties in up-scaling the process [102].

1.6.3 Functionalization

The surface properties of CNTs are paramount for their hybridization with other components. The formation of large bundles due to van der Waals interactions between hydrophobic CNT walls further limits the accessibility of individual tubes. Functionalization of CNTs can enhance their dispersion in aqueous solvent mixtures and provide a means for tailoring the interfacial interactions in hybrid and composite materials. Functionalization techniques can be divided in covalent and non-covalent routes, which will be described in greater detail in Chapter 3.

Covalent functionalization requires the formation of a chemical bond with a surface carbon, which means the disruption of the graphitic structure and thus harsh reaction conditions. The simplest way is the aforementioned ultrasonication in oxidizing acids under elevated temperatures that results in carboxyl- and other oxygenated functionalities [104, 105]. It is very difficult to control the type, amount and exact location of these groups, which typically accumulate near defects and CNT tips due to enhanced reactivity of these sites [106, 107]. However, a great variety of covalent functionalization strategies have been developed over the last few years (see Chapter 3) that provide a wide range of functional groups. SWCNTs have been the focus of research because their high curvature induces enhanced reactivity that allows sidewall functionalization (Fig. 1.3). In contrast, the low reactivity of MWCNTs, *i.e.* essentially as inert as graphite, requires the presence of structural defects for covalent functionalization (Fig. 1.3). Covalent functionalization offers a very stable modification that can withstand high pressure and temperature, convection and sonication and has therefore been realized with aryl diazonium salts [108], azomethine ylides [109], nitrenes [110], and organic radicals [111]. Furthermore, fluorine functionalization [112] has been carried out which allows subsequent interactions with alkyllithium [113] and Grignard [114] reagents or terminal diamines [115]. However, introducing an additional covalent bond induces a change in hybridization towards sp^3 hybridized carbon atoms. Since the outer CNT layer is responsible for a good part of the conductance properties of CNTs

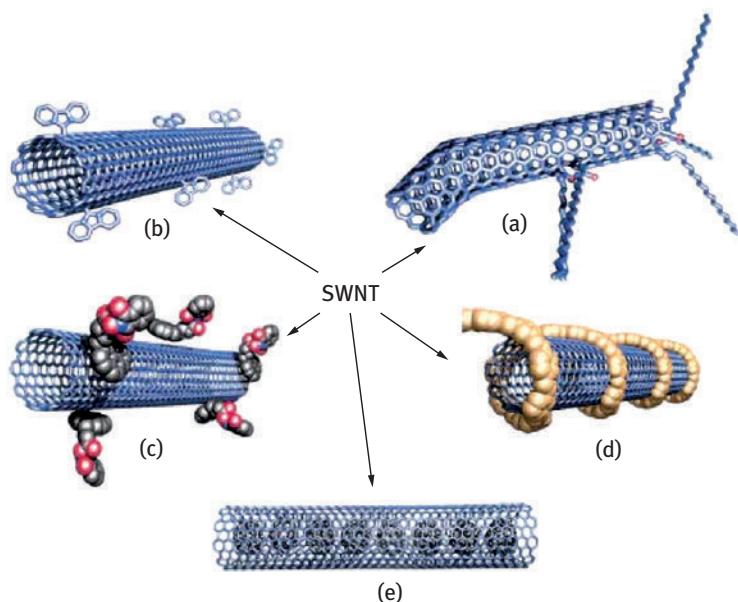


Fig. 1.3: Functionalization pathways for SWNTs: (a) defect-group functionalization, (b) covalent sidewall functionalization, (c) noncovalent exohedral functionalization with surfactants, (d) noncovalent exohedral functionalization with polymers, and (e) endohedral functionalization with, for example, C_{60} . For methods (b)–(e), the tubes are drawn in idealized fashion, but defects are found in real situations. From [103] with kind permission of Wiley.

as well as for their tensile strength (compare Section 1.3.2), covalent functionalization has a considerable, typically negative impact on their properties.

The alternative **noncovalent functionalization** does not rely on chemical bonds but on weaker Coulomb, van der Waals or π - π interactions to connect CNTs to surface-active molecules such as surfactants, aromatics, biomolecules (*e.g.* DNA), polyelectrolytes and polymers. In most cases, this approach is used to improve the dispersion properties of CNTs [116], for example via charge repulsion between micelles of sodium dodecylsulfate [65] adsorbed on the CNT surface or a large solvation shell formed by neutral molecule (*e.g.* polyvinylpyrrolidone) [117] around the CNTs.

One good example of noncovalent functionalization for subsequent hybridization is the use of benzyl alcohol (BA) [118]. π - π interactions between the aromatic ring of BA and the CNT sidewalls result in a good dispersibility in ethanol. Furthermore, BA offers a well-ordered and well-distributed functionalization [119] of hydroxyl groups on the sidewalls of the CNTs that can be used to hybridize the material with a large number of metal oxides using conventional chemical methods [60].

1.6.4 Assembly

The macroscopic design of CNT materials is an important factor regarding possible applications. Due to their anisotropy (see Section 1.3), the respective orientation and ordered structure can strongly affect the macroscopic properties of CNTs. Numerous attempts have been made in this direction, including different kinds of aligned CNTs [120]; CNT carpets [121], films [122, 123] and fibers [124]. Of these, this chapter will only focus on the latter.

In contrast to early post-synthesis attempts of fiber formation [125, 126], a more advanced route produces CNT fibers directly from a CVD oven [84]. It uses a CVD setup with an oxygen-containing carbon source and a catalyst mixture of ferrocene and thiophene. At temperatures around 1150 °C the forming aerogel can be drawn by winding it onto a rotating rod, collecting a continuous flow of fiber onto a spindle. That way, fibers can be wound at speeds up to 100 m/min with strengths beyond 2 GPa/SG, which make them some of the world's strongest fibers [124].

1.7 Summary

Carbon nanotubes comprise a very promising material for various applications and especially as an active component in composites and hybrids as will be documented in the other chapters of this book. Harnessing these nanoscopic assets in a macroscopic material would maximize CNTs' potential and applicability. The choice of synthesis technique and purification method, which define size, type, properties, quality and purity of CNTs as well as their processability, is crucial for their implementation into composites and hybrids.

For example, the exceptional electronic properties of CNTs are most distinct in metallic nanotubes, having a very high conductivity. In a realistic application as photosensitizer, however, a semiconductor is required, which implies further demands on the chiral structure of the CNTs (see Section 1.3.2). The use of a hypothetical CNT-inorganic hybrid with a semiconductor coating on the CNT surface in a dye-sensitized solar cell (DSSC) [127] also implies the need for closed caps. Otherwise, electrolyte could leak inside the nanotube channel, leading to a direct CNT electrolyte interface, and thus, to a short circuit. As a consequence, the need for closed tips reduces the options for surface functionalization, because a harsh acid treatment would also lead to an opening at the tips. One answer to this problem could be the use of CNTs with a defect-rich surface, defects being a possible nucleation point and reactive site for possible coatings. The trade-off for this, however, may be increase electrical resistance caused by the larger amount of defect sites in the CNT walls.

It is still a great challenge to obtain control of the different characteristics and the specific properties of CNTs that restrict their use in commercial real-life applications. However, considering the ongoing progress in research and development on CNTs

and other nanocarbons as well as their hybrids and composites, combined with the steadily increasing industrial production of CNTs, the future of CNTs appears bright and promising.

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2 Synthesis, characterisation and properties of graphene

2.1 Introduction

As a result of its ultra-thin, two-dimensional structure, coupled with its remarkable combination of physical properties, graphene has become one of the most studied nanomaterials of recent times. Combining high mechanical strength and stiffness [1] with electrical conductivity surpassing that of copper, as well as low optical absorption [2] has led to a wide range of possible applications for graphene. These include polymer composite reinforcement [3–6], solar cells [7, 8], transparent conducting films [9, 10], membranes [11, 12] and batteries [13] amongst many others.

2.2 Properties

Graphene has been ascribed a wide range of superlative properties, such as the thinnest, lightest, strongest material known to man. Being only one atomic layer thick, the claim for the thinnest material is perhaps obvious, and this also contributes to its high level of optical transparency. Single-layer graphene absorbs 2.3% of the incident light, a value that can be defined by fundamental constants, $\pi\alpha \approx 2.3\%$ and is almost invariant across the visible range [14]. The electrical properties have been extensively probed [15] with electron mobility of up to $230,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at a carrier density of $2 \times 10^{11} \text{ cm}^{-2}$ for suspended and annealed samples [16]. For samples on a substrate, the mobility is typically an order of magnitude lower due to scattering from the substrate phonons [17]. It should be noted however that these values were obtained at low temperature (5 K) with the highest room temperature mobility having been measured using high- κ dielectric solvents, as $\sim 7 \times 10^4 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ [18].

The combination of low optical absorbance and high electrical conductivity has attracted a lot of interest for transparent conductor applications. When coupled with its flexibility, it is widely seen as a possible replacement for indium-doped tin oxide (ITO), which has a sheet resistance of $\sim 100 \Omega/\text{cm}$ at 90% transparency. By growing graphene on copper foils, sheet resistances of $\sim 125 \Omega/\text{cm}$ at 97.4% transparency have been achieved [19]. This has been improved by combining four layers with doping of the graphene, giving resistance of $\sim 30 \Omega/\text{cm}$ at 90% transparency, all done on 30-inch roll-to-roll production scale.

Indentation testing of suspended graphene flakes has yielded a stiffness of $\sim 1 \text{ TPa}$ for pristine, monolayer graphene, with a strength of $\sim 130 \text{ GPa}$ and strain to break of $\sim 25\%$ [1]. This gives a stiffness to strength ratio of ~ 8 , close to the value of 9 predicted by Griffith [20]. These values are in close agreement with those of bulk graphite

(in-plane) and carbon nanotubes. As for carbon nanotubes, graphene has been incorporated into polymer matrices to provide an enhancement in mechanical properties [21]. For example, incorporating graphene into a polyurethane matrix allowed the properties of the resulting composite to be tuned between thermoplastic-like behavior (low stiffness, low strength, high strain to break) and thermoset-like behavior (high stiffness, high strength but low strain to break) [22]. Indeed, by careful control of the graphene loading, a composite with high stiffness, high strength as well as high strain to break could be produced.

The thermal conductivity of suspended graphene has been calculated by measuring the frequency shift of the G-band in the Raman spectrum with varying laser power. These measurements yielded a value for thermal conductivity of $4840\text{--}5300 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ [23], better than that of SWCNTs, with the exception of crystalline ropes of nanotubes, which gave values up to $5800 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ [24]. Even when deposited on a substrate, the measured thermal conductivity is $\sim 600 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ [25], higher than in commonly used heat dissipation materials such as copper and silver.

2.3 Synthesis

2.3.1 Micromechanical cleavage

Micromechanical cleavage (Fig. 2.1(a)) is a technique that has been used by crystallographers for many years to obtain samples of well-defined crystal faces. In 1999 it was suggested that this method could be used to obtain few, or even single atomic layers of graphite, *i.e.* graphene [26]. In 2005, Geim *et al.* published results showing successful micromechanical cleavage of single layer graphene [27]. This technique involves using sticky-tape to repeatedly peel layers of the crystal from the bulk, eventually reaching single atomic layer thicknesses. As well as graphene, the authors demonstrated exfoliation of several layered materials including MoS_2 , NbSe_2 and BN. The identification of monolayers of these materials was enabled by optical microscopy when deposited on a suitable substrate.

This method is capable of producing large flakes, of high quality, offering the highest mobilities of any production method [28–30], with room temperature values of up to $20\,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ reported [29]. Due to its low throughput it is not a feasible option for large-scale production, but it remains a widely used method for producing good quality graphene for research applications.

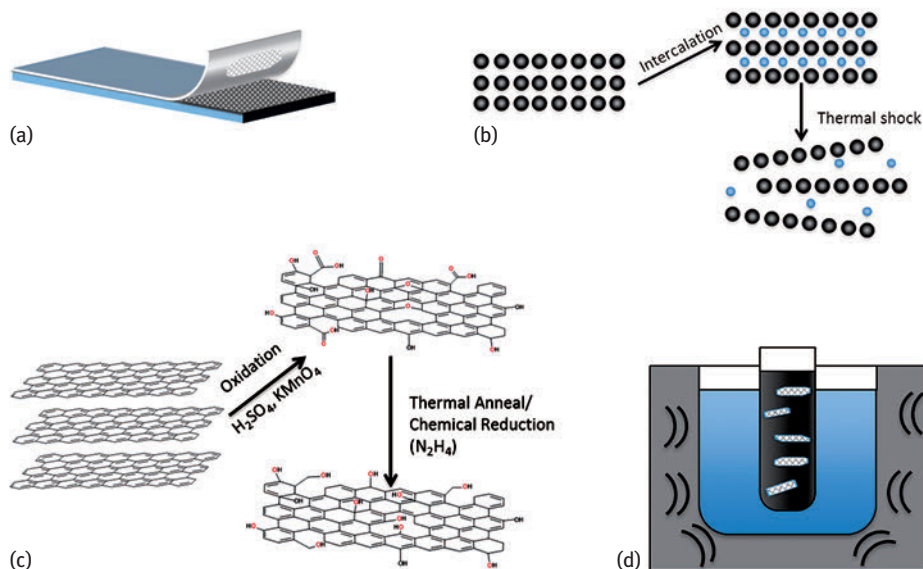


Fig. 2.1: “Top-down” synthesis methods. (a) Micromechanical cleavage; (b) ion intercalation; (c) graphite oxide; (d) liquid-phase exfoliation.

2.3.2 Liquid phase exfoliation

In contrast, exfoliation of graphene in liquid environments offers a route to large-scale production, from simple starting materials. There are various approaches that have been developed to enable effective exfoliation of graphene in liquids.

2.3.2.1 Intercalation

While the interlayer van der Waals bonding is weak in comparison to the in-plane bonds, it nonetheless presents a barrier to exfoliation of graphene from the crystal. One approach to overcoming this barrier is to first weaken these bonds by intercalation (Fig. 2.1(b)). The resulting graphite intercalation compounds (GIC) have a long history [31, 32], and have been studied and used for their own properties (including high conductivity, superconductivity and energy storage) rather than as a route to two-dimensional materials. This approach forces small molecules or ions in-between the layers of carbon atoms in pristine graphite, increasing the interlayer spacing and weakening the van der Waals forces between them. A wide range of compounds have been used as intercalants, including metal fluorides, metal chlorides and alkali metals. The degree of intercalation is described by a “stage” number, indicating the number of carbon layers between intercalation layers, *i.e.* stage 1 compounds have intercalant between every carbon layer, stage 2 compounds have intercalates between ev-

ery second carbon layer. The introduction of these intercalating compounds increases the interlayer spacing by as much as three times [33], and so they offer a good starting point for graphene production [33–36]. With the layer spacing thus increased, and the bonding correspondingly weakened, it is then relatively easy to separate the layers. While this is often described as being spontaneous, in all cases, at least some level of mechanical agitation or mixing is applied [34, 37, 38].

While GICs allow high yield production of graphene [34–36], they have the drawback of often requiring controlled atmospheres for their preparation and storage, as they tend to oxidize in air [32–36], although graphene intercalated with FeCl_3 has been reported to be stable in air for up to one year [39]. This lack of stability, coupled with the additional processing steps involved in their preparation has limited the use of this approach to date as a graphene production method.

2.3.2.2 Graphite oxide

An alternative approach to weakening the interlayer bonding in graphite is to first oxidize the graphite, which was first investigated by Brodie in 1859 [40]. The process involving reaction with potassium chloride (KCl_3) was modified by Staudenmaier to use concentrated sulfuric acid and adding the KCl_3 stepwise during the process, and TEM images published by Ruess and Vogt in 1948 showed single sheets of graphene oxide. These reactions however yield chlorine dioxide (ClO_2) gas, which can explosively decompose into chlorine and oxygen. A safer and quicker method was developed by Hummers that avoided these explosive by-products, using sulfuric acid, sodium nitrate and potassium permanganate [41].

The oxidation reaction (Fig. 2.1(c)) introduces functional groups to both the basal plane (hydroxyl and epoxide) and flake edges (lactone, phenol and quinone) [42–45]. These groups weaken the van der Waals forces between the layers, as well as making the resulting flakes hydrophilic, allowing them to be dispersed easily in water [42, 46] and simple organic solvents [42, 47]. This exfoliation is achieved through either sonication [42, 48], stirring [49] or thermal expansion [50]. While this approach can yield large flakes [51], the functional groups strongly affect the properties of the graphene, in particular the electrical conductivity [10, 52]. The graphene oxide can be chemically [45, 46, 53–55] or thermally [10, 50, 56] reduced, in order to remove the functional groups, and a range of chemistries has been developed to achieve this. The use of alkali solutions has been used since the 1960s [45], and hydrazine [53], hydrides [47, 55], hydroquinone [55] and p-phenylene [54] have all been used. A mechanism involving UV-assisted photocatalysis has also been demonstrated, wherein GO is reduced as it accepts electrons from irradiated TiO_2 nanoparticles [57]. The reduction has also been shown to be possible using a camera flash [58], and focused sunlight [59]. However, none of these methods is able to completely return GO to pristine graphene.

Although the electrical properties of GO are significantly inferior to pristine graphene, the presence of the functional groups on the flakes can be a considerable advantage when considering composites [6].

2.3.2.3 Pristine graphite

Although the weakening of the intersheet bonding through graphite intercalation or graphite oxide allows easier subsequent exfoliation, it is not necessary. Graphene has been successfully exfoliated from pristine graphite without any prior pre-treatments through ultrasonication in solvents [60–63] and aqueous solutions [63–67] (Fig. 2.1(d)). Exfoliation occurs due to hydrodynamic forces associated with cavitation (formation and collapse of bubbles in liquids) during the sonication process [68–70]. These cavitation events can create local temperatures of 5000 K and pressures of several hundred atmospheres, sufficient to overcome the intersheet bonds.

Graphene is most effectively dispersed in solvents in which the interfacial energy between the graphene and the liquid is minimized [71]. If the difference in surface energies is too high (or too low), the graphene flakes will re-aggregate and sediment out of the dispersion. By measuring the concentration of graphene dispersed in a wide range of solvents with varying surface energies, it was found that those with surface energy of $\sim 70 \text{ mJ/m}^2$ are most effective [72, 73]. This is in close agreement with contact angle measurements for the surface energy of graphite ($\sim 62 \text{ mJ/m}^2$). Many solvents with surface energy close to this value (e.g. NMP, DMF, GBL, CHP) have drawbacks with regards to toxicity [74, 75], and all have high boiling points ($> 150^\circ\text{C}$), making removal of solvent difficult. Exfoliation in low boiling point solvents, which also lack the issues of toxicity, has been demonstrated [76], although the concentrations achieved are lower than in surface energy matched solvents.

Stabilization in water (surface tension $\sim 72 \text{ mN/m}$) can be achieved through the use of surfactants [77] such as SDBS [78] or sodium cholate [79], or long chain polymers such as polyvinyl alcohol. While this allows a non-toxic and easily removed solvent to be used, the presence of the surfactant or polymer molecules can be detrimental to the subsequent applications [80].

The yield of these sonication approaches is low ($\sim 1 \text{ wt\%}$ graphene) and the unexfoliated graphite material needs to be separated from the graphene dispersion. Typically this is achieved through centrifugation, which allows a selection of flake sizes by controlling the applied centrifugal force [81]. Furthermore, by recycling the sediment back through the process with fresh solvent, the overall yield can be increased. The use of density gradient centrifugation can also be used to isolate monolayers of graphene [79, 82], where the density of the flake is modified by the surfactant coating, allowing separation. Rate-zonal separation has also been used to produce graphene dispersions with a narrow range of lateral flake sizes [83].

2.3.3 Precipitation from metals/CVD

As well as the “top-down” methods described above, it is also possible to produce graphene with “bottom-up” approaches (Fig. 2.2). Growth of graphite on transition metal surfaces was first described in the 1940s [84], with details of the mechanism described in the 1970s [85]. This synthetic graphite is formed by precipitation of carbon from Co, Ni or Pt annealed at high temperature, with single layer graphene formed as islands on the surface (Fig. 2.2(a)). A similar mechanism leads to the formation of “Kish” graphite from molten iron during steelmaking as the supersaturated iron cools [86, 87]. The solubility of carbon in most metals is only a few wt% and the best graphite growth is obtained from metals that do not form carbides, such as Ni, Cu, Pt and Au [48, 88]. Metals such as Ti, Hf and Zr are not suitable as they form stable carbides [89, 90], as well as having a large lattice mismatch with graphite.

Various techniques have been used to deposit the carbon onto the metal surface, including physical vapor deposition, chemical vapor deposition and flash evaporation. When using a pure carbon source, PVD or flash evaporation is used to deposit the carbon on the surface. The substrate is then heated to allow the carbon to diffuse into the metal as a solid solution. Upon cooling this carbon precipitates out as graphitic layers. The thickness of the graphite film obtained is controlled by the carbon solubility, metal thickness and cooling rate [91]. Careful control of these parameters allows single layer graphene to be grown over large areas [92].

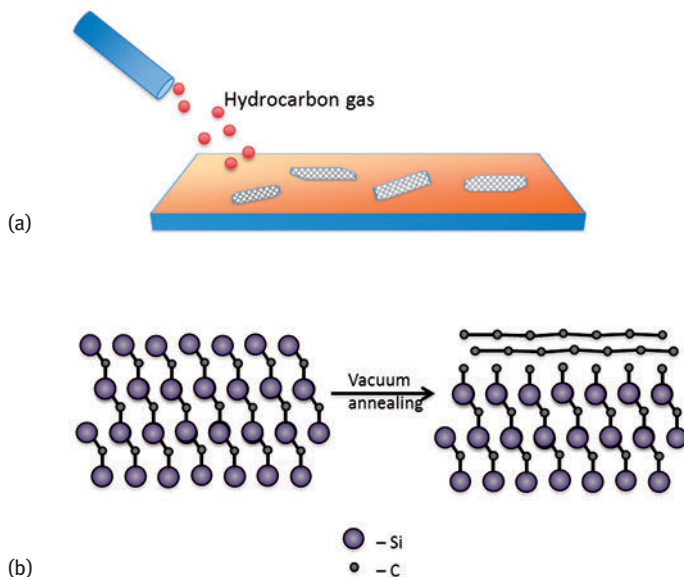


Fig. 2.2: “Bottom-up” synthesis methods. (a) Catalytic vapor deposition; (b) epitaxial growth from SiC.

Chemical vapor deposition is widely used for growing thin films, and has been successfully used to grow graphene, most notably on copper [92]. While it was initially thought that growth on copper was self-limiting to monolayer graphene [88], recent work has shown this not to be the case [93]. Indeed the parameter space for successful growth of good quality graphene on Cu is somewhat small, as a result of low catalytic activity of Cu and relatively low sublimation temperatures. An alternative material is nickel, which has a better catalytic activity, allowing lower growth temperatures, as well as theoretically ideal lattice matching on the {111} crystal faces [94]. For both metals, the growth is controlled by a balance between the flux of carbon onto the surface of the catalyst and the diffusion into the bulk [95]. Growth of graphene layers only occurs on the catalyst surface, and so the second layer grows underneath the initial monolayer, and is proposed to only occur after complete coverage of the monolayer. By control of this carbon flux balance, the carbon concentration in the bulk of the catalyst can be limited, giving very little precipitation upon cooling [95].

Due to the growth mechanism, the resulting graphene film is polycrystalline, with the domain sizes governed by the nucleation rate of the initial islands. This in turn can be controlled by the temperature and pressure in the reaction chamber, with single crystal domains of up to 0.5mm observed. The use of bi-metallic catalyst films has also been demonstrated to reduce the nucleation density of graphene, giving larger final domain sizes [96].

One drawback of both the previous techniques is that most applications most suited to graphene produced in these methods require it to be on an insulating substrate. CVD has been attempted on various insulating substrates, including sapphire [97], quartz, ZrO_2 [98], MgO [99] and Si_3N_4 [100] with some limited success, but much more work is required in this area. Graphene has also been deposited on quartz by spray pyrolysis of sodium ethoxide [101] although characterization of this material has shown it to be highly defective in nature.

2.3.4 Epitaxial growth from SiC

One solution to the problem of an insulating substrate is epitaxial growth from SiC, which goes back to 1896, when graphite was produced for lubrication applications [102]. Silicon is thermally desorbed from the surface of a SiC crystal, and the resulting carbon layer undergoes a surface reconstruction to form graphene [103, 104] (Fig. 2.2(b)). Initially this graphene layer is covalently bonded to the SiC underneath, but can be detached by hydrogen intercalation [105–107]. Furthermore, the process is not self-limiting [104], and further graphene layers will be formed beneath this initial one, with the bottom layer always bonded to the underlying SiC.

Control of the annealing atmosphere [108–110] and choice of SiC face from which Si is desorbed [110, 111] offer some control over the domain sizes. For example, graphene growth is much faster on the C-face than on the Si-face [110, 111], while an-

nealing at near atmospheric pressures yields domains almost 1000 times larger than under UHV [105, 109].

A major drawback to this method is the cost of SiC wafers, which are upwards of 15 times the price of Si wafers. Graphene has been grown from a thin SiC layer deposited on sapphire, but the properties were markedly inferior compared to graphene produced from bulk SiC [112].

2.4 Characterization

The characterization of graphene often involves several techniques in conjunction in order to build up a complete picture of the material. The techniques typically include electron microscopy, Raman spectroscopy, X-ray photo-emission spectroscopy (XPS), Fourier-transform infrared spectroscopy (FTIR) and thermal-gravimetric analysis (TGA).

Electron microscopy can most obviously provide information on the lateral dimensions of the graphene produced. Transmission electron microscopy can also be used to measure the number of atomic layers in a graphene sample. One of the most straightforward methods to assess this is by simply counting the edges visible in transmission electron micrographs. While this is often used, it has a limitation of missing any overlapping edges, and as a result tends to underestimate the number of layers. A more reliable method to confirm monolayer graphene is electron diffraction, comparing the relative intensity between the $\{\bar{2}110\} - \{10\bar{1}0\}$ diffraction spots [113, 114] (Fig. 2.3). For monolayer graphene, the inner, $\{10\bar{1}0\}$ spots have a higher intensity, whereas for bi-layer or more the outer, $\{\bar{2}110\}$ spots have a higher intensity. The effect is more clearly seen if the diffraction pattern is recorded as a function of tilt angle. This approach however can only be used to distinguish between monolayer and multilayer. A more quantitative approach is to use electron energy loss spectroscopy (EELS) to determine the number of layers. The thickness of the graphene layer can be shown to be given by $t = \lambda \ln(I_t/I_0)$ where λ is the mean free path for energy loss, I_0 is the intensity of the filtered image (using the zero-loss peak) and I_t is the total intensity of the (unfiltered) image [115]. By measuring the spectrum from a folded flake, where the number of layers can be confirmed by electron diffraction, a value of λ can be obtained, allowing the number of layers to be determined. It has also been shown that high resolution imaging using an annular dark-field detector in scanning-TEM allows not only structure information such as grain boundaries [116] but also identification of the nature of substitutional defects [117].

While electron microscopy is an invaluable tool for characterization of graphene, it is a costly and often time-consuming technique. In contrast, Raman spectroscopy is a quick and easy method to obtain a wide range of properties of graphene, including flake size, layer number, defect density, and doping levels amongst others [118].

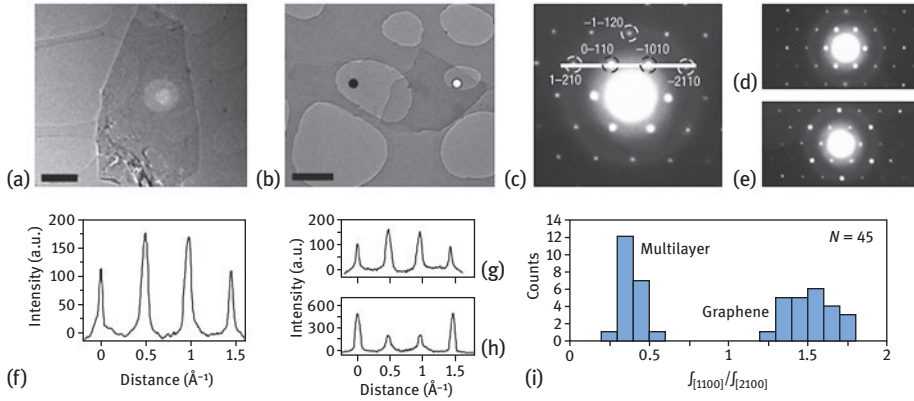


Fig. 2.3: Evidence of monolayer graphene from TEM [72]. (a) and (b) High-resolution TEM images of solution-cast monolayer (a) and bilayer (b) graphene (scale bar 500 nm); (c) electron diffraction pattern of the sheet in (a), with the peaks labeled by Miller-Bravais indices; (d) and (e) electron diffraction patterns taken from the positions of the black (d) and white spots (e), respectively, of the sheet shown in (b), using the same labels as in (c). The graphene is clearly one layer thick in (d) and two layers thick in (e); (f)–(h) Diffracted intensity taken along the $1\bar{2}10$ to $2\bar{1}10$ axis for the patterns shown in (c)–(e), respectively; (i) Histogram of the ratios of the intensity of the 1100 and 2110 diffraction peaks for all the diffraction patterns collected. A ratio > 1 is a signature of graphene.

A typical Raman spectrum for graphene consists of three main peaks of interest, the D-peak at $\sim 1350 \text{ cm}^{-1}$, the G-peak at $\sim 1580 \text{ cm}^{-1}$ and the 2D peak (sometimes called G') at $\sim 2700 \text{ cm}^{-1}$ [119, 120] (Fig. 2.4). While the G-peak, the result of in-plane phonon mode, is present in all graphitic carbon materials, the D-peak, an in-plane “breathing mode” of the 6-membered rings, only becomes Raman active in the presence of defects. The ratio of these two peaks is commonly used as a measure of the defect density of graphite materials, as it is for carbon nanotubes. However, it should be noted that as well as vacancies and sp^3 -type defects, the D-peak is also seen at the edges of graphene sheets [121]. As the intensity of the G-band is proportional to the area sampled ($I(G) \propto L_a^2$) whereas the intensity of the D-band is proportional to the total length of the edge ($I(D) \propto L_a$), the ratio $I(D)/I(G) \propto 1/L_a$, gives an estimate of the flake size or domain size [122, 123]. Therefore, as the size of graphene flakes decreases, the D/G intensity ratio will increase even in the absence of basal plane defects [124]. While this holds for samples with low basal plane defects, it needs to be adjusted for samples with higher point defect densities. For a sample with an average defect separation of L_D probed by a laser with spot size L_L , there will be, on average, $(L_L/L_D)^2$ defects probed, and so $I(D) \propto (L_L/L_D)^2$. The G-band intensity will be proportional to the area probed ($I(G) \propto L_L^2$) and so $I(D)/I(G) \propto 1/L_D^2$ [120]. Due to the origin of the D-band, this picture fails at very high defect density, as the material tends towards amorphous carbon, at which point the D-band intensity begins to fall with increasing defect density [125].

The number of layers, in contrast, can be obtained by examination of the shape of the 2D (also known as the G') peak, which is a second order process of the D-peak, and is always Raman active. While for single layer graphene, this comprises a single peak, with intensity up to 4 times the intensity of the G-peak, 2-layer graphene is fitted by 4 peaks (due to splitting of the electronic band structure [119]). In a similar way, the peak shape varies with increasing layer number until by 5 layers it is almost indistinguishable from that of bulk graphite, with two peaks with intensity $\sim 1/4$ and $1/2$ of the G-peak.

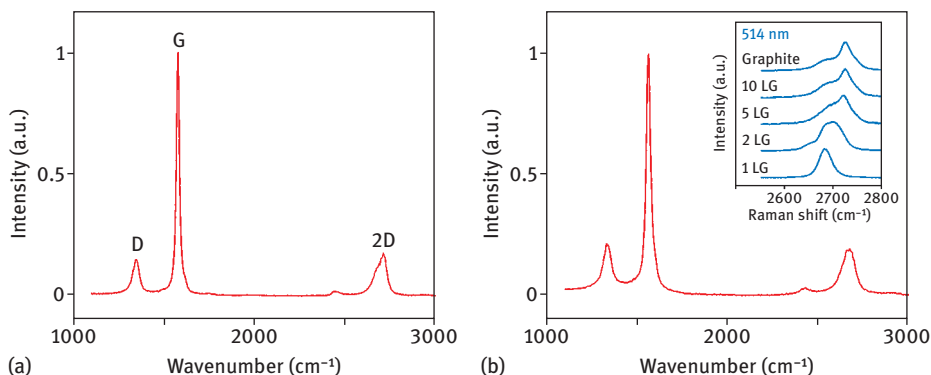


Fig. 2.4: Typical Raman spectra of: (a) graphite, with peaks labeled as discussed in the text; (b) graphene (liquid-phase exfoliated). Inset: Evolution of 2D-band with increasing layer numbers [120].

Further characterization of graphene routinely uses AFM to obtain both the number of layers and lateral sizes of flakes [126]. The presence of residual surfactant on the surface of the flakes needs to be taken into account in order to obtain an accurate measure of layer number [127]. X-ray photo-emission spectroscopy (XPS) is also widely used to characterize any functional groups and defects [128–130], as well as to indicate the presence of residual solvent molecules [129]. Standard chemical analysis techniques are also widely used to identify the nature of any functional groups, as well as the degree of functionalization. Elemental analysis provides a quantitative measure of the C/O/N ratio in the material, though this needs to be combined with a Karl–Fischer titration, due to the hygroscopic nature of functionalized graphene [131]. Fourier-transform infrared (FTIR) spectroscopy is also widely used to characterize the nature of the functional groups [58, 132].

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