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Processing Carbon Nanotubes

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1. Introduction

Due to their combined superior chemical and physical properties, carbon nanotubes (CNTs) are recognized to have a huge potential in many fields of applications (Ajayan, 1999; Rao et al., 2001; Dai, 2002; Van Noorden, 2011). These molecular-scale tubes of graphitic carbon are one of the stiffest and strongest fibers known. Besides, they have remarkable electronic, optical, thermal and chemical properties. For these reasons their interest in both academic and industrial areas is unique. Nevertheless, the as-produced material is extremely difficult to process. Development of CNT-based devices or composites of interest for new applications has been consequently hindered. CNTs are hydrophobic and incompatible with a majority of solvents, including monomers and polymers; they indeed have a high tendency to agglomerate. Moreover, CNTs and especially single-walled carbon nanotubes (SWNTs) are assembled in bundles of generally several tens of tubes. Development of efficient processes and chemical treatments that are able to control the quality of the CNT samples and to induce both their dispersion and partial or complete debundling remains highly challenging.

CNTs can be produced using different methods that basically consist in heating carbon-containing solid or gas. On the contrary to the preparation of multi-walled carbon nanotubes (MWNTs), SWNT growing requires a metal catalyst. The characteristics of the samples depend on the control and the choice of the experimental parameters used for the synthesis. A better understanding of the growth mechanisms has permitted the development of mass production processes (Grobert, 2007). Nevertheless, their uniformity (length, diameter, chirality), the quality of their walls (number of defects) and also their purity are still partially controlled. The quality of the samples has to be improved in order to benefit of the exceptional properties of CNTs in new materials. Depending on the type and the synthesis method, the CNTs can differently behave through the applied chemical treatments. Whatever the synthesis method, CNT samples persistently contain several kinds of heterogeneities: (i) carbonaceous species like fullerenes, amorphous carbon, graphitic and carbon particles, …; (ii) impurities such as residual metallic catalyst often protected by more or less graphitized carbon shells or polyhedra; (iii) defects at the CNT surface or oxygenated grafted functions, (iv) dispersion in diameter, chirality and morphology (aspect ratio) and (v) aggregation into bundles. These heterogeneities represent a major obstacle for both the establishment of universal behaviors and the development of efficient processing methods.

Nano-scaled particles exhibit an enormous surface area being of several orders of magnitude larger than that of conventional fibers. This surface area can potentially act as a

powerful interface but it is also responsible for the high tendency of CNTs to form agglomerates. It appears that the commonly used procedures for manufacturing composites with conventional fibers or other-carbon-form do not show the hoped results. Indeed, CNT samples particularly and unusually behave. Hence original chemical treatments and processes have to be proposed and optimized (Kuzmany et al., 2004; Tasis at al., 2006; Karousis et al., 2010); and efforts have to be made to disperse the CNTs prior to their incorporation within the chosen surrounding medium to obtain the desired device or material.

In this paper, we first give an overview of the characterization techniques commonly used to follow surface and structural modification of CNTs upon chemical treatments; the respective sensitivity and the limits of each technique are also briefly discussed. The second part is dedicated to the description of the main kinds of CNT samples (obtained from different synthesis methods) and the question of their purification is in particular considered. In the following section, after giving the parameters that are relevant regarding chemical treatments to process CNTs, we will focus on the treatments commonly used to induce the dispersion of the CNTs in a surrounding medium (solvent, monomer or polymer) and the methods leading to modify the CNT reactivity. The last part reports on the elaboration and the characterization of CNT-based composites taking into account their particular multi-scale character.

2. Characterization techniques

Characterization of CNT samples is a difficult task. Their inherent heterogeneity (discussed in the following part) is one of the main reasons for that statement. It is complex to obtain an unambiguous knowledge of their behavior based on the recorded data from one characterization technique. The usually and unavoidable employed approach is the use of several complementarily techniques. The most common analytical techniques used to characterize chemically modified CNTs are transmission electron microscopy (TEM), scanning electron microscopy (SEM), thermogravimetry analysis (TGA), Raman spectroscopy and XPS (X-ray photoelectron spectroscopy). Added to them, several other techniques can be used to specifically determine the nature of the attached chemical groups or their localization on CNT samples; for that purpose, TGA-MS (mass spectrometry) coupling technique, EXAFS (extended X-ray absorption fine structure) or adsorption volumetry are of interest.

The electron microscopy techniques (TEM and SEM) allow a qualitative and local examination of the morphology and the composition of the samples; by increasing the number of the observed zones, they can be reliable in the determination of the behavior of the CNT samples (Monthioux et al., 2001). The accuracy of electron microscopy being in constant progress, it permits to go further in the structural details of the analyzed species, including CNTs. EDS or EDX (energy-dispersive X-ray spectroscopy) for the elementary analysis at a specific location of the sample during observations can be used to determine the metal content after a purification process or the presence of one specific element belonging to the grafted functions. The main advantage of these techniques is that they allocate to separately analyze the behavior of the CNTs, the carbonaceous or catalytic impurities.

The TGA examines the weight lost of the CNT samples as a function of the temperature (usually from room temperature to 800°C-1000°C). In oxidative conditions (air or oxygen),

the recorded weight loss corresponds to the combustion of the carbonaceous species of the samples. This oxidation treatment gives rise to their successive combustion as a function of their respective stability (Landi et al., 2005). At the end of the gasification process, only the oxidized catalysts remain. First, this technique is used to quantify the metal content in CNT samples after a purification process. In the example reported on Figure 1a (from Landi et al., 2005), the metallic oxides content is reduced from 9.6 wt% to 7.1 wt% after refluxing in a NHO_3/HCl acidic solution for 14h. The raw sample is named 'SWNT-HO' and the sample obtained after reflux is named 'SWNT-Reflux'. Second, the situation is a little bit complicated regarding the analysis of the nature and/or the content of the different carbonaceous species in the samples. Even if it is obvious that well-graphitized species will be more stable than amorphous carbon, the removal temperature range of CNTs and more- or less-ordered carbon species can be rather large and difficult to identify. However, TGA can be useful to evidence modification of CNT structure after treatments. For example, an increase of the CNT quality or concentration through a purification process or an introduction of defects through a chemical functionalization gives rise to modifications for both the recorded weight losses and the related temperature domains. It is commonly reported that CNTs decompose at higher temperature than amorphous carbon species. As illustration, Figure 1b (from Landi et al., 2005) shows the first derivative weight-loss curves for the samples previously mentioned. Raw SWNT-HO sample shows two major contributions of the weight loss with a prominent peak maximum at 427°C and a minor shoulder at 560°C, attributed to gasification of amorphous carbon and SWNTs, respectively. For 'SWNT-Reflux' sample, the two contributions are shifted to higher temperatures, namely, peak maxima at 503 and 598 °C, respectively.
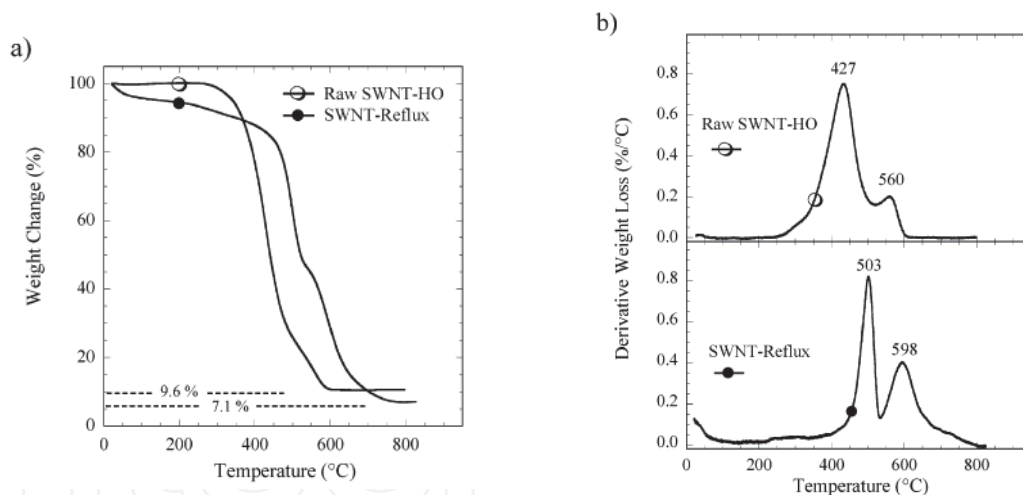

Fig. 1. TGA data for a raw SWNT (SWNT-HO) and SWNT-HO that has been treated using an acidic solution (SWNT-Reflux). SWNT-Reflux is obtained after refluxing raw SWNT-HO sample in a NHO_3/HCl acidic solution for 14h. The TGA was ramped at 10°C/min under air at a gas flow rate of 60 sccm. a) TGA data for raw SWNT-HO (O) and SWNT-Reflux (●) samples. b) TGA data from the first derivative analysis of the weight loss (%/°C) for raw SWNT-HO (O) and SWNT-Reflux (b) samples. The peak maxima for the prominent thermal decomposition features are labeled for clarity. From (Landi et al. 2005). Copyright 2005 by the American Chemical Society.

As it is reported in the work of Landi and coworkers (Landi et al., 2005), the ability to assign temperature regions of combustion for SWNTs and carbon impurities would be of great

importance for the optimization of purification processes. Nevertheless, a selective decomposition of carbon impurities if it exists remains an open question.

Under inert gas, TGA-MS coupling technique consists in analyzing the detachment of functions that have been initially grafted to the CNT surface (Chattopadhyay et al., 2005). The nature of the bonds created between the introduced functions and the CNTs can be identity from the release temperature domain (Lejosne et al., 2011). A molecule simply physisorbed or π-stacked will be detected at lower temperature than a group which is covalently linked to the sample surface. As a complementary analysis, MS investigation allows having a feedback of the nature of the functions that were effectively attached at the sample surface.

Raman spectroscopy is a widely used technique for the characterization of CNT samples (Burghard, 2005; Graupner, 2007). It is a powerful technique because the signal of CNTs is enhanced compared to that of the carbon impurities. Several features are modified upon chemical treatments and Raman spectroscopy allows probing the quality of CNT structure, the possible selectivity of reaction with respect to the electronic properties (metallic or semiconducting) (Dyke et al., 2005) or an induced electron transfer. A typical Raman spectrum of SWNTs shows three characteristic bands: the radial breathing mode RBM (100–400 cm^{-1}), the D mode ($\approx$1350 cm^{-1}) and the tangential (C=C vibrations) stretching G mode (1500–1600 cm^{-1}).

At low frequency, RBM corresponds to the radial deformation of the carbon-carbon bonds. For SWNTs in bundle, the SWNT diameter can be calculated as follows (Jorio et al.,   2003):

$$\omega_{RBM} = A/d_t + B \qquad\qquad (1)$$

where the A and B parameters are determined experimentally. For typical SWNT bundles in the diameter range $d_t = 1.5\pm0.2$ nm, $A = 234$ cm^{-1} nm and $B = 10$ cm^{-1} has been found for SWNT bundles.

The intensity of the D-band is known to be related to introduction of defects in the CNT structure. The increase of the ratio of the intensity of the D band over the intensity of the G band, I_D/I_G, is commonly used to prove the covalent nature of the functionalization of CNTs since the attachment of the grafted groups leads to the breaking of C=C bonds (Dillon et al., 2005). The area of the D band is also reported to be sensitive to a presence of deposit of carbon layers on CNT surface. The removal of such deposit by oxidation for example possibly leads to a decrease of I_D/I_G ratios (Osswald et al., 2005). Heating functionalized CNTs under vacuum or inert gas leads to the removal of functional groups and restores the initial low-defected structure. The obtained CNT samples after annealing show thus a reduced I_D/I_G. Figure 2 (from (Dyke & Tour, 2003)) shows three Raman spectra of raw SWNTs (A), covalently functionalized SWNTs (B) and of functionalized SWNTs after heating at 750°C under argon (C). I_D/I_G increases after the functionalization process because of the attachment of functional groups on the SWNT sidewalls and it decreases after heating due to the detachment of the groups and the recovering of SWNT structure.

The G band corresponds to the tangential mode of vibration of the C=C bonds in CNTs (Jorio et al., 2002). The G band is mainly composed of two or three identifiable components even if it can be usually more complex to be fitted. A simple analysis can be carried out considering the two most intense peaks that basically originate from the symmetry breaking of the tangential vibration when the graphene sheet is rolled to make a cylindrically shaped tube. They are labeled G$^+$ for atomic displacements along the tube axis, and G$^-$ for modes with atomic displacement along the circumferential direction. The difference between

semiconducting and metallic SWNTs is evident in the lineshape of the G$^-$ feature, which is broadened for metallic SWNTs in comparison with the Lorentzian lineshape for semiconducting tubes. G band can be sensitive to chemical treatments. First, for defective SWNTs after functionalization, an additional contribution, referred as the G* band, at high wavenumber is added to the conventional G band (Cataldo, 2000; Vigolo et al., 2009a). Second, reaction of SWNTs with electron-donors or -acceptors induces a shift of the G band. The reaction between alkali metals (donors) and CNTs is accompanied by an electronic transfer giving rise to an electron enrichment of the CNT structure. The G band of the obtained reduced CNTs can be then down-shifted of several tens of cm^{-1} (Sauvajol et al, 2003).
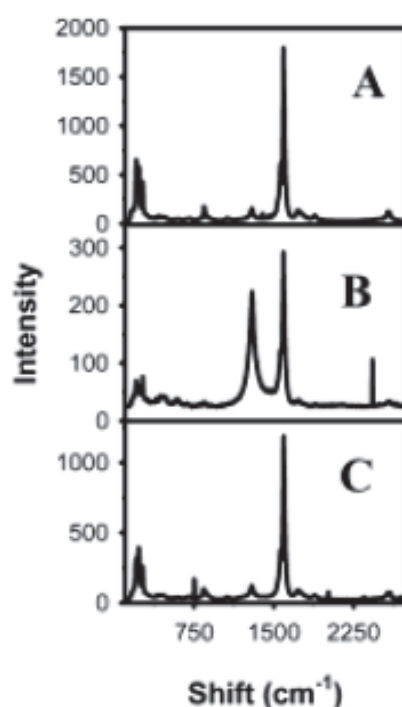

Fig. 2. Raman spectra (780.6 nm excitation) of (A) raw SWNTs, (B) functionalized SWNTs, and (C) functionalized SWNTs after TGA (10 °C/min to 750°C) in argon. From (Dyke & Tour, 2003). Copyright 2003 by the American Chemical Society.

Infrared (IR) spectroscopy is recognized to be useful for the study of SWNT sidewall chemistry. As a complementary technique of Raman spectroscopy, IR spectroscopy can be used to identify the functional groups and especially oxygenated functional groups added to the tube walls thanks to their characteristic vibrational modes (U.J. Kim et al., 2005a). The range expected for C-O stretching modes in ether, ester, alcohol, or phenol functions is around 1100 cm^{-1} and in the 1700 cm^{-1} domain, the bands can be assigned to carbonyl (C=O) stretching in ketone, aldehyde, or carboxylic acid groups. For aldehyde groups, the C-H stretching and bending vibration generally appears in the 2700-2900 cm^{-1} range. The O-H stretching modes are found in the 3100-3600 cm^{-1} range.

X-ray (XRD) and neutron diffraction techniques may help to ascertain the quality and crystalline nature of the treated CNT samples as opposed to amorphous carbon material. XRD, in particular, allows analyzing the state of oxidation of the catalyst through a purification process, for example (Vigolo et al., 2010a).

XPS (X-ray Photoelectron Spectroscopy) technique is widely used to determine atomic compositions and to qualitatively analyze different elements on the CNT surface especially upon oxidative treatments; it is also sensitive to the presence of structural defects on the nanotube surface. The C1s peak of non-treated CNTs shows a peak at 284.1 eV. The peak at 285.5 eV is attributed to defects on the nanotube structure (Datsyuk et al., 2008). Detection of oxygen-containing functional groups is evidenced by several contributions at 286.7, 288.3 and 290 eV. Finally, the π–π* transition loss peak is generally detected at 291.5 eV. The relative augmentation of the contributions related to the presence of oxygen with respect to that of pure carbon evidences the formation of C=O or C-O covalent bonds at the CNT surface. Figure 3 (from Liu et al., 2007a) shows that the C–O component after functionalization (SHR15) is increased compared to other components from the decomposition of C1s peak in agreement with the attached functional groups.
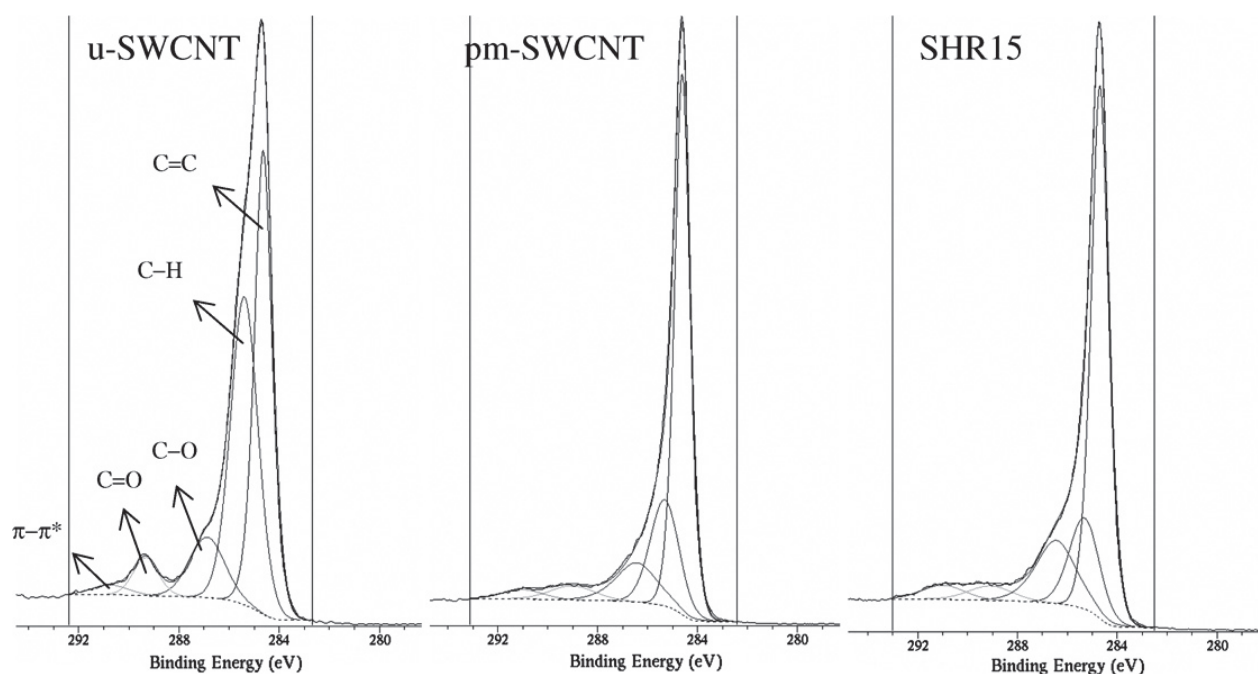

Fig. 3. Decomposition of C1s curves of as-produced SWNTs (u-SWCNT), product of control experiment (pm-SWCNT) and SWNTs that have been functionalized by methoxyphenyl (-PhOCH$_3$) functional groups through using a microwave-assisted reaction for 15 min designated as SHR15. From (Liu et al., 2007a) Copyright 2007 by Elsevier.

Near edge X-ray absorption fine structure (NEXAFS) can be used at the oxygen or carbon K edge to probe the bonding modification of the oxygen or carbon atoms in the sample upon a chemical treatment (Banerjee et al., 2004; Wang et al., 2010). CNT structure and chemical composition of oxygenated functional groups grafted to the CNT surface can be then analyzed using NEXAFS spectroscopy. In the case of C K-edge spectra, the CNTs are characterized by a sharp C–C σ* transition at 285.4 eV, three σ* transitions from 289.9–298 eV, and broad (σ+σ) transitions from 301–309 eV. The region between 287 and 290 eV mainly corresponds to the C–O bonding, with 287.6 eV assigned to C=O π* transition and 288.2 eV assigned to C–O σ* transition. The O K-edge spectra are usually also analyzed as complementary data.

As it can be commonly done for porous systems, the determination of adsorption-/desorption-curves with nitrogen at 77 K can be used to characterize the specific surface

area of the CNTs according to the well-known Brunauer, Emmett, and Teller (BET-method). Since a chemical treatment can induce modifications of CNT surface, such analysis can provide a valuable feedback regarding the occurrence of the chemical treatments (C.M. Yang et al., 2002).

By using gas such as xenon or krypton, the adsorption isotherms exhibit specific profile with several steps and plateaus (Arab et al., 2007; Goudon & Lasjaunias, 2008). The steps are especially related to the existence of different adsorption sites related to CNT bundle morphology; each step being positioned at a characteristic pressure different from the characteristic pressure of the carbonaceous impurities of the samples. The isotherm of a CNT sample can be considered as a signature of the surface of the CNTs themselves. It is hence possible to selectively prove the occurrence of the chemical treatment on the CNT surface (Vigolo et al., 2009b).

3. Description of CNT samples

3.1 Synthesis methods and related characteristics of the samples

The CNT synthesis methods have been recently highly improved leading to the development of mass production processes (Sadeghian et al., 2009; Lehman et al., 2011). Although it is easier to produce significant quantities of MWNTs than SWNTs, their structure is less well understood than that of SWNTs because of their greater complexity and variety. Multitudes of exotic shapes and arrangements have also been observed under different processing conditions. The variety of forms may be interesting but also has a negative side because they diverge from the ideal sp^2 cylindrical structure and the CNT properties are consequently diminished.

CNTs can be synthesized using both high-temperature and low-temperature processes. CVD (Chemical Vapor Deposition) process is classified in the low-temperature methods. It is based on the reaction between a carbon containing flowing gas molecules and catalyst particles often above 1000°C. Arc discharge and laser ablation methods are based on sublimation of a graphite target which occurs at relatively high temperature (1000-3000°C).

In the case of CVD methods, the growth process involves heating a catalyst material to sufficient temperatures (550-1200°C) in a tubular furnace and flowing a hydrocarbon gas through the reactor for a period of time under vacuum. The growth mechanism is based on the dissociation of carbon containing molecules which is catalyzed by a transition metal (typically Ni, Fe or Co) (Gavillet et al., 2002; Deck & Vecchio, 2005; Esconjauregui et al., 2009). After dissolution in the metal particle, a precipitation phenomenon leads to the formation of tubular carbon solids in sp^2 structure. Materials grown over the catalyst, MWNTs or SWNTs, can be obtained as non-ordered soot, densely aligned bundles or as individual array deposited on the substrate (Maruyama et al., 2002; Bronikowski 2006; Singh et al. 2003; Vigolo et al., 2008). These advanced processes allow having a certain control of the diameter and the orientation of the CNTs (Yamada et al., 2006; Willems et al., 2000; N.S. Kim et al., 2002; Y. Chen et al., 2005).

For the synthesis of SWNTs in mass quantities, particular conditions are required in the HiPco process (Nikolaev et al., 1999). It allows producing high-quality and narrow-diameter SWNTs. The metal catalyst is formed *in situ* when $Fe(CO)_5$ or $Ni(CO)_4$ is injected into the reactor (900 to 1100°C) along with a stream of carbon monoxide (CO) gas and at a pressure of 30 to 50 atm. The reaction to make SWNTs is the 'disproportionation' of CO by nanometer-size metal catalyst particles.
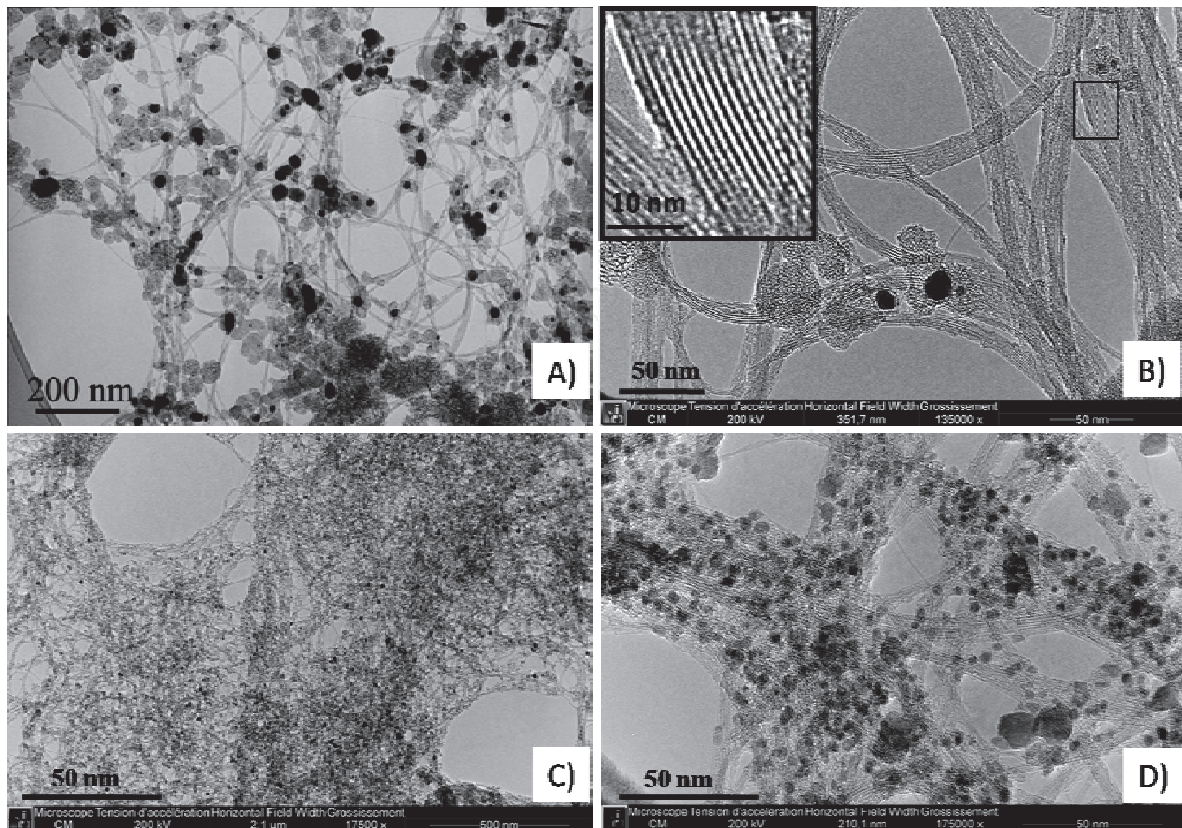
Fig. 4. TEM images at different magnifications showing arc-discharge as-produced SWNTs (A and B) (prepared in a home-made reactor) and SWNT synthesized by the HiPco process (C and D) (purchased from NanoIntergris Inc).

In principle, arc discharge and laser ablation are similar methods, both use a metal-impregnated or pure graphite target or electrode. The selection of which kind of CNT to be produced depends on the purity of graphite and the presence of catalyst. SWNTs could only be formed by adding metal catalysts (Fe, Ni, Y, Co) to graphite. MWNTs and also fullerenes can be synthesized when pure graphite is used instead. In a typical arc discharge synthesis, a low-voltage (~12 to 25 V) and high-current (50 to 120 A) power supply is used (Journet et al., 1997; Shi et al., 1999). An arc is produced across a 1-mm gap between two graphite electrodes of 5 to 20 mm in diameter. An inert gas such as He or Ar is used for the reaction, at a pressure of 100 to 1000 torr. The diameter distribution of SWNTs made by this method is roughly between 1.3 and 1.5 nm.

The characteristics of the CNTs (quality, defect amount, diameter distribution) and the nature of the impurities mainly depend on the synthesis method (Figure 4). Mass produced-SWNTs prepared by CVD (including HiPco) are usually more-defected and have a broader diameter distribution leading to less-ordered bundles than those obtained by high temperature synthesis processes (Figure 5 from U.J. Kim et al., 2005b). The carbonaceous nonnanotube impurities in the samples obtained by these latter are usually in larger concentration and show a larger variety of species compared to those included in the samples obtained by CVD. Both high temperature and CVD as-produced-CNT and especially SWNT samples contain metal residue coming from catalyst required for their growth. These catalysts are often protected by carbon shells and more or less graphitized carbon particles; and they are difficult to efficiently remove. This is especially the case for arc-discharge SWNT samples.
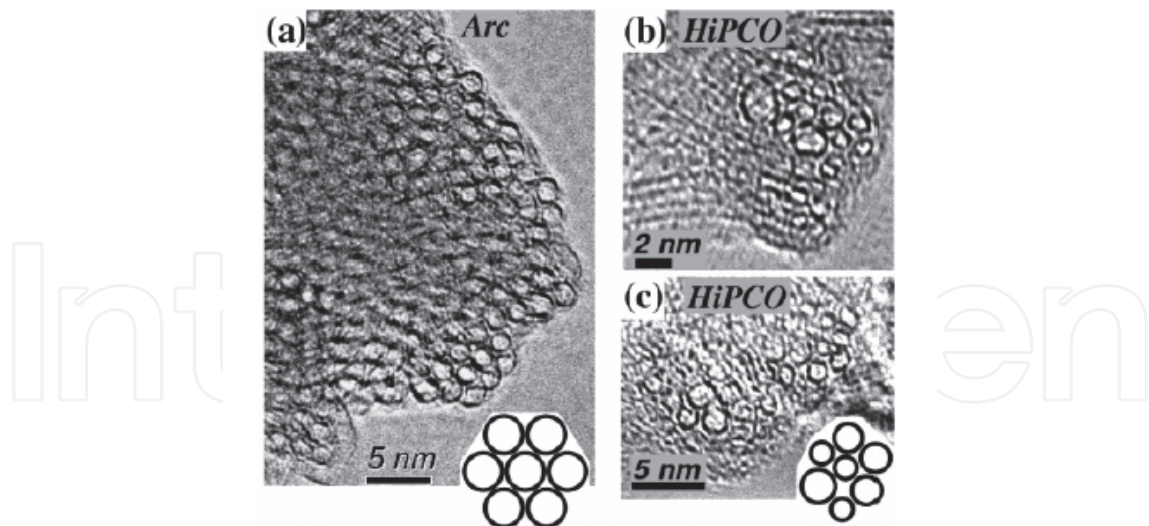
Fig. 5. TEM images of as-grown SWNT bundle cross-section produced by an arc-discharge method (a) and (b, c) SWNT bundle from HiPco materials. Insets are schematic representations of the spatial arrangement of SWNTs in the bundle for each material. From (U.J. Kim et al., 2005b) Copyright 2005 by the American Chemical Society.

3.2 Purification and purity

Even if the growing mechanisms are now better understood, it remains difficult to achieve both high-purity and high-yield CNT samples from the production methods. The as-produced soot persistently contains a part of nonnanotube species: (i) carbonaceous impurities showing large range of size and cristallinity from completely amorphous carbon to more or less ordered or well-graphitized particles and (ii) particles of residual metal catalyst required for the synthesis of SWNT-type. Numerous treatments and procedures for mass purification have been proposed, they are based on physical processes and/or chemical treatments (Hou et al., 2008; Cho et al., 2009). The physical methods are based on the difference in size, density, aspect ratio, magnetic properties between the impurities and the CNTs. They generally involve several steps of centrifugation (A. Yu et al., 2006) or filtration which prevent CNTs from severe damage. Most of the chemical procedures involve dry or wet oxidation process and/or an acid treatment. Such treatment is difficult to render selective towards the impurities because CNT are as well sensitive to the used oxidative process (Landi et al., 2005; Sen et al., 2003; Smith et al., 2003; Martinez et al., 2003;Vigolo et al., 2010a). Rigorous optimization of the experimental parameters has to be performed and adapted to the sample source. The carbonaceous impurities showing a large range of structural organization consequently lead to a large scale of stability. Moreover, inherent heterogeneities can be responsible for non controlled behaviors. The final quality of the CNTs (concentration and sidewall-defect amount) can be high but the yield consequent to the attack and the consumption of the CNTs is often disappointing. Subsequent high temperature annealing of the samples is required to restore the cristallinity of the CNTs and to remove the functions that have been grafted at their surface by the previous chemical treatments. Figure 6 (from Martinez et al., 2003) shows TEM images of SWNT samples at a raw state (a) and after each chemical treatment of the followed purification procedure. After nitric acid refluxing (b), SWNTs appear damaged due to the introduction of defects in their structure and a possible intercalation of HNO_3 molecules within the bundles. Oxidation

treatments being also aggressive to the SWNTs, bundles (c) appear as well attacked. Annealing under Ar atmosphere at 950°C for 10 h (d) is able to remove the defects and the sidewall functions introduced through previous treatments and to restore the SWNT structure.
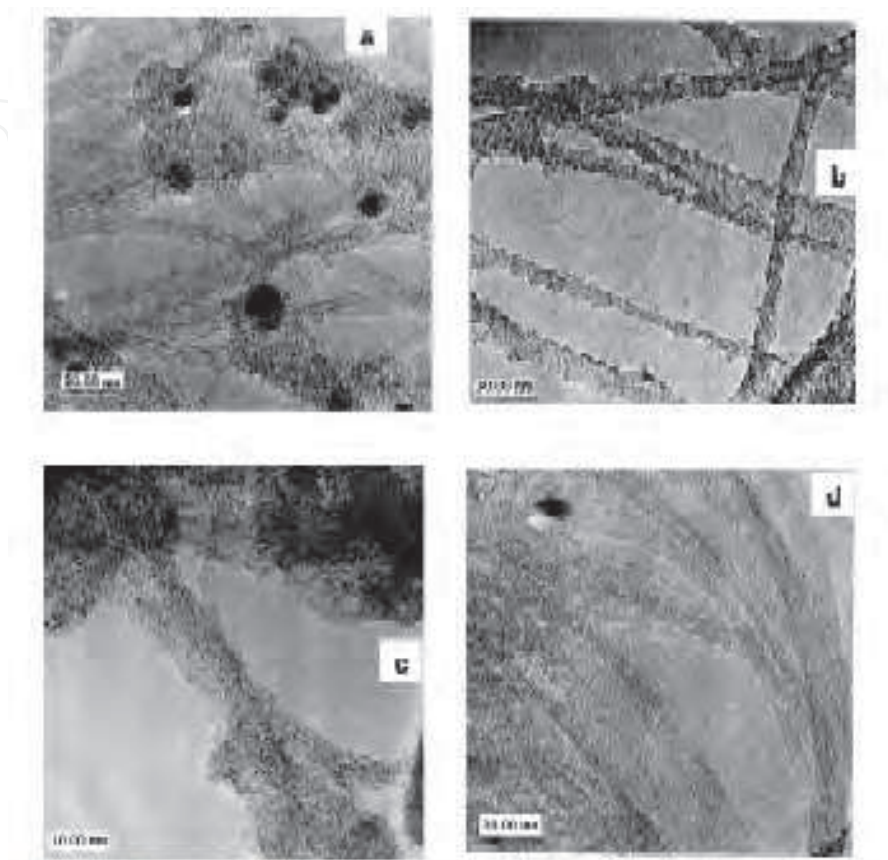

Fig. 6. TEM images of raw SWNT material (a), nitric acid-treated sample (b), air-oxidized sample (c), and annealed sample (d). From (Martinez et al. 2003) Copyright 2003 by Elsevier.

A long-standing issue involving the complete elimination of the metal catalysts from SWNT soot remains to be addressed. It is recognized that these metallic impurities (especially Ni, Fe, Co) can affect both magnetic and electric properties of the CNT samples; as well as defects that can be introduced in the CNT structure during the chemical treatments (Ellis & Ingham, 2006; Kolodiazhnyi & Pumera, 2008). Alternative nonconventional methods that combine selective elimination of catalytic impurities and weak sample-consumption have been developed. The sample is simply heated up under halogen gas (usually chlorine) combined or not- with an oxidation treatment (Zimmerman et al., 2000; Vigolo et al., 2010b). The efficiency of such one-pot process is due to the favored formation of metallic chlorides that are able to induce a mechanical stress on the protecting carbon shells leading to their fracture. In the meantime, the formed metallic chlorides being highly volatile at the used conditions, they are spontaneously eliminated from the sample by sublimation; they simply deposit out of sample at a colder location.

The assessment of CNT purity is really challenging (Arepalli et al., 2004); it does not exist a dedicated characterization technique allowing determining selectively the concentration of CNTs. The currently used techniques for the characterization of the treated samples are

MET, TGA and Raman spectroscopy. TEM allows a qualitative description of the SWNT concentration and the degree of their wall damaging. TGA carried out under oxidative atmosphere is supposed to lead to an assignment and a quantification of the present carbonaceous species from the observed temperatures of removal. Nevertheless, it is difficult to discriminate from the temperature of elimination of CNTs to that of other carbonaceous species. Raman spectroscopy can help in characterizing the damaging of the tubes upon the used treatment.

4. Modification of CNT surface properties

CNTs are often entangled according to the production process and they have high tendency to rapidly re-aggregate if no special surface agent or treatment is used to maintain them in a dispersed state. Several means can be used to modify the CNT surface properties, indispensable step for their characterization, their manipulation, their processing or their incorporation in materials (Figure 7 from Hirsh, 2002). It can be achieved by the use of surfactants (Vigolo et al., 2000; Dror et al., 2005), polyelectrolytes (Grunlan et al., 2006), biological molecules (Qiao & Ke, 2006)… that are able to reduce the interfacial energy between the CNT sidewalls and a solvent (Niyogi et al., 2002; Hirsh, 2002; Karousis et al.,
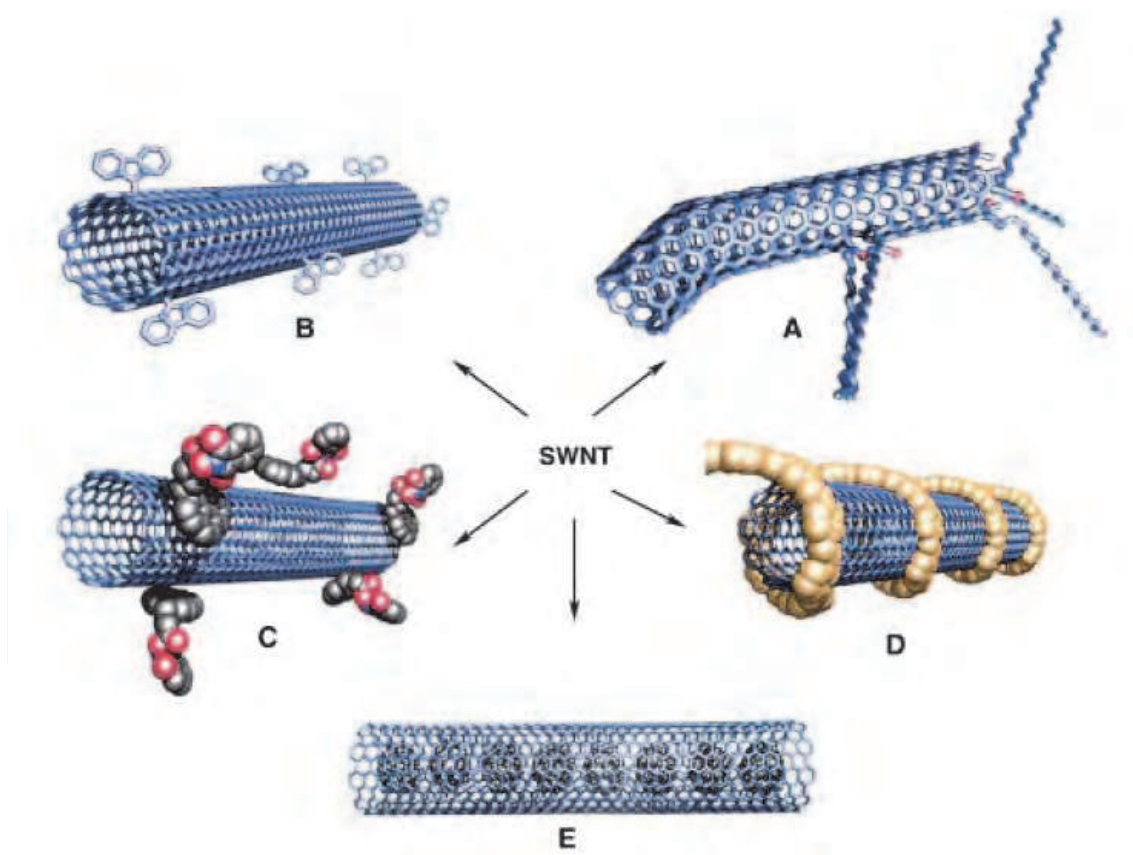

Fig. 7. Possible functionalization approaches for SWNTs. Functionalization possibilities for SWNTs: A) defect-group functionalization, B) covalent sidewall functionalization, C) noncovalent functionalization with surfactants, D) noncovalent functionalization with polymers, and E) filling tube cavity of SWNT, for example, C_{60}. From (Hirsch, 2002) Copyright 2002 by John Wiley and Sons.

2010). These physically adsorbed coatings are indeed able to counter-balance the van der Waals attractive forces between the CNT bundles and can also lead to the debundling and CNT individualization (Grossiord et al., 2005). Two others approaches are usually proposed to increase the affinity of the CNTs towards a surrounding media. Covalent functionalization which consists in the attachment of a chemical group, generally having a hydrophilic character, is recognized to be an efficient way to obtain well-quality CNT dispersions. An alternative soft-chemistry route which is based on an electron transfer between an alkali metal and the CNTs allows obtaining high-stable CNT dispersion. This process avoids any introduction of defects in CNT walls since only their electronic structure is modified. These two last mentioned processes are described in more details in the following sections.

4.1 Covalent functionalization

The use of surfactant molecules or polymers which are physically adsorbed onto the CNT surface has the advantage of not altering the CNT surface and they can facilitate their manipulation. However, for manufacturing CNT-based composites, their removal during the process is difficult and their presence in the final materials can be responsible for diminishing the composite properties. Indeed, since the remaining molecules are situated at the CNT surface, they can drastically reduce the interaction between the CNTs and the polymer matrix. The chemical functionalization which consists in covalently grafting functional groups on the CNT surface is commonly used to induce both the dispersion of CNTs in solutions of monomers or polymers and good CNT-polymer interaction.

Covalent functionalization can be realized by either modification of surface-bound carboxylic groups situated on the CNTs or direct addition of reagents to the CNT sidewalls by radical attack for example (Sun et al., 2002; Dyke & Tour 2004b). In the first category, CNTs are simply submitted to an oxidation process using HNO_3 for example (H. Yu et al., 2008). Oxygen-containing groups including carboxylic acid functions are either directly formed on intrinsic defects or are added at the CNT surface (Zhang et al., 2003). The treated CNTs can be easily dispersed in many solvents (Rosca et al., 2005; Tchoul et al., 2007) and the attached acid functions can be used as sites to attach a variety of functional groups (Niyogi et al., 2002; Wepasnick et al., 2011). In the second category, the functional groups are directly added on the CNT sidewalls without using a preceding acid attack. The developed procedures are often based on the generation of radicals that open the C=C bonds of the CNT structure. In that case, the pre-existing defects are not the favored sites but the addition mechanism rather involves an introduction of additional defects. (Dyke & Tour, 2004a; Liang et al., 2004; Mickelson et al., 1998; Ying et al., 2003). Various functional groups such as alkyl, aryl or fluorine can be covalently attached at the CNT sidewalls. Dispersability of CNTs in various solvents and in polymers can be successfully increased by using a functional group having a good affinity towards the surrounding medium. Changes in the affinity of the functionalized SWNTs towards the solvent can be merely evidenced by dispersion tests. Figure 8 shows photographs of dispersions (in DMF) of SWNT samples that have been submitted to a functionalization process in three steps. Functionalized samples are well dispersed after steps 1 and 3 (dark solution); on the contrary, the dispersion quality of SWNT-PhOH is much reduced after step 2 of the chemical process.
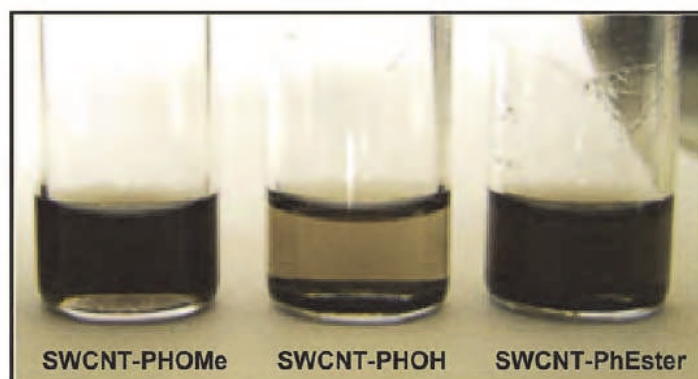
Fig. 8. Photographs of dispersions of functionalized SWNTs in DMF after each step of a chemical procedure. The photographs have been taken two weeks after the dispersion preparation. From (B. Vigolo et al., 2009b) Copyright 2009 by Elsevier.

methodology	addend	characterization techniques	degree of functionalization	highest solubility
diazonium[23,27,29,31]	aryl	UV/vis/NIR, Raman, TGA, XPS, ATR-IR, AFM, TEM	1 addend in every 10 carbons in SDS/water and 1 addend in every 25 carbons in organic solvent or neat	0.8 mg/mL in DMF
diazonium in oleum[30]	aryl	UV/vis/NIR, Raman, TGA, XPS, ATR-IR, AFM, TEM	1 addend in every 20 carbons	0.25 mg/mL in H$_2$O
fluorination[28]	fluorine	ATR-IR, AFM, STM, VTP-FIMS, UV/vis/NIR, Raman, TGA	1 addend in every 2 carbons	1 mg/mL in 2-propanol
radical chemistry[32]	alkyl	Raman, ATR-IR, UV/vis/NIR, TGA	1 addend in every 6 carbons	not given
dissolving metal reduction (Billups reaction)[38]	alkyl, aryl	TEM, AFM, Raman, ATR-IR, TGA MS	1 addend in every 17 carbons	not given
azomethine ylides (Prato reaction)[39]	pyrrolidine	UV/vis/NIR, Raman, TEM	1 addend in every 100 carbons	50 mg/mL in CHCl$_3$
nitrene[40]	aziridene	XPS, AFM, TEM, NMR, UV/vis/NIR, Raman	1 addend in every 50 carbons	1.2 mg/mL in DMSO
Bingel reaction[41]	cyclopropane	AFM, ^{19}F NMR, XPS	1 addend in every 50 carbons	not given
dichlorocarbene[42]	cyclopropane	mid-IR, Raman, EDS, UV/vis/NIR, AFM, thermal	1 addend in every 25 carbons	not given

Table 1. Common SWNT sidewall functionalization methodologies. From (Dyke & Tour 2004b) Copyright 2004 by the American Chemical Society.

Numerous chemical routes have been developed; they are able to attach various functional groups at the CNT sidewalls. They are based on the use of a highly reactive intermediate which is required to attack the carbon nanotubes. As example, table 1 gives the mainly used methods. The aim here is not to enter into details for each method of functionalization but focus the discussion on the related functionalization levels: pertinent parameter for CNT-based materials. Based on its high reactivity with graphite, fluorination was chosen for initial studies (Mickelson et al. 1998). In that case, the very high functionalization level can be found since one C-F function is present every 2 carbon atoms on the CNT. The second methodology involves the well-known substitution by benzenediazonium salts; it leads obtaining CNT being less functionalized with 1 function every 10-20 carbons (Dyke & Tour, 2004a). Arylation and alkylation of CNTs often used as preliminary step for numerous functionalization procedures, can be also obtained by radical reactions for which the degree of functionalization depends on the used process for the generation of the radicals as we will see (Ying et al. 2003; Liu et al., 2007a). SWNTs can be as well modified using cyclization

reactions using reactive carbene and nitrene reagents to attack the SWNT walls (Holzinger et al., 2003). Cyclopropanation of SWNTs under Bingel reaction conditions has also been reported (K.S. Coleman et al., 2003). In the case of the functionalization process developed by Billups and coworkers, the reaction leads to ultrahighly lithiated SWNTs (1 lithium atom per 2.2 carbon atoms) that can be further treated with numerous electrophiles including alkyl halides, aryl halides, and even vinyl monomer. Interestingly, functionalized SWNTs are obtained in an individualized state (Liang et al., 2004).

As we have just seen, depending on the chemical mechanism and procedure, the obtained levels of functionalization can be relatively elevated. Integration of covalently functionalized CNTs in polymer matrix could induce good stress–strain transfer between nanotubes and polymer guarantying interesting mechanical properties in composite materials (c.f. section 5). Nevertheless, the breaking of CNT conjugated π system may have negative impact on properties (conductivity, in particular) of the obtained composites (Garg & Sinnott, 1998; Byrne & Gun'ko, 2010; Bose et al., 2010). This is the reason why, for composite processing, the functionalization levels have to be controlled and maintained relatively low in order to avoid a strong alteration of the CNT structure. However, grafting degrees are not easy to master and they mainly depend on the involved mechanism of reaction and the means used to facilitate the reaction (Syrgiannis et al., 2010). Chemical reactions assisted by micro-wave are recognized to lead to higher functionalization degree than those obtained by thermally-assisted reactions(Liu et al., 2007b). The chemical procedure we have developed is based on the direct attack of the sp² carbon on the CNT surface. It advantageously allows having a certain control of the yield of functionalization without the introduction of a large number of defects (Liu et al., 2006; Vigolo et al., 2009b). The obtained low yield of functionalization is efficient enough to modify the surface properties of the CNTs but preserve their structural integrity (Dossot et al., 2007). The other main difficulty regarding the integration of functionalized-CNTs in polymer matrix concerns the homogeneity of the functionalization degree on the CNT surface over the several milligrams of the used CNT sample for composite elaboration (Vigolo et al., 2009c). Because of the high tendency of CNTs to form aggregates, accessibility of reactants to CNT surface has to be improved by using pre-dispersion process (usually done by ultrasounds). Depending on the used solvent which is conducted by the functionalization treatment itself, the CNTs are often poorly dispersed.

4.2 CNT reduction: dispersion and debundling

Development of soft chemistry processes such as intercalation reactions is highly challenging for both dispersion and debundling of the SWNT bundles. Indeed, CNTs have demonstrated an amphoteric character since they can be doped or intercalated either by electron-donors or -acceptors (Duclaux, 2002). These reactions are accompanied by an electronic transfer that has been evidenced by means of several techniques such as transport measurements (Grigorian 'et al., 1998; Fischer, 2002) or various spectroscopies and especially Raman spectroscopy (Bendiab et al., 2001; G. Chen et al., 2005). This electronic transfer could as well play a major role in the dispersion process of SWNT bundles. To our knowledge, only donor-type reactions with SWNTs have been successfully used for this purpose. Donor-type reactions are carried out with the strongest reducing metals: the alkali metals. Three routes are possible. The chemical reduction can be thermally assisted (i) in vapor phase or conducted (ii) in liquid phase at room temperature; or, (iii) based on an electrochemically process. The electrochemical intercalation that was mainly studied with lithium is known to induce damages of the SWNTs by progressive solvent co-intercalation.

In-situ X-ray diffraction evidences an irreversible loss of the "triangular" lattice of SWNTs (Fischer, 2002). Routes (i) and (ii) do not show any alteration of SWNT structure. Light alkali metals, lithium and sodium were firstly chemically intercalated into SWNTs using the liquid phase method in THF solutions with several radical anions (naphtalene, benzophenone, anthraquinone, benzoquinone) at ambient temperature (Petit et al., 1999). Heavy alkali metals such as potassium could also be successfully intercalated by means of the same method. In that case, within the obtained compounds, intercalated alkali cations are surrounded by solvent molecules (THF, for example). Figure 9 gives a scheme of two ternary intercalation compounds and reveals that the intertube distance depends on the size of the alkali metal.
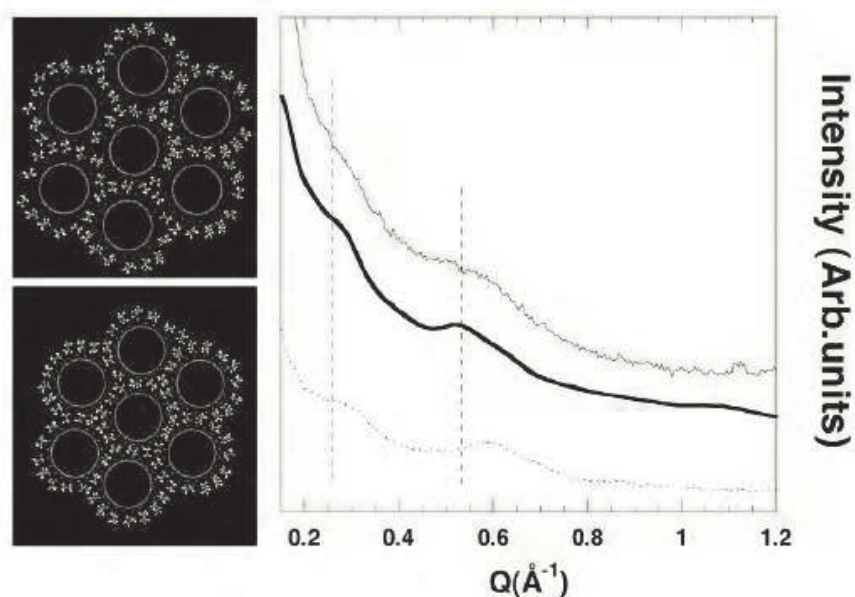

Fig. 9. Left part: Structure of the $KC_{5.88}$-THF (top) and the $LiC_{5.88}$-THF (bottom) compound after energy minimization. Right part: Experimental Neutron Diffraction patterns of the $KC_{5.88}$-THF sample (upper line) and the $LiC_{5.88}$-THF (lower dotted line, shown for comparison). The bold line is a calculated Neutron Diffraction pattern of the $KC_{5.88}$ sample involving the structural parameters described in the text. From (Cambedouzou et al., 2005) Copyright 2005 by the American Physical Society

In the case of intercalation in liquid phase, the electronic transfer was estimated from optical absorption response of the formed radical ion. Heavy alkali metals could be intercalated into SWNTs using vapor phase method (Duclaux, 2002; Duclaux et al., 2003; Vigolo et al., 2009c). The reaction temperature depends on the used alkali metal, more precisely on its vapor pressure. Contrary to the previous method, the vapor-phase process allows preparing binary compounds. The structure of the intercalated materials strongly depends on the quality and the structural parameters of the SWNT sample. For heavy alkali metals, an expansion of the 2D lattice is often observed (Duclaux, 2002). This expansion is reported to be due to the occupation of the interstitial channels. However, the precise location of the alkali metal atoms and the type of sites preferentially occupied are difficult to determine. Moreover, from different observations and measurements, it is possible to claim the absence of intercalation stages in SWNT system contrary to that could be observed in graphite intercalation compounds. The level of chemical intercalation is then difficult to control. The

excess of reagent with respect to carbon materials during the chemical reactions leads generally to "saturated" materials. However, the intercalation process itself remains poorly understood because it is not a straightforward process. Indeed, it involves some modifications of both the SWNT electronic structure upon a reduction reaction and the structural parameters subsequent to the intercalation of guest species within the host structure. Two main forces oppose each other throughout the chemical process: favorable forces resulting from the electron transfer and non favorable mechanical forces acting against an increase of the 2D lattice. As for graphite intercalation compounds, the obtained structure mainly results from the balance between these two opposite forces.
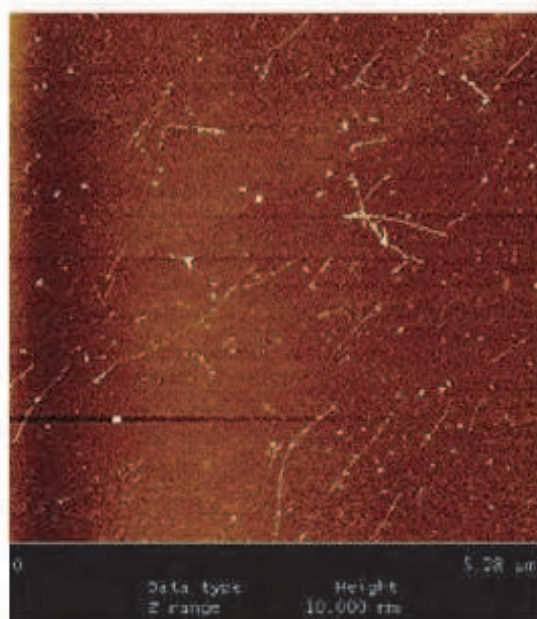

Fig. 10. AFM height image of electric arc SWNTs deposited on mica from solution after debundling process of ternary intercalation compounds prepared by a liquid medium intercalation method. Height measurements show a height of about 1 nm on all nanotubes measured consistent with the presence of isolated SWNTs in the solution. From (Pénicaud et al., 2005) Copyright 2005 by the American Chemical Society.

Beyond the precise understanding of the intercalation process itself, the preparation of SWNT-intercalation compounds is of great interest since the obtained reduced SWNTs are able to be dispersed and partially or completely debundled. Indeed, these intercalation compounds can be assimilated to salts capable to dissolve in aprotic polar solvents such as NMP (1-méthyl-2pyrrolidone), DMF (dimethyl formamide) or DMSO (dimethyl sulfoxide) (Pénicaud et al., 2005; Vigolo, et al. 2009c). Such dissolution-like mechanism is spontaneous avoiding the need of sonication or other high energy mechanical mix methods which can damage CNTs. The obtained dispersions are highly stable as long as they are kept in inert atmosphere. Polarity is a key parameter for minimizing the mixing energy of particles in a solvent. The electron transfer between carbon atoms on the CNT surface and the intercalated metal, increasing the surface reactivity, is very helpful for the dispersion of CNTs in polar solvents. Regarding the question of the preferentially occupied sites, the dispersion stability indicates that alkali metal atoms certainly occupy the external sites and the groove sites of the bundles. Moreover, locally the presence of alkali metal atoms in the interstitial sites (between two tubes within a bundle) will favor the debundling process since the increase of

the 2D lattice has already taken place. The dispersion process is then expected to lead to the debundling of the nanotubes between which alkali metals were inserted. The degree of debundling will then depend on the level of filling of interstitial channels. Indeed, if the interstitial channels are not occupied at all, preserved bundles should be observed after dispersion. On the contrary, in the case of a complete occupation of the interstitial sites, complete debundling of SWNTs leading to their individualization is observed. This is the case of SWNTs reduced by alkali metals in liquid phase (Pénicaud et al., 2005). It is then possible to prepare solution containing individualized SWNTs (Figure 10).

In the case of binary compounds prepared by vapor phase, only partial debundling is observed, explained by a non compete filling of the interstitial sites especially favored at the ending and the external part of the bundles. This partial debundling leads to hyperbranched structures of CNTs (Figure 11).
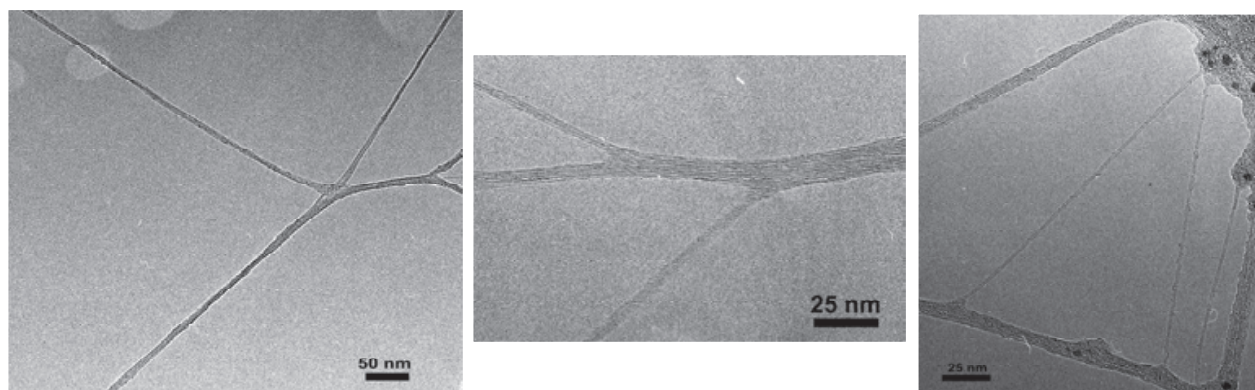

Fig. 11. TEM images of SWNT bundles after the debundling process of binary alkali metal-SWNT compounds prepared through a vapor-phase intercalation process.

This method involving a CNT reduction reaction is of great interest since it allows the formation of individual CNTs or hyperbranched structures of CNTs reducing that way the size of the usually obtained bundles and increasing the developed interfacial surface. Obtaining transparent and conducting composites or antistatic coatings are some of the most challenging applications of CNTs. High-quality dispersions of debundled non-defected SWNTs can be of great interest for manufacturing such new CNT-based composites.

5. CNT-based composites: multi-scale materials

CNTs are recognized to be the ideal filler to obtain superior composites (J.N. Coleman et al., 2006). Their high aspect ratio combined to their lightness is one of the fundamental requirements for reinforcement of polymer matrices. The challenge consists in successfully transfer both the remarkable mechanical and conductive intrinsic properties of the CNTs at the macroscopic scale of the composite materials. Dispersion is known to be certainly the most fundamental issue. Efficient load transfer cannot be achieved if CNT aggregates remain within the polymer matrix; CNTs have to be randomly dispersed in bundled or isolated state. Their alignment is also reported to enhance the mechanical properties along the CNT axis (Xie et al., 2005). High interfacial strength between CNT surface and the polymer matrix is also an indispensable requirement to induce efficient stress transfer within the composites (Cadek et al., 2004; Gorga et al., 2006).

Various procedures have been developed for the preparation of CNT-based composites (Fiedler et al., 2006; Ma et al., 2010; Spitalsky et al. 2010). Functionalization is widely used to achieve both the dispersion of CNTs and a good wetting between CNTs and polymer chains. Indeed, the procedures that consist in simply mixing non-treated CNTs in the polymer system (either solubilized in a solvent or used in a melting state) present the advantage to be compatible with large-scale production but re-agglomeration phenomenon is still difficult to avoid. Two main approaches for the incorporation of functionalized CNTs in polymer matrices have been developed: *grafting to* and *grafting from*. Their principle is here briefly recalled. The "grafting to" method consists in the attachment of already preformed end-functionalized polymer molecules to functional groups on the CNT surface (Z. Yang et al., 2005). The main limitation of this technique is that the initial binding sterically prevents diffusion of additional macromolecules to the surface. The "grafting from" method consists in first grafting monomer-like functional groups on the CNT surface; the polymerization reaction being further initiated in the monomer solution, the formed polymer chains are directly bound to the CNTs. This method requires a strict control of the amount of the initiator but allows efficient polymer-CNT binding (Jia et al., 1999). Such *in situ* polymerization method in the presence of the functionalized CNTs has been successfully developed (Velasco-Santos et al., 2003; Putz et al., 2004; Vigolo et al. 2009a). The main advantage of this method is the possibility of creating covalent bonds between a modified CNT surface and the polymer matrix.

Nanotube/Polymer Composite	Nanotube Functionality	Preparation Techniques	Y_{poly} [GPa]	Y_{Max} [GPa]	NT content [wt%]	dY/dV$_f$ [GPa]	Reference and Year
CVD-MWNT/methyl and ethyl methacrylate P(MMA-co-EMA)	Octadecylamine	Solution casting	1.64	2.62	10	15	[131] 2004
SWNT/epoxy	Large organic groups	Solution casting and curing	2.02	3.4	4	95	[77] 2004
SWNT/polyamide 6 (PA6)	PA6	Solution casting and melt spinning	0.44	1.2	1.5	120	[132] 2005
SWNT/PVA	Hydroxyl	Solution casting	2.4	4.3	0.8	305	[133] 2005
CVD-MWNT/PVA	Ferritin protein	Solution casting	3.4	7.2	1.5	380	[134] 2005
MWNT/PC	Epoxide	Solution casting and injection molding	2.0	3.8	5	95.5	[135] 2006
MWNT/PMMA	PMMA	Melt mixing and extrusion	2.7	2.9	3	18.15	[136] 2006
CVD-MWNT/PVC	CPP	Solution casting	0.56	0.9	1	115	[129] 2006
CVD-MWNT/PS	CPP	Solution casting	1.48	2.63	1	304	[129] 2006
SWNT/copolymers of styrene and vinyl phenol (PSVPh)	Carboxylic acid	Solution casting	1.5	2.1	5	24.25	[44] 2006
CVD-MWNT/PU	Carboxylic acid	Solution casting	0.05	0.42	20	4.5	[46] 2006
SWNT/biosteel (synthetic spider silk)	Octadecylamine	Solution casting	1.6	1.9	0.125	381	[122] 2007
SWNT/PAMAM	Epoxy	Solution casting and curing	2.76	3.49	1	153	[56] 2008
CVD-MWNT/Kevlar	PVC	Solution casting	1.5	2.5	2	300	[64] 2008
CVD-MWNT/epoxy	TETA	Cast molding	1.56	2.4	0.6	355	[126] 2008
CVD-MWNT/PS	Butyl	Solution casting	1.29	1.63	0.25	433	[130] 2008

Table 2. Mechanical properties of polymer composites containing functionalized CNTs. From (Byrne & Gun'ko, 2010) Copyright 2010 by John Wiley and Sons.

Both conductivity and mechanical properties (see table 2,) of composites containing functionalized CNTs cover quite a large domain (Byrne & Gun'ko, 2010). Mechanical performance of the obtained materials showing the highest Young's modulus of 7.2 GPa (Table 2) is to a certain extent disappointing compared to Young's modulus of the CNTs being more than 100 times higher. It is however essential to remind, that the measured properties depend on the CNT type, the treatment used to modify CNT reactivity and the used preparation technique. It is indeed difficult to directly compare the values of Young's modulus

to estimate the effectiveness of a given CNT-polymer system. Moreover, the rate of increase of the Young's modulus (dY/dV_f) as a function of the concentration of CNTs within the matrix is reported to be a most pertinent parameter for a quantitative evaluation of the induced reinforcement (Cadek et al., 2004). The interfacial area in CNT-based-materials plays a fundamental role in the reinforcement mechanism and dY/dV_f indeed quantifies the efficiency of the interfacial area to reinforce the obtained materials (table 2).

Micromechanical mechanisms for the reinforcement phenomenon in CNT-based composites are not easy to ascertain due to the multi-scale character of the materials. The interfacial stress transfer could be analyzed by means of fiber pullout model. If adhesion between CNT surface and polymer matrix is efficient, crack propagation tends to be inhibited by a bridging phenomenon increasing the toughness of the material. Reinforcement is thus provided by the positioning of elongated nanoparticles perpendicular to the cracks reinforcing the brittle polymer zone by CNT bridges. Resulting CNT pullout could be useful to characterize mechanical reinforcement in CNT-polymer composites (Hwang et al., 2004; Cooper et al., 2002).
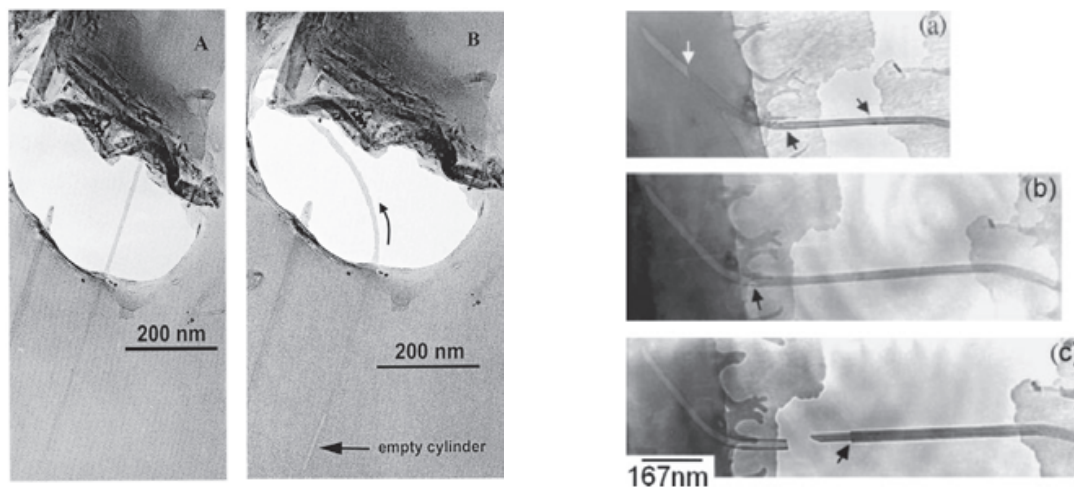

Fig. 12. TEM images of a MWNT crossing a hole in CNT polymer composites: the fiber pullout model. On the left side (from Cooper et al., 2002) (a) TEM image of a nanotube bridging a matrix hole. The bridging nanotube in this image has a diameter of 8.2 nm. (b) TEM image of same specimen following partial pull-out by means of a scanning probe microscope (SPM) tip. The direction of the tip movement was from right to left across the hole; The larger arrow shows the direction of the tip movement; the small arrow indicates the empty cylindrical hole left behind after partial pullout. Copyright 2002 by the American Institute of Physics. On the right side (from Hwang et al., 2004), TEM images of MWNT bridges in PMMA (poly(methyl methacrylate) matrix taken at different times a) t=0, b) t=4, and t=10 min. Copyright 2004 by John Wiley and Sons

Added to the development of tailored preparation procedures, studying CNT-based materials requires tools, techniques and methods that are able to relate the behavior at the molecular scale to the composite properties at a macroscopic scale (Wagner & Vaia, 2004). Beyond the experimental parameters or the nature of the CNT-polymer system, the mechanisms that take place at the CNT-polymer interface have to be better understood; they are indeed recognized to be the key for the CNT-based composite processing.

5. Conclusion

To summarize, significant progress has been achieved in the area of CNT processing. A range of new chemical treatments that are tailored in agreement with the desired application of the CNTs have demonstrated interesting results. Among them, covalently functionalized CNTs have been shown to improve both dispersion and polymer–CNT interaction. Avoiding damaging of the CNT structure upon chemical functionalization or purification procedure is still challenging. Further, the exact influence of the pre-treatments on the chemical and physical properties of the CNTs is difficult to assess. Regarding CNT-based composites, the prevailing problems of dispersion and stress transfer are not completely being overcome. However progress in this area has to be continued for the development of selective and innovative chemical treatments that will hopefully help for manufacturing of CNT-based devices and materials.

6. Acknowledgment

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Carbon Nanotubes - Synthesis, Characterization, Applications

Edited by Dr. Siva Yellampalli

Carbon nanotubes are one of the most intriguing new materials with extraordinary properties being discovered in the last decade. The unique structure of carbon nanotubes provides nanotubes with extraordinary mechanical and electrical properties. The outstanding properties that these materials possess have opened new interesting researches areas in nanoscience and nanotechnology. Although nanotubes are very promising in a wide variety of fields, application of individual nanotubes for large scale production has been limited. The main roadblocks, which hinder its use, are limited understanding of its synthesis and electrical properties which lead to difficulty in structure control, existence of impurities, and poor processability. This book makes an attempt to provide indepth study and analysis of various synthesis methods, processing techniques and characterization of carbon nanotubes that will lead to the increased applications of carbon nanotubes.

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