NANOSCIENCE AND NANOTECHNOLOGY SERIES



Nanotechnologies and Nanomaterials Applied to Chemical Sensors and Biosensors

Applications to the Environment, Medicine and Health

> Pierre Camille Lacaze Benoît Piro Jean-Christophe Lacroix





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Contents

Port 4 Nonemeterials Amplification Separation	
Recognition and Transduction	1
Chapter 1. Nanomaterials.	3
1.1. Carbon nanomaterials	3
1.1.1. Fullerenes	3
1.1.2. Carbon nanodiamonds (NDs)	6
1.1.3. Carbon quantum dots.	8
1.1.4. Carbon nanotubes	11
1.1.5. Graphene	16
1.1.6. Graphene quantum dots	28
1.2. Inorganic nanomaterials	32
1.2.1. Metal nanoparticles	33
1.2.2. Metal nanoclusters (MNCs)	36
1.2.3. Semiconductor QDs	37
1.2.4. Two-dimensional inorganic lamellar nanosheets	40
1.2.5. Metal organic frameworks (MOFs)	44
1.2.6. Methods for manufacturing MOFs.	45
1.3. Conclusions	49
Chapter 2. Separation and Amplification Techniques	53
2.1. Principle of the PCR technique applied to the concentration amplification of DNA traces	53

vi Nanotechnologies and Nanomaterials Applied to Chemical Sensors and Biosensors

2.2. Sequencing techniques	57
2.3. Separation techniques for product mixtures	61
2.3.1. Chromatography techniques	61
2.3.2. Electrophoresis techniques	65
2.4. Conclusions	87
Chapter 3. Recognition Principles.	89
3.1 The different molecular or chemical identification techniques	90
3.1.1 Ion detection using synthetic ligands	90
3.1.2. Immunological recognition: antibodies, nanobodies	20
and peptides	92
3.1.3. Identification using nucleic acids: antamers	96
3.1.4. Recognition by molecularly imprinted polymers	97
3.1.5. Recognition followed by transformation: enzymes	21
and catalysts	100
3.1.6 Recognition of gaseous species	104
3.2. Sensor networks and artificial intelligence	108
3.2.1. Basic principles	108
3.2.2. Application to chemical sensors	110
3.3. Conclusions.	112
Chapter 4. Physico-chemical Transduction Techniques	115
	110
4.1. Electrochemical methods.	116
4.1.1. Potentiometric analysis	117
4.1.2. Voltametric analysis	118
4.1.3. Impedancemetry	121
4.2. Piezoelectricity for gravimetric analysis.	124
4.2.1. Quartz crystal microbalance	124
4.2.2. Surface acoustic wave sensors	126
4.3. Field effect transistors	128
4.3.1. Operating principle of an FET	128
4.3.2. Main FET devices applied to chemical analysis	130
4.4. Optical and optoelectrochemical detection methods	139
4.4.1. Luminescence of molecules	139
4.4.2. Electrochemiluminescence	142
4.4.3. Photoelectrochemistry	159
4.4.4. Raman scattering spectroscopy	168
4.4.5. Surface- and plasmon-enhanced resonance scattering	170
4.5. Conclusions	178

Part 2. Environmental and Biological Sensors	181
Chapter 5. Ion and Gas Sensors	183
 5.1. Membrane electrodes for potentiometric pH measurement. 5.2. Ion selective electrodes (ISE) 5.2.1. Toward ISEs with very low detection limits 5.2.2. Solid contact ISEs 5.2.3. Conclusions on ISE electrodes 5.3. Gas sensors 5.3.1. Gas sensors based on nanostructured metal oxides 5.3.2. Gas sensors based on conductive polymers 5.3.3. Gas sensors based on two-dimensional thin-film materials 5.3.4. Sensor networks and their use in artificial noses 	184 186 189 191 199 200 200 200 203 208 221
5.4. Conclusions	232
Chapter 6. Biosensors for Health	235
 6.1. Blood sugar, uremia and cholesterol 6.1.1. Blood sugar 6.1.2. Uremia 6.1.3. Cholesterol 6.2. Biomarkers 6.2.1. Cancer biomarkers 6.2.2. Cardiac disease biomarkers 6.2.3. Stress biomarkers 6.3. Pathogens 6.3.1. Virus detection 6.3.2. Toxin detection 6.4. Conclusions 	236 236 246 251 254 256 260 266 275 275 284 286
Conclusion	287
References	289
Index	333

Introduction

The environment, health and the agri-food sector are areas that are subject to very strict regulatory standards with an increasing use of detection and analysis systems (sensors) to carry out the numerous controls and verifications. A sensor is thus a device that measures, continuously where possible, either a physical quantity (temperature, pressure, light intensity, object position, acceleration, etc.) or detects and accurately measures the concentration of a chemical or biological compound present in the surrounding environment.

Long before nanotechnologies emerged, the design of all kinds of chemical sensors was a hot topic in analytical chemistry. The operation of a chemical or biochemical sensor involves a cause and effect relationship between three entities: the compound to be analyzed (analyte)¹, the receptor and a transduction device that transforms the interaction between the analyte and the receptor into a measurable signal, which, depending on the case, can be electrical, electrochemical, optical, thermal or gravimetric (Figure I.1).

One of the oldest commercialized systems is probably the electrochemical detection of glucose in the blood of the human body, initially proposed by Clark and Lyons in 1962 (Clark and Lyons 1962), which carries the greatest number of associated research studies and has seen the greatest technological evolution. This is how various enzymatic or non-enzymatic detection systems subsequently emerged, based on nanomaterials, and were miniaturized and designed as portable systems, making it possible to carry out precise continuous measurements of glucose in the blood (Wang 2008), with a semi-invasive approach (e.g. by insertion of a transcutaneous needle) or by new methods aiming toward non-invasive systems (Chen et al. 2017).

¹ Analyte refers to the chemical entity that we wish to identify and/or quantify.



Figure 1.1. Working principle of a chemical sensor or biosensor Adapted from Chambers et al. (2008). For a color version of this figure, see www.iste.co.uk/lacaze/nanotechnologies.zip

Over the last few decades, numerous increasingly efficient chemical and biological sensors have been manufactured, including receptors made of carbon nanomaterials (carbon nanotubes [CNTs], graphene and carbon nanodots) as well as inorganic nanomaterials (various shaped metal nanoparticles, nanocrystals, nanowires, semiconductor quantum dots [QDs]). The advantages provided by these nanomaterials are significant, particularly when they are involved in the design of systems involving electrical or optical transduction. In the case of graphene and CNTs, their very high conductivity as well as their very high charge mobilities, which are susceptible to significant variations as soon as slight surface modifications occur, make them extremely sensitive receptors. Furthermore, the very high specific surface areas of these materials (~2,600 m²/g for graphene) mean that, in the form of an atomic monolayer, they are capable of adsorbing significant quantities of the compound to be measured and, therefore, of producing a high intensity transduction signal, much better than that obtained with other micron-sized carbonaceous materials.

In parallel with this research, significant efforts have been devoted to the "portability" of very high sensitivity sensors equipped with various transduction systems, with a signal amplification effect based on the development of the sensor in the form of a field-effect transistor (FET). The ultimate design objective is that these sensors have total autonomy in terms of operation based on the capture and transformation of surrounding energy into electrical energy (e.g. self-charging power systems) (Kausar et al. 2014; Pu et al. 2018a).

This book at a glance

Our objective is to analyze the different challenges faced in the design of a sensor and to show what methods are used to, on the one hand, separate the analytes from a mixture and, on the other hand, choose a physical method that gives an intense transduction signal leading to selective detection. This book therefore has two parts: the first is a description of the most common nanomaterials used in the making of sensors and the physical methods to identify and separate these nanomaterials; the second is more applied and describes the different sensors used in the environmental and biomedical fields.

Part 1: nanomaterials, separation, amplification, recognition and transduction

Chapter 1 describes the properties of some of the most important organic and inorganic nanomaterials. We highlight the main contribution of new carbon nanomaterials such as CNTs, graphene, carbon nanodots, conductive polymers in thin layers, but also various forms of inorganic nanomaterials (nanowires, nanotubes and nanosheets), which have allowed enormous progress in the design of portable detection and analysis systems (Kim et al. 2019).

Chapter 2 is devoted to separation methods of compound mixtures and concerns the different chromatography and electrophoresis techniques. Furthermore, DNA amplification techniques necessary for element identification and sequencing, often present only in trace amounts, are also briefly described.

Chapter 3 develops the main analyte–receptor recognition systems, which generally involve pairs of self-assembling molecules, with very high affinities for each other, as observed with the protein pairs avidin–biotin, antibody–antigen, as well as associations between complementary DNA strands.

Chapter 4 describes the characteristics of the main physical methods used to produce a transduction signal, based essentially on the use of electronic, electrochemical, piezoelectric or optoelectronic devices, illustrated using some examples.

Part 2: environmental and biological sensors

Chapter 5 is devoted to chemical sensors specific for environmental issues. It mainly concerns the analysis of mineral salts and gases in terms of toxicology. This is a field that has seen significant developments in ion-selective (membrane and

ionophore) electrodes (ISE), subsequently adapted to the production of all-solid portable devices with, in the latter case, a strong involvement of nanomaterials. The same evolution occurred for the analysis of gases, applied mainly to a few toxic gases.

Chapter 6 focuses primarily on biomedical analysis problems. Innovative solutions are proposed with the contribution of nanomaterials (Lin et al. 2018) being decisive. The real-time control of the primary molecules secreted by the body is a main focal point that we describe in the case of glucose, urea and cholesterol, three key chronic disease-causing molecules. Biomarkers of certain diseases (cancers, heart diseases, etc.), food pathogens, as well as viruses and bacteria are also areas covered, for which portable analysis devices are proving decisive for their effective prevention.

Part 1

Nanomaterials, Amplification, Separation, Recognition and Transduction

Nanomaterials

This chapter¹ is not an exhaustive review of nanomaterials. Its objective is to describe some of the carbon-based and inorganic nanomaterials, frequently used in the design of sensors. Some nanomaterials with opto-electronic properties that have not really been used in the design of sensors but also have specific properties that have led to their application in the biomedical field, in particular in biological imaging, will also be described.

1.1. Carbon nanomaterials

Fullerenes, carbon nanotubes (CNTs), nano-diamonds (NDs) and carbon quantum particles or carbon quantum dots (CQDs) were all discovered before the 2000s, followed by graphene in 2005. Due to their remarkable physicochemical properties, fullerenes, CNTs and graphene (G) have given rise to innumerable applications and their exploitation has remained continuous, but with a much quicker development of G compared to fullerenes and CNTs.

1.1.1. Fullerenes

In 1985, Kroto et al. (1985) discovered Buckminsterfullerene C_{60} (hereinafter referred to as fullerene C_{60}) and revealed its balloon-shaped structure, consisting of an assembly of sp² carbon atoms, organized in the form of pentagons (12) and hexagons (20). Fullerene chemistry then developed and gave rise to a multitude of applications, in fields as diverse as electronics, energy, biology and medicine. Along with C_{60} and C_{70} , the two most stable forms (Figure 1.1), new fullerenes were subsequently synthesized, with more carbon atoms.

¹ This chapter is inspired by one of our previous books entitled *Nanotechnology and Nanomaterials for Energy* (Lacaze and Lacroix 2021). We have reused some illustrations.

1.1.1.1. Electrophilic and antioxidant properties of fullerenes

The electrophilic nature of fullerenes allows the formation of anions with six negative charges, corresponding to the acceptance of six electrons by lower unoccupied molecular orbitals (LUMOs). The progressive electrochemical reduction in six steps of C_{60} and C_{70} shows that the six reduction states of fullerene can be obtained with good stability (Xie et al. 1992) (Figure 1.1).



Figure 1.1. (a) Image of fullerene C_{60} . Adapted from Balch et al. (1998). (b) Voltametric redox curves of C_{60} in solution in an acetonitrile/toluene mixture at low temperature (-10° C). Adapted from Xie et al. (1992). For a color version of this figure, see www.iste.co.uk/lacaze/nanotechnologies.zip

COMMENT ON FIGURE 1.1.— The red and white symbols (a) represent the C atoms in front and behind the projection plane. The reduction curve obtained by a potential sweep from -0.5 to -3.5 V (blue arrow) clearly shows the six reduction peaks, each corresponding to a gain of one electron. The reverse oxidation curve from -3.5 to -0.5 V (red arrow) shows six oxidation peaks, corresponding to the six intermediate and successive anionic states, thus proving the stability and reversibility of these six redox states. Scan rate: 100 mV/s.

This electronic affinity has been exploited in the fields of medicine and biology. C_{60} and its derivatives, functionalized by various hydrophilic groups, have been used in the fight against cancer and AIDS (antiretroviral therapy against HIV-1). Functionalized by carbohydrate chains, they have also proven to be good antibacterial agents. Their high affinity for radicals, a property resulting from radical addition to the many fullerene double bonds, means that they are considered as "radical sponges". They are powerful antioxidants, used in biology to neutralize radical oxygen species (ROS), such as the superoxide ion $O_2^{-\bullet}$, hydroxyls HO[•] or hydrogen peroxide H₂O₂, particularly impressive regarding DNA and certain

proteins. All these properties used for medical purposes have been described in review articles (Bakry et al. 2007; Lalwani and Sitharaman 2013; Acquah et al. 2017; Castro et al. 2017).

1.1.1.2. Chemical reactivity and exofunctionalization

Given their cage-shaped carbon structure, involving only covalent bonds between sp² carbons, fullerenes are naturally hydrophobic and therefore insoluble in aqueous environments. Their use for biological purposes requires transformations to make them hydrophilic, which is achieved by the grafting of hydroxyl groups (COOH or OH), corresponding to exofunctionalization reactions, typically carried out with C₆₀, and some commercially produced fullerenes (C₇₀, C₈₀, etc.), however at high prices, because of the difficulties in producing them in large quantities (Taylor and Walton 1993; Georgakylas et al. 2015).

Among all the products derived from fullerenes, fullerenols and carboxyfullerenes, obtained by grafting hydroxyl or carboxylic groups onto the surface of fullerenes, have the advantage over simple fullerenes in that they are soluble in aqueous and biological media. This is the case of hexacarboxylated fullerenes (carboxyfullerenes), which are fullerenes with three pairs of carboxylic acids, composed of a mixture of two stereoisomers, C3-C₆₀ and D3-C₆₀ (Figure 1.2)².



Figure 1.2. Structure of the two stereoisomeric carboxyfullerenes C3-C₆₀ and D3-C₆₀ as per Dugan et al. (1997). For a color version of this figure, see www.iste.co.uk/lacaze/nanotechnologies.zip

Like simple fullerenes, but with the added advantage of solubility in aqueous media, they have strong antioxidant properties, including the ability to destroy the peroxide ion O_2^{\bullet} , a toxic by-product of cell metabolism. This property makes them very good neuroprotective agents, and research in this area is still ongoing (Dugan et al. 1997; Ali et al. 2004; Gharbi et al. 2005; Ye et al. 2015).

² Both isomers, $C3-C_{60}$ and $D3-C_{60}$, obtained by reacting ethyl 2-bromomalonate with C_{60} in the presence of NaH, belong to different symmetry groups (C3 and D3).

1.1.1.3. Endometallofullerenes (EMFs)

The presence of a cavity allows the encapsulation of chemical species, which is of interest for the design of various markers, used for example in medical imaging. As early as 1985, Smalley et al. identified with mass spectrometry the first fullerene with 60 carbon atoms containing a lanthanum atom (Heath et al. 1985). A few years later, they isolated several metallofullerenes with 60, 70, 74 and 82 carbon atoms, the latter $La@C_{82}^3$ being the only one that is stable in contact with air (Chai et al. 1991).

What is remarkable is that for all these new compounds there is no metal release when the compound is placed in a biological medium, which is a considerable improvement compared to metal chelates. This stability is likely due to the transfer of electrons between the La atom and the fullerene, which leads to the ion pair $La^{3+}@C_{82}^{3-}$, and to the fact that fullerene meshes are small enough that they prevent diffusion of the ion La^{3+} outward.

This discovery, which opened promising prospects in the medical field for diagnostic and therapeutic applications, triggered significant research into the synthesis of new EMFs, with some having applications in cancer therapy. Thus, gadolinium fullerenol $Gd@C_{82}(OH)_{22}$, initially used as a contrast agent in nuclear magnetic resonance imaging (MRI), also turned out to have a strong anti-cancer activity, different from that of simple fullerene, with low cytotoxicity (Kang et al. 2014)⁴.

1.1.2. Carbon nanodiamonds (NDs)

Although known since the 1960s⁵, they only began to be exploited at the end of the 1990s when they were produced by detonation of a mixture of explosive

³ The notation $La@C_{60}$ indicates that the lanthanum atom is inside the cage formed by the fullerene.

⁴ The gadolinium ion (Gd^{3+}) , used as a contrast agent in NMR imaging, has the disadvantage of being very toxic. This toxicity can be greatly reduced when Gd is encapsulated in a hydrophilic fullerene, soluble in biological media, after exo-functionalization by OH or COOH groups of the fullerene molecule.

⁵ First discovered by Danilenko et al. in 1963 and overlooked by the scientific community, they were synthesized a second time in 1982 by another Russian team, during research into the synthesis of diamonds using the detonation technique in a pressurized chamber (Danilenko 2004). Obtained in the form of carbonaceous soot and considered uninteresting by-products, they only really began to interest scientists when they realized their functionalization capacity and areas of exploitation in the biomedical field.

products (trinitrotoluene [TNT] and trinitrobenzene [TNB]) (Greiner et al. 1988). These nanomaterials are now produced commercially. They are used for medical, diagnostic and therapeutic purposes, or to improve the mechanical properties of plastics.

From a mechanical point of view, NDs inherited properties from pure diamonds. They are characterized by their very high hardness and a very high Young's elasticity modulus, making them ideal for use in polishing hard surfaces (ceramics). Their very high chemical stability also allows them to be used in very aggressive environments. Two other particularly interesting properties are their fluorescence and biocompatibility, which make them suitable for biomedical applications (diagnosis and treatment) due to their easy surface functionalization.

Fluorescent nanodiamonds (FNDs) are a new family of nanomaterials, with sizes between 35 and 100 nm (Hsiao et al. 2016) and characterized by the presence of a structural defect inside the crystal (Figure 1.3(a)). This defect, called the nitrogen-vacancy (NV) defect, corresponds to a coupling between a vacancy (absence of a carbon atom in the lattice) and a nitrogen atom, adjacent to the vacancy. It can be easily created by irradiation of NDs crystallites with a helium (He⁺) or proton (H⁺)⁶ ion beam. The processed NDs (equivalent to n-doped NDs) emit stable red fluorescence when excited by a laser. The intensity of the fluorescence depends on the concentration of NVs, which itself is higher the higher the energy of the He⁺ ion beam used for their manufacture (the concentration of NVs can vary between 10 and 30 ppm in relation to the number of carbon atoms; when unprocessed their concentration is less than 1 ppm)⁷.

Their biocompatibility, high stability, absence of toxicity as well as their high fluorescence intensity in the red make them diagnostic tools of choice in biology rather than inorganic quantum dots (QDs), which are most often made up of toxic elements Cd, Se, Pb, etc. (Chambers et al. 2008).

⁶ The sub-micron diamond powders used to make FNDs are obtained at high temperature and high pressure and contain approximately 100 ppm of nitrogen atom impurities dispersed throughout the diamond structure. Under the effect of ion bombardment, vacancies (V) are produced, their migration and their proximity to nitrogen atoms (N) leads to the formation of NVs centers.

⁷ NVs centers can exist in two forms NV° and NV⁻, with NV⁻ dominating. NV⁻ determines the magneto-optical properties due to its different spin numbers $m_s = 0$ and ± 1 . NVs are characterized by a strong absorption band centered at 550 nm and an intense fluorescence band around 685 nm, with a high quantum yield (70%) (Schirhagl et al. 2014).



Figure 1.3. Fluorescence of ND nanocrystals with NV defects. (a) Structure of an NV defect. (b) Fluorescence spectrum of FNDs (size 35 nm) obtained by laser excitation at 532 nm. (c) Differences between the fluorescence lifetimes of an FND (pink) and that of biological tissue (cell) due to the presence of endogenous fluorophores (green). According to Hsiao et al. (2016). For a color version of this figure, see www.iste.co.uk/lacaze/nanotechnologies.zip

COMMENT ON FIGURE 1.3.— An NV defect results from the proximity between a nitrogen atom (impurity due to the preparation of NDs) and a vacancy corresponding to the absence of a carbon atom. The ovals shown in purple (a) correspond to the dangling bonds of the carbon atoms neighboring the vacancy. The rectangle colored in pink (b) represents the spectral operating window for NDs, for which the autofluorescence of a biological tissue (green curve in c) is negligible. The fluorescence of the NDs can thus be detected by imposing a delay of 10 ns between the excitation and the detection of the emission (c).

1.1.3. Carbon quantum dots

Less than 10 nm in size, they comprise a graphitic sp^2 carbon core, corresponding to fragments of graphene or graphene oxide (GO), linked together by sp^3 carbons. They contain significant amounts of oxygen on their surface, mainly as COOH, carbonyls and hydroxyl groups (Lim et al. 2015) (Figure 1.4).

Discovered by chance during the preparation and purification of CNTs (Xu et al. 2004), they quickly generated great interest because of their fluorescence properties, which make them potential biomedical imaging reagents. As with NDs, their non-toxicity is also an additional advantage, favoring their use in the medical field over inorganic QD semiconductors, which are often made with heavy metals.



Figure 1.4. Structure of carbon quantum dots (CQDs) showing the association between graphene oxide and graphene fragments. According to Lim et al. (2015) and Demchenko and Dekaliuk (2013)

Unlike inorganic QDs, for which the absorption is determined by the band gap, CQDs are characterized by a very wide absorption band resulting from plasmonic absorption of the π^8 orbitals. This absorption band covers a large part of the UV-visible spectrum and extends into the near infrared spectrum, thus intercepting a large part of the solar spectrum (Fernando et al. 2015).

Two main emission mechanisms, not always easy to identify, are responsible for the fluorescence of CQDs. The first results from transitions between energy levels of sp^2 carbon bonded domains. The second is less obvious and it involves the surface defects present on the CQDs. A third type of mechanism, corresponding to up-conversion, has also been identified, where an emission is observed in the visible due to an excitation in the red (Figure 1.5).

The photoexcitation of CQDs is said to produce a separation of charges in the carbon cores. Their recombination with surface defects produces fluorescence, which also explains the great diversity of emissions, different from that observed with inorganic semiconductor QDs, characteristic of their band gaps.

One of the most striking characteristics of CQD fluorescence emission is the dependence of the emission spectrum on the excitation source. This has been attributed to different factors, such as the quantum size effect, the defects and surface states present in CQDs, the presence of fluorophores with different conjugation lengths, the radiative recombination of electron-holes due to sp^2 carbon clusters within a sp^3 carbon matrix, each of which are decisive and can contribute to fluorescence (Wang and Hu 2014).

⁸ Plasmonic absorption corresponds to a collective excitation of π electrons delocalized over several benzene cycles.



Figure 1.5. Luminescence of an aqueous solution of CQDs produced by laser ablation of a graphite powder. (a) Absorption (ABS) and luminescence spectra obtained by excitation at different wavelengths (from 400 to 600 nm in 20 nm increments – from left to right). (b) Photographs of the luminescence of solutions of CQDs functionalized with polyethylene glycol (PEG) with a molar mass of 1,500 and comprising two amino groups at its chain ends $-CH_2NH_2$ (PEG_{1500N}). (c) The same solutions of CQDs are directly photographed after excitation at 400, 450 and 694 nm. According to Sun et al. (2006). For a color version of this figure, see www.iste.co.uk/lacaze/nanotechnologies.zip

COMMENT ON FIGURE 1.5.– CQDs (a) are functionalized by poly(propionylethyleneimine-co-ethyleneimine) (PPEI-EI), and the intensities are normalized to the quantum yields. Normalization is performed relative to peak intensity. The photographs in (b) correspond to an excitation at 400 nm of the CQDs and are obtained after passing the emitted light through color filters of 450, 500...690 nm.

The fluorescence quantum yields of most CQDs are typically around 10%; in some cases, however, high yields of around 80% have been observed and seem to be linked to the presence of nitrogen resulting from the precursors used during pyrolysis (citric acid and ethylene diamine) (Zhu et al. 2013).

Finally, for certain CQD preparation conditions, multiphoton absorption was also observed, corresponding to the up-conversion of the emitted photons, which is an essential property for biomedical imaging, where excitation can be produced in the near-infrared spectrum (800–900 nm) with very high penetration of biological tissues (several mm). Such a property was discovered by Sun and colleagues (Cao et al. 2007), with CQDs of sizes of around 5 nm, passivated by a nitrogen-containing polymer (polypropionylimine-co-ethylenimine).

Given the ease of their production and the numerous functionalization possibilities of their surface, the production of various multifunctional probes can be considered. By combining, for example, magnetism and luminescence properties, MRI and fluorescence imaging can be performed simultaneously. Such a result has been demonstrated with the fixation of nuclear resonance contrast agents (gadolinium complexes) on fluorescent CQDs (Bourlinos et al. 2012).

Their solubility in an aqueous medium makes them diagnostic agents and very good vectors for transporting drugs to diseased biological cells. For instance, platinum salt-based anticancer drugs have been bound onto CQDs (Zheng et al. 2014a). Other applications have also been described (Wang and Hu 2014; Hu et al.2019a) and relate to optoelectronics (photovoltaics and electroluminescence), energy and its storage (supercapacitors and electrodes for lithium batteries) and analytical chemistry with the design of various sensors based on optoelectronic phenomena (Molaei 2020; Nazri 2021).

1.1.4. Carbon nanotubes

Iijima (1991) was the first to show the formation of multi-wall carbon nanotubes (MWCNTs) through the electrical discharge between carbon electrodes under a reduced argon-pressurized environment. He thus obtained a mixture of MWCNTs with diameters between 4 and 30 nm, approximately 1 μ m long, made up of two to seven concentric tubes. Single-wall carbon nanotubes (SWCNTs) were obtained shortly after using cobalt-based catalysts (Bethune et al. 1993). These nanotubes have walls with a structure identical to that of graphene, which is made up of an assembly of sp²-hybridized carbon atom monolayers, forming regular hexagons between them.

Since the first productions and characterizations of CNTs, numerous manufacturing and separation techniques have been introduced by several teams and are described in several articles (Grobert 2007; Hersam 2008; Komatsu and Wang 2010; Chen et al. 2014a). Essentially, the vaporization of carbon by laser ablation, the electrical discharge between graphite electrodes, catalytic chemical vapor decomposition (CCVD), the HiPco process (decomposition of CO under high pressure)⁹ and the use of silica nanoparticles doped with Co (Co-MCM 41)¹⁰ are the

⁹ The HiPco (high-pressure carbon monoxide) process was developed in the 1990s at Rice University. It makes it possible to obtain high purity SWCNTs by reacting carbon monoxide mixed with iron pentacarbonyl Fe(CO)₅ at high temperature (900–1,100°C) under a pressure of 30–50 atmospheres. The amount of CNTs produced using this process is around 450 mg per hour and provides a SWCNT mixture with 10 distinct chiralities (Bronikowski et al. 2001).

main CNT manufacturing methods. The choice of catalyst, as well as the carbon precursor fragmentation technique, is crucial. The CCVD technique is the most widespread as it is more likely to produce SWCNTs in large quantities, which is more favorable for production on a commercial scale (Figure 1.6).

The CVD technique typically involves introducing a gaseous carbon source (ethylene, acetylene, toluene, CO, etc.) mixed with a carrier gas (H₂, argon) into a reactor. The gas mixture, heated to a high temperature of at least 600° C corresponding to the decomposition of the carbon precursor, comes into contact with the catalyst (in the form of metal nanoparticles) on which the CNTs will develop.

The old electrochemical route is also the subject of research into the production of large quantities of carbon nanomaterials, such as graphene, carbon fibers, CDs and CNTs. The reduction of CO_2 in the form of molten carbonate is a solution that was recently developed by the Pint group to produce CNTs and has the merit of converting CO_2 into high added value products (Douglas and Pinta 2017).



Figure 1.6. Simplified schematic of the CVD device used to produce CNTs. Adapted from Gore and Sane (2011)

Most manufacturing techniques produce CNT mixtures of multi-walled (MWCNTs) and single-walled nanotubes (SWCNTs) with different architectures, corresponding to distinct chiralities. The improvement of separation methods and the development of new catalysts, making it possible to increase the selectivity in the production of CNTs with a determined configuration or chirality, are important research topics.

¹⁰ MCM-41 is a particular zeolite whose pores can be adjusted between 2 and 10 nm. After depositing a thin layer of cobalt on its internal walls, the zeolite can be used as a nanoreactor to produce SWCNTs (Lim et al. 2003).

1.1.4.1. Chirality of carbon nanotubes

The formation of SWCNTs can be thought of as the result of rolling up a graphene fragment in a particular direction, defined by a C_h vector (Figure 1.7). This C_h vector, known as the chirality vector, is defined by the sum of vectors **a**₁ and **a**₂, forming a 60° angle between them. C_h is equal to n **a**₁ + m **a**₂, and the CNT with a chirality of (n, m) is thus obtained by rolling up the graphene fragment according to the direction of the vector C_h to connect the two ends of the vector. This makes the SWCNT circumference equal to the length of the C_h vector (Bachilo et al. 2002).

This chirality is particularly important because it determines the electrical properties of CNTs and, consequently, their use in fields such as nanoelectronics, photovoltaics, energy storage and sensors.



Figure 1.7. Formation of an SWCNT defined by the rolling up of a graphene fragment along the direction of the chiral vector $C_h = na_1 + ma_2$. Adapted from Wang et al. (2015). For a color version of this figure, see www.iste.co.uk/lacaze/ nanotechnologies.zip

COMMENT ON FIGURE 1.7.– The C_h vector (red arrow) equal to $14a_1 + 4a_2$ corresponds to the formation of an SWCNT with the chirality (14,4). An angle of Θ with respect to the a_1 vector axis defines an SWCNT (4,14) with R-type chirality (rectus), which has the same diameter as S-SWCNT (14,4) (sinister (S) chirality). The blue hexagons correspond to the most common CNT chiralities obtained synthetically with diameters between 0.7 and 2 nm.

For SWCNTs with different chiralities (n,m), two limit forms, Armchair (n,n) and Zigzag (n,0) structures, are important and correspond to Θ angles of 0° and 30° , respectively (Figure 1.8). The Armchair (n,n) configuration has a metal-like conductivity; the Zigzag configuration (n,0) and SWCNTs of chiralities (n,m) also have metal-like conductivities but only when the difference between n and m is a multiple of 3 (Maultzsch et al. 2005) and are semiconductors when it is not the case. Band gaps are less than 1 eV and decrease as the CNT diameter increases (Odom et al. 1998).



Figure 1.8. Examples of CNTs with different configurations. (a) Examples of two SWCNTs (14,0) and (8,8) constructed from a graphene sheet, rolled according to the vectors (14,0) (red) and (8,8) (green) and corresponding to the two Zigzag and Armchair configurations. (b) Images of single-walled (SWCNT), double-walled (DWCNT) and multi-walled (MWCNT) CNTs. Adapted from Schnorr and Swager (2011). For a color version of this figure, see www.iste.co.uk/lacaze/ nanotechnologies.zip

Each configuration (n, m) corresponds to a distinct Raman spectrum and a particular CNT diameter, which allows them to be identified. The frequency of the Raman Radial Breathing Mode band (RBM), corresponding to the radial mode of vibration of the nanotube (ω_{RBM}), is linked to the diameter (d) by the relation:

 $\omega_{RBM} = A/d + B$

A and B are experimentally determined constants (Bachilo et al. 2002; Maultzsch et al. 2005).

1.1.4.2. Some properties and applications of CNTs

The list of their properties is particularly long and well summarized in several review articles (De Volder et al. 2013; Yang et al. 2015; Ferrier 2021; Dai 2022).

CNTs are characterized by their high conductivity due to their metallic character. Wei et al. (2001) showed that MWCNTs could withstand current densities greater than 10^9 A/cm² over 2-week periods at temperatures between 200 and 250°C without observing any CNT degradation or variation in conductivity. CNT semiconductors are also characterized by extremely high electron and hole mobility properties, far beyond silicon, reaching up to 79,000 cm² V⁻¹ s⁻¹ (Dürkop et al. 2004). The band gap widths are inversely proportional to the CNT diameter and are approximately 1 eV for diameters of 1 nm, a value comparable to that of silicon (Kataura et al. 1999).

The thermal conductivity in the axial direction of a CNT is very high $(3,500 \text{ Wm}^{-1} \text{ K}^{-1} \text{ for a SWCNT 2.6 } \mu\text{m}$ in length and 1.7 nm in diameter, while for copper, a very good thermal conductor, it is only 385 Wm⁻¹ K⁻¹; Pop et al. 2006). On the other hand, the thermal conductivity in a radial direction is very low at only 1.52 Wm⁻¹ K⁻¹, almost a thermal insulator in this direction. This difference between the two orientations explains that for films made up of CNT assemblies arranged disorderly, the thermal conductivity is only 1,500 Wm⁻¹ K⁻¹ (Koziol et al. 2017). Note that, under a vacuum, these CNTs resist up to temperatures of 2,800°C and 750°C under an air atmosphere.

Ideal CNT structures lead to exceptional mechanical characteristics, with a tensile strength of 100 GPa (10^{11} Pascal), Young's modulus of 1 TPa (10^{12} Pascal), and an elongation at break of 18%. Such values were obtained with CNTs that were several centimeter long and defect free. The use of CNTs as polymer reinforcement fibers with the production of CNT/polymer composite materials is a key application area that has been the subject of numerous studies (Sun et al. 2013; Chen and Yan 2017a).

Obtaining self-supported films of agglomerated CNTs, leading to a buckypaper structure, coupling very good mechanical and electrical properties, is a commercially available product with numerous potential applications. Note that 6 μ m thick buckypaper sheets can be made simply by vacuum filtration of an MWCNT dispersion; the film obtained has an elastic modulus of 3 GPa and a conductivity of about 2 \times 10⁴ S/cm, a function of the deformation state, which makes it a possible sensor for detecting movements (Degraff et al. 2017).

CNTs are widely used in nanoelectronics, energy, mechanics, biomedicine and sensors. Their use in the production of biosensors has been the subject of recent

research (Ferrier 2021; Dai 2022). Their exceptional properties have made CNTs successful and have encouraged many companies to develop large-scale preparation techniques. Over a few years (between 2004 and 2011), global production of CNTs has increased from 200 kg to 4,500 tons per year, a 22,500-fold increase (De Volder et al. 2013), reaching around 20,000 tons in 2022¹¹. The cost of SWCNTs, however, remains high: it depends on the packaging method and varies depending on the companies that manufacture them. In 2020, the lowest prices were between \$80 and \$100 per kg, and the price of industrial-grade MWCNTs varies between \$200 and \$400 per kg.

1.1.4.3. Conclusion

CNTs are a family of nanomaterials whose strategic importance has continued to grow. Due to their exceptional electrical and mechanical properties, they have given rise to many applications thanks to very broad commercialization. However, obtaining large quantities of highly pure CNTs with a specific chirality is still challenging.

1.1.5. Graphene

Geim et al. were the first to isolate a fragment of graphene by mechanically exfoliating a sheet of graphite. The prepared graphene film is extremely stable, and a range of electrical and mechanical measurements can easily be done¹². Moreover, monolayer of graphene can be easily identified by Raman spectroscopy. A characteristic line (G) appears at 1,584 cm⁻¹, as well as another line (2D or D') close to 2,700 cm⁻¹, whose width increases as the number of graphene layers increases (Ferrari et al. 2006; Graf et al. 2007; Bonaccorso et al. 2010).

The physical, chemical and mechanical properties discovered for graphene were exceptional and it immediately became the "magic" material at beginning of the 21st century. Its unique electrical properties make it a material of choice for electronics and allowed considerable improvements in the performance of various devices used in the fields of electronics, optoelectronics, energy and biomedical analysis. Since the 2010s, graphene-based transistors have been manufactured. However, the fact

¹¹ A 2021 Fortunes Business Insights report forecasts an increase in the global CNTs market from 5.32 to 10.52 billion USD between 2021 and 2028, representing a CAGR of 10.2% for this period (ID: 5685490).

¹² The technique may seem simple but, in fact, the graphene sheet deposited on a Si substrate covered with a thin layer of SiO₂ only becomes visible if an optical contrast occurs between the silica and the graphene. This implies that the thickness of the silica layer must be comparable with that of the graphene sheet. Geim and Novoselov (Nobel Prize in Physics in 2010) recognized that it was a fortunate combination of circumstances that allowed them to highlight the graphene monolayer (Geim and Novoselov 2007).