STRUCTURAL AND ELECTRONIC PROPERTIES OF BN-DOPED CARBON NANOMATERIALS OBTAINED BY DENSITY FUNCTIONAL CALCULATIONS

INTRODUCTION

Single wall carbon nanotube has been emerged as of great interest due to variety of fascinating properties in many areas of modern technology, e.g., their field emission, electronic transport, high mechanical strength, and chemical properties. With 100 times the tensile strength of steel, thermal conductivity better than all but the purest diamond, and electrical conductivity similar to copper, but with the ability to carry much higher currents, they are very interesting. CNTs include both single-walled and multi-walled structures (Fig. 1). Singlewall CNTs (SWCNTs) (Fig. 1A) comprise of a cylindrical graphite sheet of nanoscale diameter capped by hemispherical ends. The closure of the cylinder is the result of pentagon inclusion in the hexagonal carbon network of the nanotube walls during the growth process. SWCNTs have diameters typically 1 nm with the smallest diameter reported to date of 0.4 nm. This corresponds to the theoretically predicted lower limit for stable SWCNT formation based on consideration of the stress energy built into the cylindrical structure of the SWCNT. The multi-wall CNTs (MWCNTs) (Fig. 1B) comprise several to tens of incommensurate concentric cylinders of these graphitic shells with a layer spacing of 0.3–0.4 nm. MWCNTs tend to have diameters in the range 2–100 nm. The MWCNT can be considered as a mesoscale graphite system, whereas the SWCNT is truly a single large molecule.

An infinitely long SWCNT can be imagined as a rolled up piece of a graphene sheet (two-dimensional graphite plane), in other words a cylinder, formed by wrapping up a regular hexagonal lattice. The rolling up of the honeycomb lattice is characterized by the wrapping (chiral) vector ($\bar{C}_h$), connecting two carbon atoms of the graphene sheet which coincide after folding. Each SWCNT is uniquely given by the two chiral indices, *n* and *m* ($n \geq m$), which are the two integer coefficients in the expression of the chiral vector in terms of the primitive vectors of the hexagonal lattice: $\vec{C}_h = n \cdot \vec{a}_1 + m \cdot \vec{a}_2$. The directions of the inequivalent wrapping vectors fall within a 30° region (see Figure 2). The borderline cases are the zigzag ($m = 0$) and the armchair ($n = m$) tubes. The remaining cases are the chiral tubes.

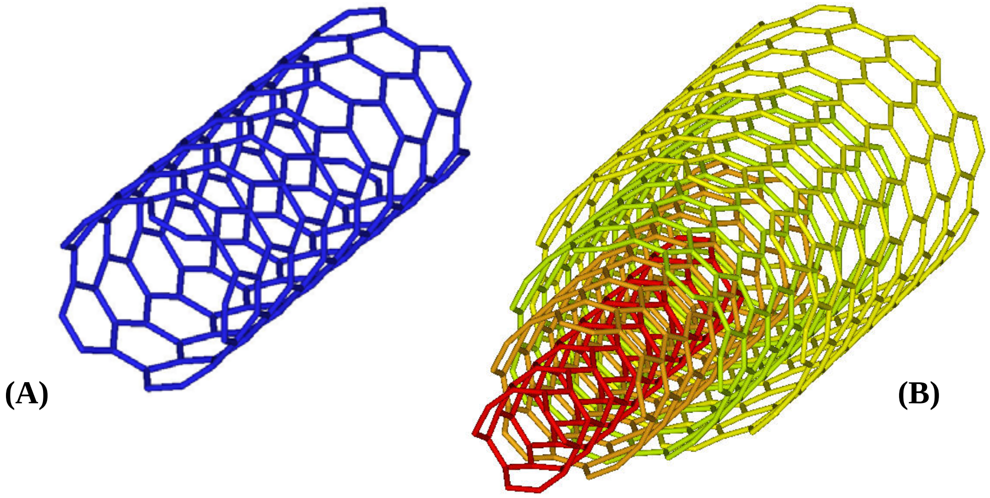

Figure 1 Schematics of an individual (A) SWCNT and (B) MWCNT.

In general, the properties of nanotubes with large enough diameters can be described by the ‘graphene folding’ approximation; we call this the ideal behaviour. However, deviations from the ideal behaviour can be expected for small diameters (large curvatures) where the discreteness of the atoms cannot be neglected. The accurate theoretical investigation of the tubes with small diameters has become important recently, because such tubes have been produced by several methods.

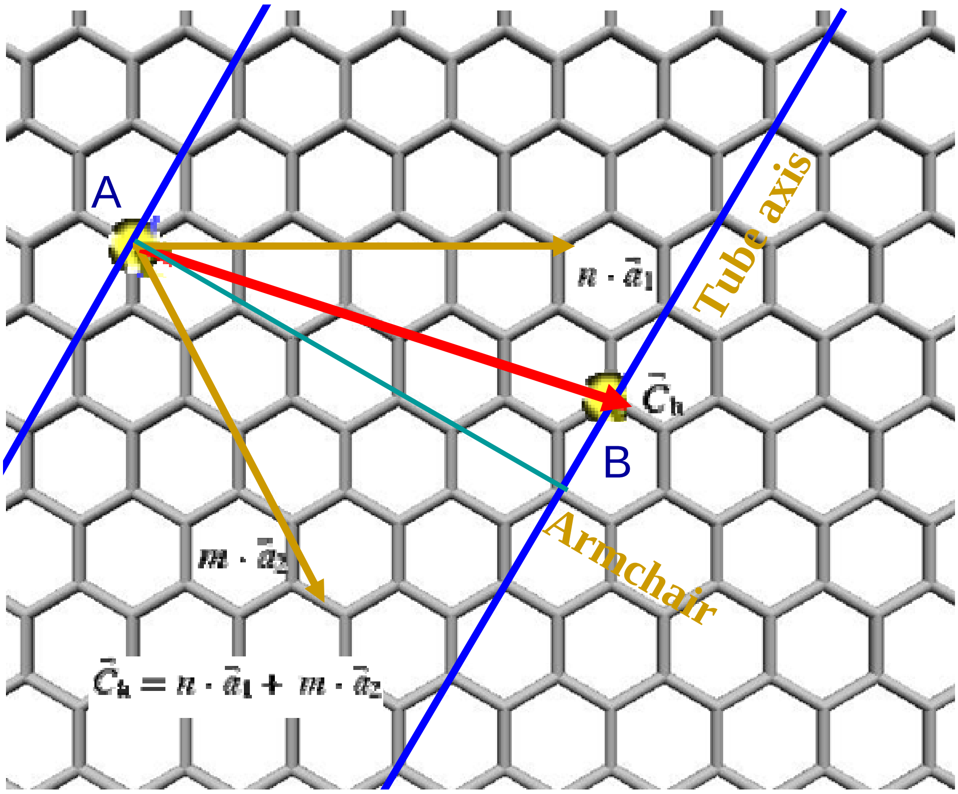

Figure 2 Determination of the chiral vector

Three different methods are now well established for the production of SWCNTs (see Table 1). Among these, the catalytic decomposition of a gaseous carbon feedstock offers the highest production rate (≈50 kgday $^{-1}$). However, despite the remarkable progress made in the synthesis methods during the last 3 – 4 years, the costs are still too high for large-scale applications of the nanotubes. The raw material usually contains amorphous carbon, fullerenes, and catalytic metal particles (e.g., Co or Ni) as impurities.

Table 1 Overview of the important synthesis procedures for single-walled carbon nanotubes.

Synthesis method	Principle	Average diameter of the tubes	Maximum production rate
Electric arc-discharge	Carbon atoms are generated through an electric arc discharge at T> 3000 °C between two graphite rods. Nanotubes are formed in the presence of suitable catalyst metal particle (Fe, Co or Ni).	1.3-1.4 nm	120 g day $^{-1}$
Laser ablation	Generation of atomic carbon at T > 3000 °C through laser irradiation of graphite, which contains appropriate catalyst particles (Fe, Co or Ni), is followed by formation of nanotube.	1.4 nm	50 g day $^{-1}$
Catalytic decomposition of gaseous hydro-carbons	Decomposition of a gaseous hydrocarbon source (e.g., an alkane or CO) is catalyzed by metal nanopartical (Co or Fe). Particles are prepared by pyrolysis of suitable precursor (e.g., [Fe(CO)$_5$]) at 1000-1100 °C under high pressure.	1 nm	50 kg day $^{-1}$

Since the emergence of carbon nanotubes, their electrical properties have attracted particular interest. According to the zone-folding approach, which derives the electronic structure of nanotubes directly from graphite, a nanotube behaves either as a metal or as a semiconductor, depending on its chiral vector. Within a sample showing no preference for specific chiralities, one third of the tubes are expected to be metallic, and the remaining two thirds to be semiconducting. Furthermore, the bandgap in semiconducting tubes is predicted to scale inversely with their diameter. Both of these predictions have been verified through numerous experimental results. Marked deviations from the zone-folding scheme are encountered only for SWCNTs that have the smallest diameters ($\leq$0.5 nm).

On top of their excellent electrical properties, carbon nanotubes possess high mechanical and chemical stability. While the latter is certainly advantageous from an application point of view, this attribute also imposes a severe hurdle for the development of methods allowing for the selective and controlled covalent functionalization of the nanotubes. This explains why it was only within the past 3– 4 years that a wider range of reliable functionalization schemes have become available.

Their ultrahigh surface-to-volume ratio makes CNTs highly suited for investigating fundamental aspects of gas adsorption. For instance, the interior region of nanotubes offers a deep well for physical adsorption, which provides an ideal example of a micro-porous material. In particular, nanotubes represent an optimal testing ground for theoretical predictions on adsorption mechanisms within 1D matter, for which only a few physical realisations exist. Moreover, the fact that all carbon atoms of the SWCNT are exposed to the surface imparts a high sensitivity of its electronic properties against binding of atoms or molecules, whereby promising perspectives for sensor applications are opened. While in the pioneering studies on SWCNT functionalization via sidewall additions, functionalization degrees of only a few percentages were reported, values exceeding 10% are attainable through the more recently developed procedures. As the amount of detects in SWCNTs is also at the few percent level (Mawhinney *et al.*, 2000), it appears plausible that in the initial experiments, the covalent linkages were mostly restricted to the sidewall defects such as Stone–Wales defect, vacancies, dopant and boron-nitride substitution.

Furthermore, appropriate chemical functionalization could make significant contributions towards the hierarchical assembly of nanotubes into ordered functional architectures. The exceptional electrical characteristics of CNTs, doubts have arisen concerning their real technological applicability in ultra-small electrical devices, which is largely due to the fact that the controlled synthesis of one specific type of tubes is hard to achieve. Furthermore, no reliable method is currently available to produce extended ensembles of aligned nanotubes, in which each tube would be located at a desired location and connected to its neighbours in a well-defined manner. Nonetheless, recent advances in linking specific groups or molecules to the nanotubes clearly testify the strong potential of chemical functionalization not only for tuning the tubes' electronic properties, but also to enable their assembly into more-complex architectures required for integrated device operation. Chemical functionalization furthermore imparts increased solubility to the nanotubes, thus opening new perspectives for solution-based chemical transformations and spectroscopy. The fast progress made in these directions has led to the prediction that the field of nanotube chemistry will successfully rival that of the fullerenes. One intriguing example is a specifically designed amphiphilic peptide which enables SWCNT to self-assemble into fibers containing nanotubes aligned along the fiber axis (Dalton *et al.*, 2004). This approach represents a promising alternative to methods that involve tube alignment during the growth (Wang *et al.*, 2004). Finally, several potential biomedical applications are emerging for functionalized SWCNTs, including their use as scaffold for the directed growth of neuron cells (Lu *et al.*, 2004).

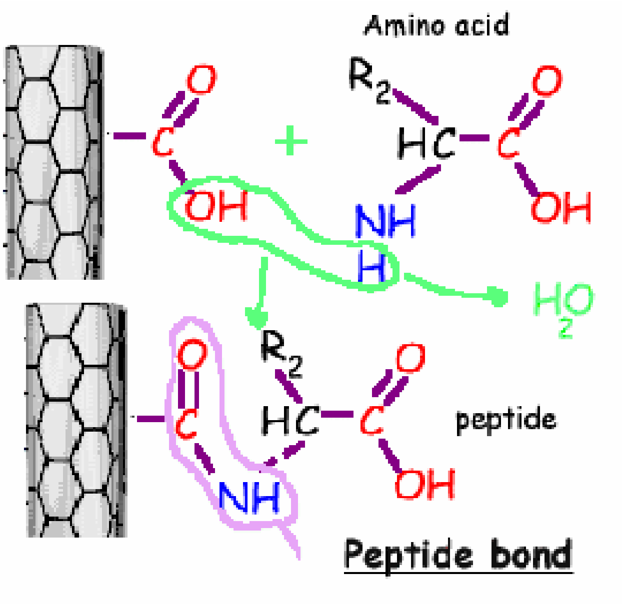

Figure 3 Peptide formation from the reaction of between amino acid and carboxylic acid attached on side-SWCNTs

One of the most important applications of CNTs in analytical chemistry is that in the sensor field. Carbon nanotubes combine in a unique way high electrical conductivity, high chemical stability and extremely high mechanical strength. These special properties of both single-wall (SW) and multi-wall (MW) CNTs have attracted the interest of many researchers in the field of electrochemical sensors. The relevant sensing mechanics are attributed to the sensitive conductance change of SWCNTs caused by charge transfer between SWCNTs and adsorbed molecules (Peng and Cho, 2003). As found in experiments, these adsorbed molecules affect the electronic transport properties of SWCNTs via physisorption or chemisorption. However, it is a pity that some biomolecules can not be detected by intrinsic CNT devices (Goldoni *et al.*, 2003), since they can not be adsorbed on the surface of SWCNTs. So considerable experimental and theoretical works have focused on improving the sensing performance of SWCNTs to various desired molecules by doping or functionalizing CNTs (Bekyarova *et al.*, 2004; Fagan *et al.*, 2003; Kong *et al.*, 2001; Lu and Pan, 2004; Peng and Cho, 2003; Wei *et al.*, 2004).

During the past few years, several methods for the covalent functionalization of SWCNTs have been established that allow to persistently anchor atoms or molecules to the carbon framework of the tubes. The intact sidewall, where the curvature is considerably smaller than at the caps, and hence strain relief offers a smaller driving force for the formation of tetragonal carbons. As a consequence, sidewall functionalization in general requires quite ‘‘hot’’ addends.

The electronic, chemical and mechanical properties of CNTs can be tailored by replacing some of the carbon (C) atoms with either boron (B) or nitrogen (N). If B (has one electron less compared with C) or N (one electron more than C) replaces some C atoms, a p or n type conductor can be formed respectively. From the chemical point of view these doped structures would be more likely to react with donor or acceptor type molecules depending on the doping. The B or N doped CNT can be obtained by arc method by arching either B- or N-graphite electrodes in an inert atmosphere as described previously. Laser (Lu *et al.*, 2003) and CVD (Terrones *et al.*, 1997) methods have been also used for their production. Although not reported up to date for electrochemical sensing systems, B and N doped CNTs were attentively investigated in this work.

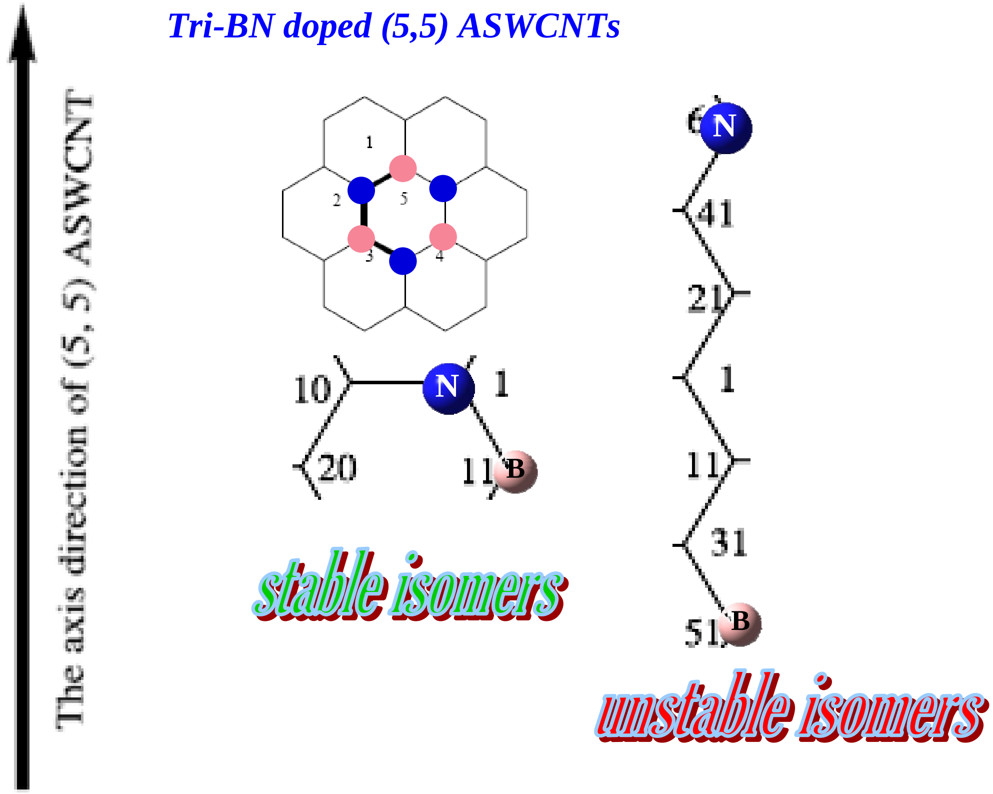

Figure 4 Positions of mono & tri BN-substitution on side-wall (5,5) armchair SWCNTs

The modifications of SWCNT have also been widely investigated to improve their electronic, chemical and mechanical properties. For instance, doping of other elements into SWCNT is one such alternatives. Boron-, nitrogen-, and boron nitride-doped carbon nanotubes have been shown their unique properties. B-doped and N-doped nanotubes correspond to p-type and n-types doping, respectively, give rise novel electron transport properties for such systems. BN-doped carbon nanotube that is isoelectronic to its original carbon nanotube, it exhibits many novel electronic, mechanic, conductive and optical properties, thus, by increasing potential applications in many fields, such as electronic devices, electronic sensors. Many efforts on investigations of BN-doped SWCNT have been reported in the literature. For example, Zhang *et al.* the systematically study on the isomers of BN-doped on (5,5) armchair carbon nanotube and found that the BN-doping increase the redox and electron excitation properties of BN-doped SWCNT system compared to the undoped

SWCNT system. Moradian and Azadi investigated the BN-doped on (10,0) zigzag SWCNT using DFT calculation and they found that the energy gap of the system can be controlled by numbers of boron and nitrogen concentration, giving smaller energy gap while increasing number of either boron or nitrogen into SWCNT. Moreover, they suggested that BN-doped SWCNT could be a potential candidate for making nanoelectronic devices.

From the chemical point of view, BN-doped SWCNT especially at the boron doped position would be expected to react with molecules consisted of electron donor group. Thus, in this study (Chapter I), we characterize the attachment of BN-doped SWCNT by the interactions between BN-doped SWCNT with a variety of nitrogen nucleophilic groups. The binding energies, structural geometries and electronic properties, *i.e.*, energy gaps, charge redistribution and densities of states (DOS) are reported. Moreover, the electron-donating property was also presented to clarify the nucleophilic strength by pK_a of all Lewis bases molecules in term of the binding energy.

In Chapter I, we focused on the electronic properties of attachment between BN-doped carbon nanomaterials and N-nucleophiles obtained by density functional theory. The results of pyridine complexed with BN-doped (5,5)SWCNT indicated that this complex are stable and exhibits metallic character effecting the energy gap decreased. Thus, in chapter II, we used the pyridine-like molecules with two active sites for improvement of electronic properties and charge transfer between each fullerene. We proposed the possibilities to modify the electronic communication between two BN-doped fullerene ($C_{58}BN$) frameworks with bridging heterocyclic compounds.

The electronic properties of several fullerene derivatives have been attracted considerable research interests due to their various properties (Zhou *et al.*, 2005). For instance, the bisfullerene compound, consisting of two fullerene centers, is one such system in the study of electronic communication between two C_{60} active centers due to their practical abilities in future optical and electronic applications. Several efforts have been devoted to explore such electronic communication by introducing various linkage species between two C_{60} centers (see ref (Balch *et al.*, 1996; Basiuk *et al.*, 2004; Dragoe *et al.*, 2000; Dragoe *et al.*, 2001; Fujiwara and Komatsu, 2002) for examples). It was found that no electronic communication has been observed for the organic-based bisfullerenes in which the large spacer between C_{60} moieties (Balch *et al.*, 1996; Dragoe *et al.*, 2000; Dragoe *et al.*, 2001; Fujiwara and Komatsu, 2002). Since the weak interactions for bisfullerene compounds might be occurred due to the less active of C_{60} itself, thus, the modifications of fullerene structure have also been introduced in which some carbons are replaced by heteroatoms, referred to as heterofullerenes. Heterofullerenes have been intensively studied to adapt electronics properties of fullerenes by which the existence of heteroatoms, i.e., B, N and BN (Vostrowsky and Hirsch, 2006). One such of common system studied is BN-doped fullerene ($C_{58}BN$). Even $C_{58}BN$ system remains the isoelectronic properties as behaved in fullerene, it has been found that the BN heteroatoms play vital role in the electronic property improvement by reducing the energy gap by ~0.2 eV (Pattanayak *et al.*, 2002; , 2003) compared to the fullerene system. As a result, the presence of BN in fullerene centers might help to promote electronic communication between two $C_{58}BN$ cages with some appropriate linkage compound species.

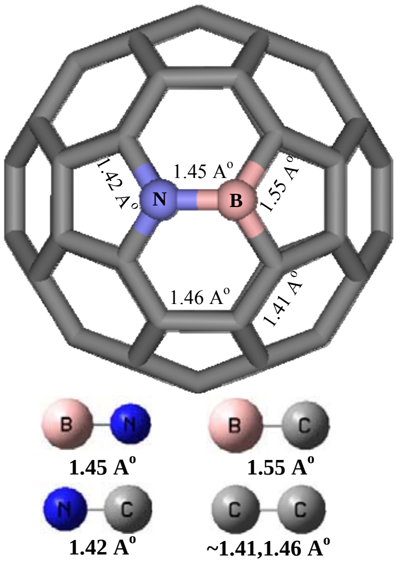

Figure 5 Geometry of BN-doped fullerene

LITERATURE REVIEW

Since the discovery of carbon nanotubes (CNTs) by Iijima (1991), carbon nanotubes (CNTs) have generated great interest in future applications based on their field emission and electronic transport properties (Ceulemans *et al.*, 2004), their high mechanical strength and their chemical properties. There is increasing potential for CNTs to be used as field emission devices (Bonard *et al.*, 2001), nanoscale transistors (Martel *et al.*, 1998), tips for scanning microscopy (Dai *et al.*, 1996) or components for composite materials (Shaffer *et al.*, 1998). CNTs are one of the most commonly used building blocks of nanotechnology.

Carbon nanotubes possess extraordinarily high tensile strength, which outreaches that of a steel wire of corresponding thickness by around one order of magnitude. This attribute combined with their high length-to-diameter ratio and low density (one-sixth that of steel) makes CNTs valuable components for mechanically reinforced composite materials. A critical issue here is the attainment of good adhesion between the matrix and the individual tubes, which is required for an effective transfer of the mechanical load onto the nanotubes. To this end, covalent coupling between the matrix and the nanotubes is currently under extensive investigation. An optimal density of covalently bonded groups on the nanotubes would ensure that sufficient linkages to the matrix are provided without impeding too much the mechanical stability of the nanotubes. A promising approach for the reinforcement of organic polymers comprises of polymer synthesis from covalently attached initiator sites. In this manner, the radical polymerization of methacrylate esters on the nanotubes has been realized. This flexible “grafting-from” approach has recently been extended to ring-opening metathesis polymerization reactions, in which SWCNTs were functionalized with rutheniumbased catalysts.

The successive discoveries of fullerenes (Kroto *et al.*, 1985) and carbon nanotubes (CNTs) around 1990 triggered a hot wave of scientific research to explore the properties and applications of these new forms of carbonous materials over the past two decades. Differing from the two long-known allotropes of carbon, i.e., diamond and graphite, fullerenes and carbon nanotubes have displayed brand-new, unique, and fascinating structural, electronic, mechanic, and optical properties and should find their power in a wide variety of applications. Some of their unique properties can be related to the curved π-conjugation within their curved hexagonal (for CNTs) or hybrid hexagon-pentagon (for fullerenes) carbon-carbon networks. The curved π-conjugation and aromaticity, as well as the related chemistry of fullerene and its larger homologues have been the subject of several review articles. Herein we review recent studies on the curved π-conjugation within small fullerenes (<C60) and single-walled carbon nanotubes (SWCNTs) as well as their unusual chemical properties that are related to their curved π-conjugation and aromaticity.

Fullerenes are convex carbon cages comprising hexagons and pentagons. This building principle follows Euler's Theorem stating that exactly 12 pentagons must be accommodated to allow closure of a carbon network consisting of *n* hexagons. The geometry and stability of fullerenes are, in most cases, governed by the so-called isolated-pentagon rule (IPR) (Kroto, 1987), i.e., the pentagons within the most stable fullerenes are surrounded by five hexagons and, hence, are isolated from each other. The smallest carbon cage that faithfully fulfills this rule is the icosahedral C_{60} (I_h) (Fowler *et al.*, 1995). Only C_{60} and fullerenes not smaller than C_{70} can fulfill the IPR. Non-IPR fullerenes with adjacent pentagons are always unstable, due to enhanced steric strain (steric effect) and resonance destabilization pertaining to the pentalene-type 8π-electron system (electronic effect). For fullerenes that cannot follow the IPR rule, the relative stability of the different isomers is directly related to the number of adjacent pentagons; the isomer with the least adjacent pentagons is most favorable . much higher than that of their large homologues, which results in a much severer steric strain on the small fullerene carbon surface (Fowler *et al.*, 1995; Kroto, 1987). Even worse, the π-conjugation within small fullerenes is more severely curved and weakened, especially at those pentagon-pentagon (PP) fusion sites. Accordingly, small fullerenes have been predicted to have narrow HOMO-LUMO gaps and high reactivity, e.g., subject to coalescence. Because of their high lability, thus far they can only be observed and experimented upon in the gas phase, whereas the efforts made for bulk synthesis of them have proven to be mostly fruitless (Piskoti *et al.*, 1998). As such, most of our knowledge regarding small fullerenes comes from gas-phase experiments and theoretical investigations. Yet, it has been shown that for carbon clusters C_n generated in the gas phase the most stable structures are probably fullerenes with $n \geq 30$, whereas small carbon clusters prefer chain or ring structures (Handschuh *et al.*, 1995). Much encouraging is the recently reported synthesis of dodecachlorofullerene ($C_{50}Cl_{10}$) (Lu *et al.*, 2004), which unambiguously provides evidence that small fullerenes can definitely be stabilized and thus synthetically approachable by functionalizing their active pentagon abutments. Other recent exciting progresses in small fullerenes include the synthesis of covalently bonded assembly of C_{36} and its derivatives ($C_{36}H_4$, $C_{36}H_4O$, and $C_{36}H_6$), the gas-phase production of endohedral metallofullerenes M@C_{28} (M) U, Zr, Hf, and Ti), and the gas-phase production and characterization of the smallest fullerene C_{20} from its long known derivatives ($C_{20}H_{20}$) followed by bromination. Because of their spherical shapes, fullerenes suffer large strain energy introduced by the deviation from planarity.

The chemical reactivity of conventional fullerenes is primarily driven by such type of curved π-conjugation. The curved π-conjugation within the carbon surfaces of fullerenes and SWCNTs can be easily analyzed using the π-orbital axis vector (POAV) method proposed by Haddon. In general, an sp^2-hybridized carbon atom prefers to form planar σ-framework with its neighbors, leaving its p_π-orbital perpendicular to the π-bonds. In fullerenes, the sp^2-hybrized carbon atom is pyramidalized; the angle between its p_π-orbital and the π-bonds is larger than 90°. The pyramidalization angle (Θ_p) for such a non-planar sp^2- hybrized carbon atom can be defined as the angle between its π-orbital and the σ-bonds minus 90°. Thus an sp^3-hybridized carbon atom (ideally tetrahedral) has a 19.5° pyramidalization angle, Θ_p, while a regular sp^2 carbon (as in a planar benzene) has a Θ_p of 0°. All carbon atoms in the icosahedral C_{60} have the same Θ_p of ~11.6°. The pyramidalization angle Θ_p of a carbon atom in the curved carbon surface is a good measure of the curvature-induced local weakening of π-conjugation, which in turn results in the chemical reactivity of fullerenes. The larger pyramidalization angle is of an unsaturated carbon atom in a fullerene, the higher reactivity it is toward addition reactions. For small fullerenes, their PP fusion apices always have the largest pyramidalization angles, thus are the most active sites subject to addition reactions. While the pyramidalization angle can be used to assess the local reactivity of carbon atoms in a fullerene and to advocate the importance of steric strain effect, the global aromaticity of such spherical molecules (electronic effect) is another factor to determine their global stability. However, it is worth noting that aromaticity is only one factor to determine the overall stability of a molecule and can only be decisive when other factors are similar or unimportant; the most stable isomers do not necessarily have the largest aromaticities.

During the past 3–4 years, considerable advances have been made towards the development of covalent and non-covalent chemical functionalization schemes for SWCNTs, which mainly target the sidewall of the tubes. A more detailed picture of how these derivatizations affect the tubes's electronic and vibrational properties is currently emerging. Of strong interest is the determination of the atomic-scale structure of the functionalized nanotubes, specifically with respect to the density, distribution and conformation of the attached groups or molecules.

The addition of atoms or molecules to carbon/carbon π-bonds results in the local formation of tetragonal, sp^3-bonded carbon centres. This process is unfavourable on a flat graphene sheet due to the stabilisation by the extensive π-conjugated bonding. In comparison, carbon nanotubes are chemically more reactive owing to their curvature. Real SWCNTs possess three regions of different reactivity:

(i) The tube caps exhibiting a high reactivity comparable to that of the fullerenes. This high reactivity stems from their pronounced curvature in two dimensions, which ensures a strong strain relieve upon conversion of trigonal into tetragonal carbon atoms. Like in C_{60}, the caps can be regarded as an assembly of distinct C=C double bonds connected by C–C single bonds, which should in principle lead to regioselectivity in addition reactions. However, due to the fact that the standard purification and/or dispersion procedures normally lead to opening of the nanotube ends (Monthioux *et al.*, 2001), the chemistry of the caps in SWCNTs remained largely undeveloped so far. In contrast, first steps have recently been made towards functionalization of the caps in MWCNTs (Basiuk *et al.*, 2004).

(ii) The intact sidewall, where the curvature is considerably smaller than at the caps, and hence strain relief offers a smaller driving force for the formation of tetragonal carbons. As a consequence, sidewall functionalization in general requires quite ‘‘hot’’ addends such as the strong oxidizer fluorine, or highly reactive species like radicals. In principle, additions to the sidewall could also proceed in a regioselective manner (Lu *et al.*, 2002).

(iii) Defects in the sidewall enhances the reactivity due to the high local strain. Once the reaction is initiated at such a site, adjacent partial double bonds may be rendered more reactive as well, allowing it to spread along the tube. A defect that is frequently encountered is the Stone–Wales defect comprising two pairs of five- and seven-membered rings, whose presence results in a locally enhanced curvature of the graphitic layer. The strongest curvature exists at the interface between the two five-membered rings, which makes addition reactions most amenable to the carbon–carbon double bond in this position (Zhao *et al.*, 2004).

The extent of curvature-induced weakening of π-conjugation within SWCNT depends on the helicity and diameter of the tube, according to the POAV analyses (Niyogi *et al.*, 2002). Besides the curvature-induced pyramidalization of π-orbitals of carbon atoms (similar to the fullerene case), curvature also induces misalignment of π-orbitals of carbon atoms within a SWCNT. As a result, the sidewall of a SWCNT could be more reactive than a flat graphene sheet; a SWCNT of smaller diameter having larger π-orbital pyramidalization and misalignment angles suffers more severe curvature induced weakening of π-conjugation and, hence, is more reactive. However, due to the different bending pattern, the nanotubes have less curvature compared with fullerenes with comparable diameters; accordingly nanotubes are generally less reactive than fullerenes, and more critical experimental conditions are required to functionalize carbon nanotubes.

While perfect infinite SWCNTs ideally have curved graphenic hexagon networks with strong, pseudo 1D π-conjugations, the presence of a variety of imperfections, such as vacancies, SW defects (Stone and Wales, 1986), pentagons, heptagons, and dopants, is unavoidable in pristine SWCNTs (Hashimoto *et al.*, 2004). These defects can be inevitably formed during the growth of CNTs or introduced by post processing (e.g., ultrasonication and oxidative cleaning). It has been shown that these defects play a pivotal role in tailoring the physical, and chemical properties (Li *et al.*, 2003; Lu and Pan, 2004) of SWCNTs. For example, defects have been shown to be of critical importance in the chemical etching and shortening of CNTs. Owing to the importance of defects in the chemistry of SWCNTs, a number of theoretical investigations have been conducted recently, mainly focusing on the chemical reactivities of the following four types of defects: vacancies, dopants (e.g., B, N, Si, etc.), ad-dimers and SW defects.

1. Vacancies. Vacancies with unsaturated dangling bonds are of course highly reactive and can readily form covalent bonds with adsorbed species. For instance, recent temperature-programmed desorption (TPD) experiments (Chakrapani *et al.*, 2003) showed that acetones can be chemisorbed on HiPCOSWCNTs, and at least five chemisorption states were formed with measured activation energies of acetone desorption ranging from 24.5 to 59.5 kcal/mol. Further theoretical calculations using hybrid quantum mechanical and semi-empirical methods and short zigzag tube models revealed that the most stable chemisorption states are due to acetones covalently bonded to atomic vacancies, while those weaker ones are attributed to the [2+2]-cycloaddition adducts of actones on the SW defects.

2. Dopants. Doping the sidewalls of SWCNTs with heteroatoms such as B and N modifies their electronic structures and chemical properties. Recent first-principles DFT calculations (Peng and Cho, 2003) predicted the following properties for the B-or/and N-doped zigzag (8,0) SWCNTs:

(i) Small polar molecules such as CO and H_2O that have electron-donative lone pair(s) can be chemisorbed onto the B sites of the B-doped and BN-doped CNTs, whereas physisorption occurs only on the intrinsic CNTs.

(ii) The B-doping drastically enhances the charge transfer capability of the CNTs. Consequently, electron transfer from the chemisorbed CO or H_2O on the B-doped and BN-doped CNTs is also enhanced as compared to the CO/CNT and H_2O/CNT physisorption systems.

(iii) B-doped CNTs are good sensors of CO and water molecules. Moreover, DFT computations (Nevidomskyy *et al.*, 2003) showed that nitrogen substitutional impurities have different effects on metallic armchair and semiconducting zigzag nanotubes: at low concentration, the defect in a semiconducting tube creates a spatially localized state, which makes the impurity site chemically and electronically active, while the impurity in armchair nanotubes is totally delocalized. Because of its electron deficiency, boron atoms doped in SWCNTs have a strong propensity to accept electrons from lithium energetically; thus, boron doping is expected to improve the Li adsorption in SWNTs (Zhou *et al.*, 2004). The electron-deficient boron doped SWCNTs, especially BC_3 nanotubes (Zhou *et al.*, 2005), are computed to absorb lithium very favorably and exhibit superior Li adsorption capabilities than the pure carbon nanotubes.

3. Stone-Wales Defect (5-7-7-5 Defect). The SW defect (an assembly of 5-7-7-5 rings) is a very important topological defect in the science of CNTs and graphites. By definition, an SW defect can be generated topologically by rotating one of the C-C bonds in a hexagonal network by 90° (Stone and Wales, 1986).

Recently, the presence of SW defects in carbon and boron nitride nanotubes was identified experimentally by combining resonant photoabsorption and vibration spectroscopy with scanning tunneling microscopy (Miyamoto *et al.*, 2004). Recent theoretical investigations showed that the central C-C bond (i.e., the 7-7 ring fusion) in the SW defective sites has a bond length with a range of 1.32-1.38 Å, shorter than that of an ordinary C-C bond (around 1.42 Å) in a defect-free SWCNT (Bettinger, 2005). This implies the central C-C bond in an SW defect can be considered as a double bond with highly localized π-electron density. Consequently, the central C-C bond in an SW defect should be more reactive than the ordinary C-C bonds of a defect free SWCNT. This is true for most of the cases concerned so far. (Dag *et al.*, 2003; Zhao and Xie, 2003) For instance, acetone was found to undergo exothermic [2+2]-cycloaddition with the central C=C bond of a SW defect in the sidewall of a zigzag (10,0) tube but does not react with a defect-free tube at all. A similar trend was predicted for the [2+2]-additions of singlet O_2 (Dag *et al.*, 2003) and [2+1] cycloaddition of methylene to the sidewalls of the defective and defect-free (10,0) tube. However, an exception exists: recent DFT computations show that the central C-C bond of an SW defect in an armchair (5,5) SWNT is chemically less reactive than perfect sites (Lu *et al.*, 2005). Note that the local carbon skeleton at the 5-7-7-5 ring fusion of the SW defect is nearly planar with a curvature induced pyramidalization angle of only ~0.3° at the C1 and C2 atoms, whereas the pyramidalization angle (~5.3°) at the C atoms of a defect-free tube is much larger. Clearly, the local curvature of the SW defect is far less severe than that of a perfect site. The much lower chemical reactivity at the defective 7-7 ring fusion can be ascribed to the constraints of its planar local structure. On the contrary, its peripheral C-C bonds (e.g., the 5-6 and 6-7 ring fusions) were predicted to be more reactive than an ordinary 6-6 ring fusion in the tube wall due to the much severe local curvatures at these sites. Thus, the local curvature introduced by the topological defect affects subtly the chemical reactivity of the sites in its vicinity.

A major milestone in the emerging area of nanotube chemistry was the development of an oxidation process for SWCNTs involving extensive ultrasonic treatment in a mixture of concentrated nitric and sulfuric acid. Such drastic conditions lead to the opening of the tube caps as well as the formation of holes in the sidewalls, followed by an oxidative etching along the walls with the concomitant release of carbon dioxide. The final products are nanotube fragments with lengths in the range of 100 to 300 nm, whose ends and sidewalls are decorated with a high density of various oxygen containing groups (mainly carboxyl groups). Under less vigorous conditions, such as refluxing in nitric acid, the shortening of the tubes can be minimized. The chemical modification is then limited mostly to the opening of the tube caps and the formation of functional groups at defect sites along the sidewalls. Nanotubes functionalized in this manner basically retain their pristine electronic and mechanical properties.

The oxidatively introduced carboxyl groups represent useful sites for further modifications, as they enable the covalent coupling of molecules through the creation of amide and ester bonds. By this method the nanotubes can be provided with a wide range of functional moieties, for which purpose bifunctional molecules (e.g., diamines) are often utilized as linkers. The examples are nanotubes equipped with dendrimers, nucleic acids, enzymes, metal complexes, or semiconductor and metal nanoparticles (Katz and Willner, 2004). Another interesting application of the carboxyl groups is the formation of an anhydride at the tube ends, through which rings of nanotubes are accessible (Sano *et al.*, 2001).

The presence of (modified) carboxyl groups leads to a reduction of van derWaals interactions between the CNTs, which strongly facilitates the separation of nanotube bundles into individual tubes. Additionally, the attachment of suitable groups renders the tubes soluble in aqueous or organic solvents, opening the possibility of further modifications through subsequent solution-based chemistry. A high water solubility of a few tenths of a gram per milliliter has recently been achieved on the basis of the carboxyl-based coupling of hydrophilic polymers such as poly(ethylene glycol) (PEG) (Fernando *et al.*, 2004). SWCNTs with a good solubility in organic solvents can be obtained by covalent or ionic (Chen *et al.*, 2001) attachment of long-chain aliphatic amines onto the carboxyl groups.

While the two-step functionalization of nanotubes through the oxidative introduction of carboxyl groups followed by the formation of amide or ester linkages does allow for a stable chemical modification, it has only a relatively weak influence on the electrical and mechanical properties of the nanotubes. By comparison, addition reactions enable the direct coupling of functional groups onto the π-conjugated carbon framework of the tubes. The required reactive species (atoms, radicals, carbenes, or nitrenes) are in general made available through thermally activated reactions, and small-diameter tubes are preferred as they show higher chemical reactivity due to their increased curvature.

While in the initial experiments aiming at addition reactions to the sidewall only one to three functional groups were found per 100 carbon atoms, the procedures developed more recently have reached functionalization degrees of at least 10%. At the present stage, however, the addition mechanisms are not yet completely understood. In principle, the addition reaction could be initiated exclusively on the intact sidewall, or in parallel at defect sites from where the reaction could proceed further. It is a matter of actual investigation as to which extent these two possibilities contribute. One exception is nanotube fluorination, for which direct addition to the defect-free sidewall appears viable. Nonetheless, the addition of fluorine has a noticeable activation barrier, due to which the reaction requires slightly elevated temperatures (T >150 ^{o}C).

Analogous to nanotube functionalization with carboxyl groups, the direct covalent attachment of functional moieties to the sidewalls strongly enhances the solubility of the nanotubes. The good solubility of nanotubes modified with organic groups has been exploited for their effective purification (Georgakilas *et al.*, 2002). In this procedure, small particles are first separated from the solution through chromatography or filtration, and then the covalently attached groups are removed through thermal annealing (T>250 ^{o}C).

The electronic, chemical and mechanical properties of CNTs can be tailored by replacing some of the carbon (C) atoms with either boron (B) or nitrogen (N). If B (has one electron less compared with C) or N (one electron more than C) replaces some C atoms, a p- or n-type conductor can be formed respectively. From the chemical point of view these doped structures would be more likely to react with donor or acceptor type molecules depending on the doping. The B or N doped CNT can be obtained by arc method by arching either B- or N-graphite electrodes in an inert atmosphere. Laser (Lu *et al.*, 2003) and CVD (Terrones *et al.*, 1997) methods have been also used for their production.

The recently developed chemical methods for chemical functionalization of carbon nanotubes have opened up a broad range of novel application perspectives. In this Section, five specific applications of (electro-) chemically modified SWCNTs are described in detail.

For many electronic applications it is of great importance to have nanotube ensembles that exhibit uniform electrical properties. While metallic nanotubes are desirable for nanoscale electrical interconnects, the fabrication of transistor devices requires exclusively semiconducting nanotubes. At present there exists no synthesis method that allows for a reliable control over the electrical properties of the produced nanotubes. The raw nanotube material thus constitutes a mixture of metallic and semiconducting nanotubes. Various methods for the separation of the two types of nanotubes have been devised. One such procedure is based upon alternating current dielectrophoresis of surfactant-stabilized SWCNTs (Krupke *et al.*, 2003), which takes advantage of the differing concentrations of freely movable charge carriers in nanotubes: Metallic nanotubes possess a high density of such carriers, which gives them a large electronic polarizability. Hence, when a suitable alternating electric field is applied, they are attracted to the regions of highest field strength, whereas the semiconducting tubes are repelled. An important disadvantage of this method is that it is limited to very small material quantities. On the other hand, chemical separation methods exploiting differences in the solubility of the two types of tubes upon doping with an electron acceptor offer an easier scalability (Chen *et al.*, 2003). However, all currently available chemical methods are still far from enabling an exclusive enrichment of one type of tube.

An alternative technique for the separation of the tubes is based on the selective destruction/functionalization of the metallic nanotubes in a tube ensemble. As one possibility, this can be achieved by applying an increasing electrical voltage across the tube ensemble until the metallic tubes are burnt off as a consequence of

Joule heating arising from the high current densities (Collins *et al.*, 2001). The procedure is performed by simultaneous application of a gate voltage to deplete the semiconducting nanotubes of charge carriers, so that exclusively the metallic nanotubes remain conductive. While this method has proven effective for the separation of single tubes, its application to samples composed mainly of bundles faces limitations. This is due to the close proximity of the metallic and semiconducting nanotubes within the bundles, which leads to a high risk of damage for the latter type of tubes. Electrochemical methods offer an elegant solution to this problem. Upon switching off the semiconducting tubes under appropriate gate control, the metallic tubes are exclusively provided with a high density of covalently coupled phenyl radicals reductively generated from aromatic diazonium salts. As a consequence, the modified metallic tubes become insulating, and the resulting ensemble shows purely semiconducting behavior. The conductance of such devices can be varied over many orders of magnitude through the voltage at the gate electrode (Collins *et al.*, 2001). The key concept of this approach is the creation of highly reactive radicals exclusively at the locations where the reaction is desired, that is, at the interface between the electrolyte and the metallic nanotubes.

The fact that all of the carbon atoms in a carbon nanotube are surface atoms makes them optimally suited for components of chemical sensors. Hence, it is not surprising that gas sensors made from individual nanotubes show good sensitivities at room temperature, in comparison to commercially available classical semiconductor sensors, which in general operate above 200°C. However, a necessary prerequisite is that the molecules to be detected must have a distinct electron donating or accepting ability, which is fulfilled, for example, by ammonia (NH_3) as a donor and nitrogen dioxide (NO_2) as an acceptor. The adsorption of these molecules on the nanotubes is associated with a partial charge transfer, which alters the charge-carrier concentration or, alternatively, the adsorbed molecules may affect the potential barriers present at the tube–electrode contacts. In any event, the resulting change in the electrical resistance of the nanotube is utilized as a sensor signal. However, for the detection of molecules that are only weakly adsorbed (e.g., carbon monoxide and hydrogen), the change in resistance is often too small. A possible method to overcome this drawback is accomplished by the modification of the nanotube sidewalls with nanoparticles made of a suitable metal. For instance, sensitive hydrogen sensors operating at room temperature can be obtained via the deposition of palladium nanoparticles either by direct evaporation or through electrodeposition. Electrodeposition offers the specific advantage of site-selectivity, since the metal decoration is restricted to the current-carrying tubes, so that the remaining substrate surface is unaffected. The operation mechanism is largely analogous to that of a palladium gate field-effect transistor realized within classical silicon technology (Lundstrom *et al.*, 1975). Specifically, molecular hydrogen is split on the surface of a Pd particle into atomic hydrogen, which diffuses to the Pd/SWCNT interface. At this interface, a dipole layer is formed, which acts like a microscopic gate electrode that locally changes the charge-carrier concentration. It should be mentioned that the recovery of this type of room-temperature-operated hydrogen sensor requires a supply of oxygen to remove the hydrogen atoms in the form of water.

Carbon nanotubes exhibit high electron transfer rates for different redox couples in various media, which has stimulated an increasing amount of research into CNT based amperometric sensors for the detection of specific analytes in solution. The length scales of CNTs are similar to that of typical biological molecules, which gives CNTs an edge over other materials in functioning as effective electrodes in bioelectrochemical sensing (Guiseppi-Elie *et al.*, 2002). In particular, their high aspect ratio and their diameter in the nanometer range make CNTs particularly well suited for direct electrochemical communication with the redox site of a protein, without requiring any mediator. When properly arranged, a nanotube should have the capability to act as a 1D channel that guides electrons towards the redox center. Direct electron transfer has been achieved with various types of CNT electrodes for cytochrome c, horseradish peroxidase, myoglobin, as well as glucose oxidase. It is noteworthy that in the latter case, the redox-active center is deeply embedded within the protein. In some cases, an oxidative pretreatment that introduces negatively charged surface groups on the CNTs was necessary to achieve high electron transfer rates. In a strategy to optimize the accessibility of the redox center, aligned CNT arrays have been fabricated using selfassembly techniques, followed by the covalent attachment of microperoxidase to the tube ends. On this basis, various types of amperometric biosensors have been fabricated (Wang and Musameh, 2003). The working principle of a glucose sensor obtained by immobilizing glucose oxidase onto SWCNTs deposited on a glassy carbon surface.

For a long time, active carbon has found widespread application as a support material in heterogeneous catalysis. Compared to this form of carbon, carbon nanotubes offer the advantage of a more defined morphology and chemical composition as well as the possibility to attach catalysts onto their surface through covalent bonds. The applicability of SWCNTs as carriers for catalytically active molecular functional units has recently been demonstrated through the covalent coupling of an organic vanadyl complex (Baleizao *et al.*, 2004). The nanotubes modified in this manner permit the catalytic cyanosilylation of aldehydes.

The adsorption strength of organic compounds on SWCNTs depends sensitively on the type of functional groups contained in the molecule. Aliphatic molecules lacking functionalities of appreciable electron-donating or -accepting capability bind only weakly to SWCNTs, as exemplified by the experimental binding energy of ~0.5 eV reported for alcohols (Yang *et al.*, 2002). Aliphatic amines, in comparison, interact more strongly with SWCNTs due to the strong donor property of the amino-groups (Kong and Dai, 2001), and hence enable to disentangle bundles into individual tubes and render them soluble in organic solvents. (Chakrapani *et al.*, 2003; Lu *et al.*, 2004)