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Hybrid carbon nanotubes: Strategy, progress, and perspectives

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We introduce the concept of meta-nanotubes, among which are hybrid carbon nanotubes (X@CNTs), which are CNTs whose hollow core is filled—fully or partially—with foreign atoms, molecules, or compounds. The article focuses on the latter, describing their potential interest and the various ways currently available to synthesize them, while providing examples of the resulting materials mainly taken from the author's works but also from literature, as characterized by means of high-resolution microscopy and related techniques. We discuss advantages and drawbacks of the various synthesis routes to help willing scientists and engineers to define a strategy for X@CNT synthesis with respect to their specific goals and expectations. Some examples of peculiar properties and behaviors of X@CNTs will be provided as well, although such related investigations are still scarcely reported because we are dealing with quite new nanomaterials.

I. INTRODUCTION

A. Time for a third generation of carbon nanotubes

Although it might not be of common knowledge,¹ the evidence for the existence of nanosized, hollow carbon filaments, i.e., carbon nanotubes (CNT), was reported first in 1952,² as a result of the thermal decomposition of hydrocarbon precursors over transition metal catalysts [a method commonly named catalyst-enhanced chemical vapor deposition (CCVD)]. They were, of course, multi-walled-type CNT (MWNTs), which can be considered the first generation of carbon nanotubes. The second generation of carbon nanotubes was born far later, in 1993, when single-walled CNT (SWNTs) were unexpectedly discovered within the carbon materials produced from electric arc experiments when a graphite anode is loaded with, again, transition metals.^{3,4} Hence, it has been approximately 13 years for SWNTs, and approximately 50 years for MWNTs (yet definitely boosted by the well-known paper by Iijima⁵ in *Nature* in 1991), that CNT have been investigated regarding their possible

synthesis routes and properties. Currently, the relevant synthesis processes are defined, and although the electric arc method is still a commercial route, it is clear that CCVD will be the main process for mass production of SWNTs in the near future, as it is for MWNTs already. Likewise, most of CNT properties are now predicted and even demonstrated for many of them. In spite of several aspects that are still worth studying further regarding synthesis (addressing cost, purity, and selectivity problems), formation mechanisms (which are not clear in many instances), and theory (e.g., electron transport in SWNT is still worth being investigated in many instances), most of the current research efforts are dedicated to the demonstration of the anticipated behaviors of CNT, and to the actual incorporation of the latter in devices. As a natural evolution of a scientific field becoming more mature, many research activities have actually shifted from nanoscience to nanotechnology. Of course, the latter is a very important research field because the specter of the previous economical and technological failure of fullerenes still haunts the engineering community, and CNT must now demonstrate that applications will actually follow the expectations. At this level of maturity of the knowledge of CNT, one might wonder whether significant scientific (i.e., not merely technological) novelty or progress may now be expected regarding

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CNT. The answer is yes, thanks to a third generation of CNT that may be named “meta-nanotubes,” which are more often the focus of scientists worldwide.

B. Introducing meta-nanotubes

One motivation for developing meta-nanotubes is to find alternative ways for overcoming some of the recurrent drawbacks of pristine nanotubes, e.g., the impossibility of obtaining a single batch of SWNTs having the same electronic behavior. Another example of motivation is providing nanotubes with properties that they do not possess at the pristine state, e.g., ferromagnetic behavior. Meta-nanotubes result from the transformation of pristine nanotubes by various ways, generally involving chemical treatments. For such nanomaterials, nanotubes are no longer considered as such, but merely as starting materials that will be used as host, substrate, mold, structural skeleton, etc. Five categories of meta-nanotubes are listed below, but others are possible. In this field, imagination has the power.

1. Functionalized nanotubes

Functionalized nanotubes are nanotubes at the surface of which various individual chemical functions are grafted (see Refs. 6 and 7), i.e., where the foreign material does not form a phase by itself. It is a quite important topic, mostly developed to address some of the major issues of pristine CNT such as reactivity, dispersability, solubility, etc., which are compulsory properties for many processes involving nanotubes. One example includes the requirements for making nanotube-reinforced composites, i.e., a good dispersion of the nanotubes within the matrix has to be obtained so that a sufficient homogeneity is reached, and a sufficient bonding between the nanotubes and the matrix has to be created so that part of the mechanical load is able to be transferred from the latter to the former. Typically, specifically SWNTs are not suitable for such a use at the pristine state because of their propensity to gather into bundles and their low surface reactivity. Functionalization may also change the electronic behavior of the whole with respect to the pristine nanotubes, for instance, by making them better electron donors. It may also be used to promote bonding between nanotubes (in view of building nanoscale assemblies), to allow nanotubes to be attached at specific sites, to align nanotubes, etc.

2. Coated nanotubes

Coated nanotubes are nanotubes at the surface of which a foreign material is deliberately fixed, as a continuous or a discontinuous coating. They are most often nanoparticles, but the category may also include nanotubes onto which complex compounds are adsorbed or bonded, such as polymers, biomolecules, etc. (see Ref. 8

and Refs. therein). In related applications, the intrinsic properties of the nanotube underneath may be of a minor importance because the nanotubes may basically be used as a substrate, while the needed properties are brought by the coating material. A major example is the use of CNT—specifically MWNTs—as a support for nanosized catalysts,^{9,10} which is one of the major current motivations for developing low-cost mass production of MWNTs. When exhibiting a somewhat defective surface (e.g., herringbone-type MWNTs from CCVD, as opposed to concentric-type MWNTs from arc plasma processes, which are too much perfect), MWNTs are able to attract and/or retain nanoparticles with sufficient nanotube/particle interaction so that the thermally induced diffusion of the latter at the nanotube surface is limited, thereby preventing impingements between particles and the subsequent coalescence of the latter. All the catalyst supports currently used (e.g., alumina foam) actually exhibit the desired surface properties, but nanotubes offer the appropriate combination of a widely open mesoporous network and high specific surface area. It is worth noting that functionalizing nanotubes so that the nanotube surface attractiveness toward the nanoparticles is enhanced may be a preliminary step in the preparation of coated nanotubes. Particle-coated nanotubes (more specifically, SWNTs) are also attractive solutions in addressing and/or interconnecting SWNTs for building nanoelectronic devices.¹¹

3. Heterogeneous nanotubes

Heterogeneous nanotubes are CNT whose carbon atoms from the hexagonal graphene lattice are partially or even totally substituted with hetero-atoms, typically nitrogen and/or boron. Obviously, one of the major consequences of such a substitution is the modification of the electronic structure—and thereby the electronic behavior—of the resulting nanotubes. Typically, as opposed to pristine SWNTs, such heterogeneous SWNTs should exhibit a metallic behavior whatever their helicity.¹² Because selectively controlling the formation of metallic or semiconductor SWNTs upon controlling the appropriate helicities is still a challenge thus far, acting on the chemical composition of SWNTs appears to be a way to obtain whole batches of SWNTs exhibiting the same electronic (metallic) behavior. Other benefits for such substituted nanotubes are the expected improvement of the resistance to oxidation or, on the contrary, the enhancement of surface reactivity toward chemical reactions specifically involving aromatic nitrogen or boron.

4. Doped nanotubes

Doped nanotubes are CNT that have been associated with electron donor or acceptor elements such as Br₂, K, Rb, etc. (or, more rarely, compounds), generally to modify the overall electronic structure and behavior (see

Refs. 13 and 14 and Refs. therein). The association is close, i.e., it is not merely a matter of coating or grafting the outer surface, and does not involve strong chemical bonding. The association mechanisms and the doping process are more related to that of intercalation compounds in graphite, and the inserted element (e.g., Li, K, etc.) is therefore found in between graphenes in MWNTs, or in between SWNTs in SWNT bundles. The doping material does not make an individual phase, as opposed to the coating materials (see Sec. I. B. 2) or the filling materials (see Sec. I. B. 5). The doping process is usually reversible, although it may not allow doping-dedoping cycles to be carried out because such doped nanotubes are unstable in some conditions, e.g., in air. However, when cycling is possible, building energy storage devices is one of the major expected applications for doped nanotubes.

5. Hybrid nanotubes (X@CNTs)

X@CNTs are CNT in which the inner cavity has been filled with foreign atoms, molecules, or compounds. They are probably the most versatile among the meta-nanotubes described here, and thereby are likely the ones that open the wider research field, regarding scientific and technological aspects. As opposed to doping, the filling constituents generally gather and associate into a phase, and the filling event may show variable reversibility upon solvating methods, specifically regarding SWNTs.^{15,16} This article is dedicated to these materials.

II. SYNTHESIS OF X@CNTS

A. A bit of history

The story of X@CNTs started 2 years after the possibility to easily synthesize nearly defect-free, concentric-type MWNTs via a catalyst-free process (i.e., the same electric arc procedure used to produce fullerenes) was reported by Iijima in 1991.⁵ Four papers were published in 1993 that reported some filling of MWNTs with various metals and compounds (PbO,¹⁷ Y₃C and TiC,¹⁸ Bi₂O₅,¹⁹ and Ni²⁰) in attempts to obtain encapsulated inorganic nanowires. However, inner diameters of MWNTs are generally quite large (an average of 5–50 nm) and filling the much smaller inner cavity (range of 1–1.5 nm) of SWNTs that were discovered in 1993^{3,4} appeared more challenging. It actually took 5 years for the first two doubtless examples of hybrid SWNTs to be reported (Fig. 1). One was the incidental discovery of the ability of fullerenes to enter SWNTs, thereby forming the so-called “peapods.”²¹ The other, involving RuCl₃²² was the first work of a long series by the University of Oxford, which has thoroughly investigated the filling of SWNTs since then (see, for instance, Refs. 23 and 24) to the extent that makes them the world leader in the field.

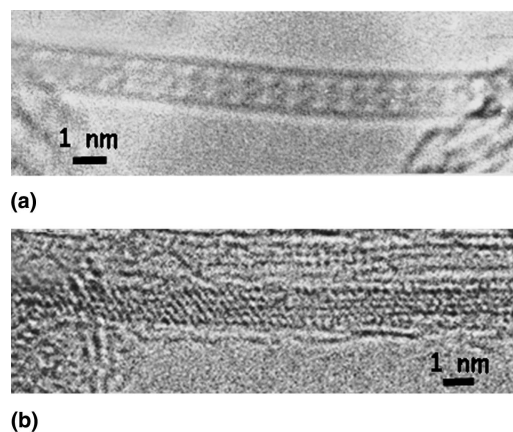


FIG. 1. Pioneering transmission electron microscopy (TEM) images in the field of hybrid SWNTs, both published in 1998. (a) The first example of C₆₀@SWNT (peapod).²¹ (b) The first example of metal@SWNT,²² in the latter, the metal is Ru and was initially introduced as RuCl₃ and then was chemically reduced. By permission of the Royal Chemical Society.

By similarity with the accepted notation for endo-fullerenes, SWNTs filled with fullerenes were symbolized as C₆₀@SWNT,²⁵ which rapidly became the overall notation for any kind of X@CNT, where X is the chemical symbol of the filling material and CNT is the nanotube type [SWNT, double-walled (DWNT), or MWNT].

B. Motivation

In a way similar to coated nanotubes for which the latter are basically considered as a mere substrate, nanotubes can be merely considered for their inner cavity, i.e., an empty volume that can be used as a nanomold and/or a nanoreactor (when the post-transformation of a previously inserted material is carried out) for the synthesis of nanomaterials. Thanks to the huge and unique aspect ratio of nanotubes, the inserted materials are enforced to adopt a genuine one-dimensional morphology, specifically considering SWNTs whose aspect ratio is much higher than that of MWNTs. On the other hand, the containing nanotubes may act as nanocapsules protecting the contained materials from any reaction with the surrounding medium, typically oxidation by contact with the atmosphere. Nanotubes may then make possible the synthesis of nanowire-like materials that could never exist if not encapsulated. Indeed, nanowires of 1 nm in diameter would rapidly turn into oxide nanowires or would even possibly collapse, as recently demonstrated by attempts to remove the carbon sheath from hybrid SWNTs.²⁶ In both cases, chances are high that any peculiar property is lost. Generally speaking, growing phases within a very confined volume allows for the formation of new nanomaterials to be expected because of the possibility opened to enforce and stabilize new combinations of chemical elements, to enforce and stabilize novel crystal structures for regular chemical phases, and to deform and stress lattices within regular structures.

Of course, new nanomaterials are mainly valuable if they come with new, or enhanced at the least, physical properties. The latter are expected from the stabilization of otherwise impossible new chemical compositions, structures, or morphologies, as described in the previous paragraph. A typical example is the ballistic transport behavior from the one-dimensional, which prevents electron scattering; the very unusual [surface atoms over core atoms] ratio, which may even reach an infinite value, i.e., all the atoms of the structure can be surface atoms; and the protection by the carbon sheath from the surface adsorption of disturbing molecules. A typical expected benefit, yet to be demonstrated, regards nanowires made of magnetic elements or compounds, and electronic interactions (typically, charge transfer) with the encapsulating graphene lattice.

Finally, should encapsulated phases not exhibit new structures, chemical composition, or physical properties, encapsulation may provide external reactants peculiar access conditions to the filling materials, thereby controlling the behavior of the latter by controlling the interaction kinetics with the surrounding medium. Of course, this could occur in a negative manner, for instance, regarding the filling material chemical reactivity that may be more or less inhibited in spite of the nanosize because of the presence of the carbon sheath. On the other hand, this modified behavior regarding chemical reactivity may be useful to some applications, for instance, slowing down diffusion kinetics and/or chemical reactivity may be very valuable in fields such as chemical catalysis, drug or pesticide delivery, etc.

Hence, encapsulating materials in CNT is likely to promote new phases, new structures, new properties, and/or new behaviors. However, any of these features will be more likely as the tube cavity diameter is smaller. Filling nanotubes whose inner cavity is below ~ 2 nm wide, as is encountered in most of SWNTs and DWNTs, will therefore be preferably considered below. Detailed review papers specifically dealing with filling MWNTs may be found in the early literature.^{27,28}

C. Filling strategy

1. Parameters

Various ways of filling nanotubes may be considered, depending on the physical properties of the material being inserted, the cavity diameter to be filled, the cost issues (if for commercial purposes), and the capabilities of the methods themselves, with all parameters being more or less interdependent.

Materials can be inserted into SWNT cavities as a solid, liquid, or vapor. Hence, relevant physical properties of the materials filling the nanotubes are primarily solubility, melting point, boiling point, and, of course, decomposition temperature, which should not be reached.

When liquids are involved (molten or dissolved material), a subsequent property of the utmost importance to consider is surface tension γ . It was experimentally observed that the surface tension of liquids should be below 100–200 mN/m to wet MWNTs,²⁹ while supporting the idea that the capillarity-driven mechanisms for filling nanotubes with liquids are obeying the Young-Laplace law and equations. Later on, this surface tension threshold was more precisely defined as 130–170 mN/m for SWNTs.³⁰ In addition to surface tension, the viscosity of the liquid material is also interesting to consider as a parameter presumably important in the filling event, at least regarding the filling kinetics. These aspects will be discussed further in Sec. IV.

In addition, it might also be interesting to know the vapor pressure of the material to be inserted to estimate, if needed, whether some vapor was introduced along with the liquid.

The nanotube inner diameter is obviously an important parameter because, on the one hand, it will determine the ultimate diameter of the basic entities (such as molecules, as a vapor or a solution) able to enter the nanotube cavity. On the other hand, it is also quite important when filling with liquids because it will contribute to the determination of the filling efficiency. Previous studies actually proposed that a minimal inner diameter for the nanotube to fill is required.³¹ Because this cut-off value depends on the surface tension of the liquid involved, it does not correspond to a single value, hence, no “magic” number for the nanotube diameter can be provided. For instance, threshold nanotube inner diameters were calculated to be 0.7 and 4 nm for molten V_2O_5 ($\gamma = 80$ mN/m) and molten $AgNO_3$, respectively.^{28,31}

In addition to the intrinsic cost of the starting materials, product recyclability, and energy supply for thermal steps, an important feature for cost issues is the number of steps included in the filling process. The latter aspects may drive the selection of the filling process, but may also drive the nanotube synthesis process because some may allow in situ filling, i.e., are able to fill nanotubes while they form.

2. In situ filling

Filling nanotubes in situ is interesting because it is a single-step synthesis procedure; it leaves the nanotube sheath intact and, depending on the synthesis process, closed (for arc-prepared nanotubes) or opened at one end (CCVD-prepared nanotubes), thereby protecting as far as possible the encapsulated material from any contact with the surrounding postsynthesis atmosphere, and it allows nanotubes to be filled with elements whose surface tension is high enough to prevent filling by wetting methods (see Sec. II. C. 3).

In situ filling was one of the two early ways that foreign materials were introduced in MWNT-type

nanotubes. Two methods allow it: one is the electric arc process,^{16,17} and the other is the CCVD process (Fig. 2). The latter is rather limited because it most often corresponds to specific conditions for which the excess metal catalyst that is needed to grow the nanotubes is trapped and encapsulated inside them. Therefore, filling nanotubes this way is basically restricted to materials that are catalysts for carbon, typically transition metals such as Ni, Co, and Fe, although examples of other types of materials encapsulated this way can be found in the literature (e.g., Cu and Ge in Ref. 33). Because catalyst metals for carbon are mainly ferromagnetic materials, it is actually quite a convenient way to produce ferromagnetic nanowires encapsulated in nanotubes,^{32,34,35} otherwise difficult to obtain (see below).

The electric arc plasma process consists in drilling a coaxial hole within the graphite anode and filling it with the ground, desired element (or a mixture of it with graphite powder). Once the electric arc is run using conditions (current, voltage, pressure, and atmosphere) similar to that used to produce fullerenes, the MWNTs

that usually grow as a cathode deposit are found partially filled with the desired element. However, efficiency and control of the filling process is lower than for the CCVD-related method, probably because of the huge temperature gradients that are typical of the plasma zone in arc-related processes, and that are also responsible for the heterogeneity in the diameter distribution of the MWNTs synthesized that way. A specific requirement for achieving successful in situ filling in arc plasma processes is that some sulfur is present, added or naturally contained as an impurity (e.g., originating from the pitch used as a binder) within the graphite anode, otherwise the filling mechanism may fail.^{36,37} Opposed to the CCVD-based method, the electric arc method is hardly able to form hybrid MWNTs encapsulating transition metals such as Fe, Ni, or Co, although some rare exceptions may be found (e.g., with Co³⁸). The reason is that as soon as such a metal is introduced into the system (by doping the graphite anode with it), it forms C-metal solid solutions droplets that are encapsulated as carbides within the MWNTs growing at the cathode, or that escape the plasma zone to subsequently promote the growth of (empty) SWNTs from them. That is actually how SWNTs were incidentally discovered, i.e., as byproducts of attempts to fill MWNTs with transition metals (Fe in Ref. 3 and Co in Ref. 4).

Interestingly, the CCVD method and the electric arc method conveniently complement each other because the former is mainly able to produce transition metal-filled MWNTs, whereas the latter is not, but is mainly able to produce MWNTs filled with many other elements.^{36–39} On the other hand, both methods exhibit severe limitations. One is that only single elements (or carbides, for obvious reasons) are able to be inserted because of the requirement of being a carbon catalyst (for the CCVD process) or because of the high temperatures involved (for the electric arc plasma process) that do not allow oxides or salts to form. Typically, inserting multi-element compounds is not possible, nor is inserting labile materials. Another major limitation is that synthesizing hybrid SWNTs this way is nearly not possible, and when it is, it comes with very low yield, in the range of a small percentage. Examples in the literature are actually very scarce and involve the electric arc process only. One involves the spontaneous formation of peapods obtained during arc experiments aiming to grow SWNTs,^{40,41} and the other is the encapsulation of Bi in SWNTs grown with Co as catalyst,⁴² both Co and Bi having previously been introduced in the coaxial hole drilled in the graphite anode, as described above.

The severe limitations related to in situ filling, specifically regarding SWNTs, have then promoted the development of ex situ filling processes.

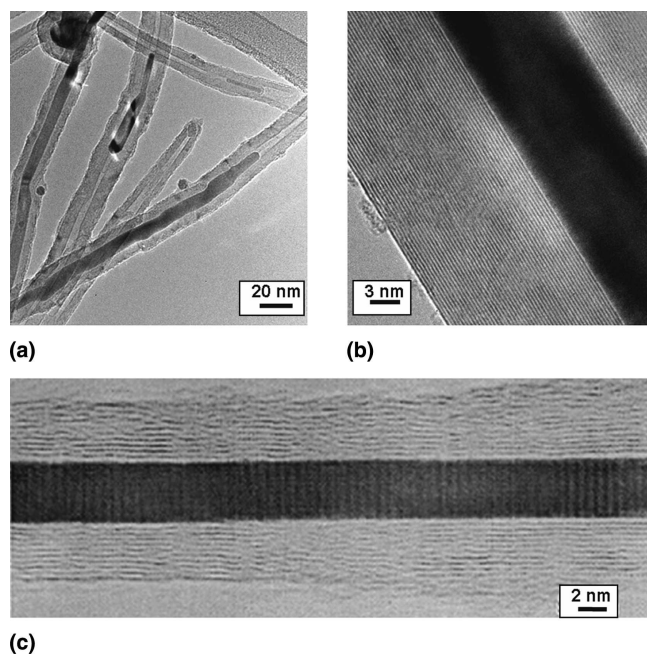


FIG. 2. (a) Low-magnification TEM image of in situ-filled MWNTs obtained via a CCVD-related process. The filling material is pure α -Fe (bcc Fe crystals). (b) High resolution of one of the Fe@MWNTs in (a). The perfection of graphenes from the surrounding carbon nanotube is shown. Lattice fringes of the contained iron crystal are not seen because of the high Z number of Fe that makes it barely transparent to electrons. The material was prepared as reported in Ref. 32, and was kindly obtained from P. Watts (University of Sussex). (c) High-resolution TEM image of an in situ-filled MWNT obtained via an electric arc plasma process. The filling material is a single crystal of pure chromium, somehow in epitaxial relationship with the surrounding graphene lattice (taken from Ref. 37 with permission of Elsevier).

3. Ex situ filling

Ex situ filling is the most versatile route because it is basically able to insert nearly any kind of material within any kind of nanotube. This was acknowledged long ago when filling MWNTs.^{27,28} Figure 3 summarizes the various experimental pathways that will be described in the following sections. Ex situ filling can be carried out following one-, two-, or three-step procedures, not mentioning the final treatment, which is needed for any of the ex situ methods to remove the excess (noninserted) material, via washing or dynamic vacuum heating (the latter may be preferred for avoiding a liquid phase step that often comes with residuals, and the filtration step that compacts the hybrid SWNT material obtained).

a. Opening the nanotubes

Except for single-step filling procedures, and unless starting nanotubes are naturally opened because of the specificity of the nanotube synthesis process (e.g., from templating), the very first step for the ex situ filling of nanotubes is dedicated to the previous opening of the latter, which can be achieved in two main ways. Both have been documented for a long while (i.e., since the early days of filling MWNTs^{16,18,43}) and consist in using thermal treatments in oxidizing gas phase (air or O₂)^{16,18} or liquid reactants that are oxidizing for polyaromatic carbon materials, typically, acids such as concentrated nitric (preferred) or sulfuric acid⁴³ or a mixture of both, but also others such as hydrogen peroxide, potassium permanganate, fluoric acid/bromine fluoride mixture, osmium tetroxide, etc.⁴⁴ Gas or liquid phase oxidation

procedures are efficient in opening MWNTs or SWNTs, although conditions have to be more severe for the former because of the higher number of graphenes per wall to attack. However, liquid phase oxidation tends to generate residuals that may more or less cover the nanotubes, thereby hindering subsequent treatments (such as filling) or investigations (such as TEM). In this regard, gas phase oxidation may be preferred. For instance, subjecting raw SWNTs obtained from arc process to a 380 °C thermal treatment (including 1 h of isothermal) in air within a tubular furnace allowing natural convection was proven in our laboratory to be able to create openings as wide as 0.7 nm or more in SWNTs with an overall weight loss in the range of 40% (not only from the nanotubes, hence variable according to the amount and type of carbon impurities, and the amount and type of catalysts). Such a treatment allows SWNTs to be subsequently filled with fullerenes with a filling efficiency in the range of 95%–100%. Interestingly, because purification procedures that are carried out on SWNTs to remove carbon byproducts (and catalyst remnants) are oxidizing treatments as well, purified SWNTs available from commercial suppliers (e.g., Nanocarblab in Russia) exhibit openings that are sufficient to allow them to be also filled (e.g., with fullerenes) with high efficiency without needing any further treatment but the filling step.

Considering the high inertness of the graphene lattice toward chemical oxidation, opening occurs at the location of structural defects (typically heterocycles) whatever the tube type. Pentagons are obviously found at the tips of nanotubes as a requirement to curve and close the graphenes involved, making nanotubes naturally able to

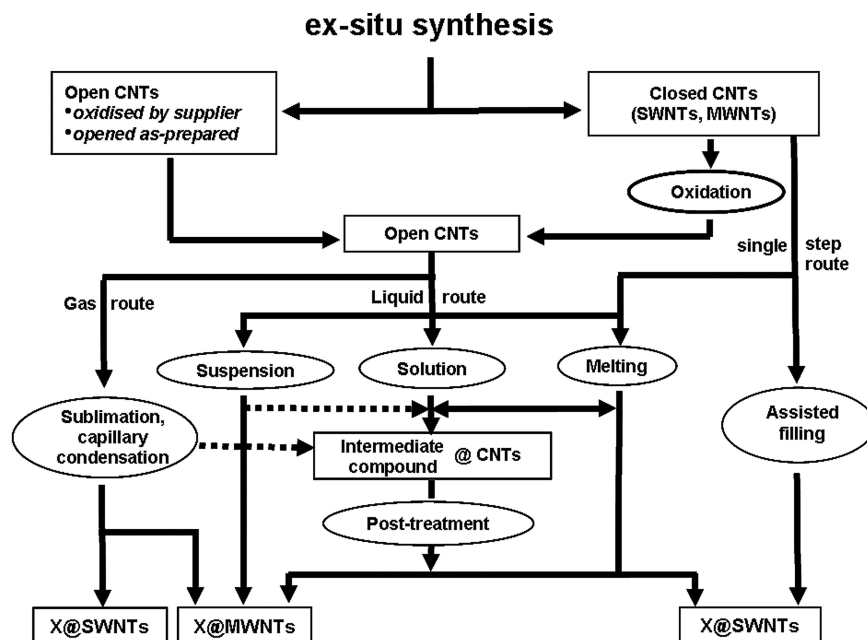


FIG. 3. Sketch of the various possible experimental routes that are possible for the ex situ filling of carbon nanotubes. Rectangles are for materials and ovals are for treatments.

be opened from the tips. However, a major discrepancy in the behavior of MWNTs versus SWNTs upon oxidation treatment for opening purpose is that the former is able to open from the tips only, whereas SWNTs are able to open from the tips and the side wall. Indeed, as discussed earlier,⁴⁵ several experimental results such as TEM investigation, electron irradiation behavior, and titration of acid-treated SWNTs have shown the presence of side defects (e.g., Stone-Wales) to be very likely, with an average proportion of one chemically attackable site every 5 nm along a given SWNT wall. Such a filling of SWNTs via side openings was further supported by calculations.⁴⁶ In contrast, should every graphene making the wall of a MWNT be defective as well (which has yet to be demonstrated), the chance for the defects from each graphene to superimpose at a given location of the wall to create a site for side opening is nil, except in the MWNT tip region where pentagons obviously superimpose from reasons related to geometric constraints and to the mechanism of the nanotube closure event.

b. The gas route

The gas route consists in putting in contact the previously opened nanotubes (MWNTs or SWNTs) and the vapor of the material to insert in them, for instance, in a Pyrex or quartz vessel that should be evacuated (primary or, preferably, secondary vacuum) before being sealed, and then heated up at the desired temperature, typically the vaporization or sublimation temperature of the filling material, or slightly above. This is the way peapods [see Fig. 1(a) and Sec. II. D. 2] are usually prepared.⁴⁷ For filling material such as fullerenes, which exhibit high electronic affinity with the graphene lattice, i.e., the nanotube surface, insertion into the SWNT cavity was proven to be a surface diffusion-driven mechanism.⁴⁷ Hence, it is highly dependent on temperature and time, but weakly dependent on the partial pressure of filling material vapor. Therefore, operating at a not-too-high temperature is necessary to minimize temperature-induced stochastic movements of the filling molecules and to give them a sufficient residence time on the nanotube surface to enable them to find the entry ports. A long processing time, in the range of several hours to 2 days, is therefore necessary to achieve high filling rates (up to 100%) provided a sufficient amount of filling material is supplied. For other types of materials to insert that do not exhibit the same affinity for the graphene lattice (e.g., ZrCl_4 ,⁴⁸ Se,⁴⁹ or Re_xO_y ⁵⁰), the filling mechanism is therefore slightly different and relates to capillary condensation. In the latter, a high partial pressure of the material to be inserted has to be developed at the vaporization/sublimation temperature or above, and the vapor condenses into the capillary porosity (i.e., the tube inner cavity) when the system is cooled down. High filling efficiencies, along with shorter processing times (e.g.,

with respect to peapod synthesis), are therefore expected for materials exhibiting high vapor pressure (e.g., Se⁴⁹). Examples are provided in Fig. 4.

This route is quite interesting and should be preferred as far as possible because of its simplicity (basically two steps, i.e., opening and filling), potentiality for a high filling rate and high purity and homogeneity of the filling material, and nondependence on surface tension requirements (see the next section). It is applicable to SWNTs and MWNTs, although examples for the latter in literature are scarce.^{49,51,52} On the other hand, a major drawback is the need for the filling material to exhibit vaporization or sublimation temperature below, say, approximately 1000 °C–1200 °C, to minimize the chances for healing the nanotube openings and/or for possible reactions with carbon. Inserting compounds (e.g., oxides, salts, etc.) this way is limited as well because candidate materials have to be able to vaporize or sublime without decomposing.

c. The liquid route

The main feature of all of the liquid route methods is their close dependence on the physical interaction between the filling liquid and the encapsulating solid, typically via the Young-Laplace law for capillary wetting. As soon as a solvent is involved, as for the suspension and the solution methods (see below, same section), wetting is not supposed to be a problem because surface tensions of usual solvents are below 80 mN/m. However, viscosity is certainly another parameter assumed to play a leading role, yet it has been scarcely considered in the literature dealing with the topic.

The suspension method is dedicated to filling with nanoparticles. Although examples (thus far involving

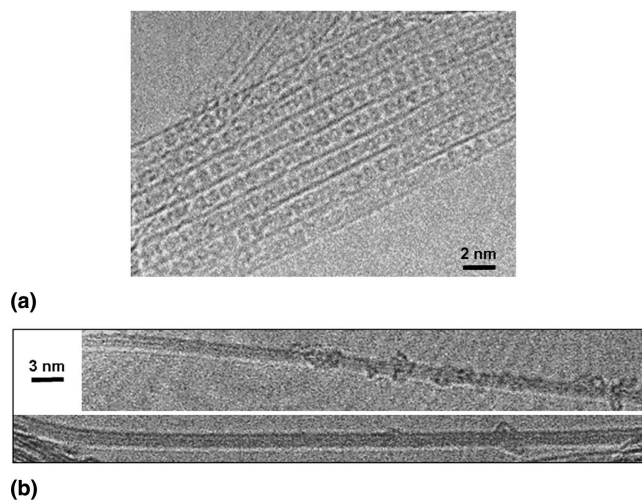


FIG. 4. Examples of hybrid SWNTs with high filling rates obtained via the gas phase route. (a) Bundle of C_{70} @SWNTs, prepared at 500 °C for 24 h in a sealed Pyrex ampoule. (b) Two examples of isolated Se@SWNTs filled over lengths longer than 60 nm, prepared at 800 °C for several hours.

MWNTs only) are still limited until quite recently,^{53,54} filling rates can be fairly high. This is not very surprising considering the large diameters of the MWNTs being filled (Fig. 5). In related experiments, open nanotubes were put into contact with a suspension of nanoparticles in a liquid at room temperature, the latter being evaporated during the experiment and/or afterward. Low volume concentrations of particles in the suspending fluid were used to maintain a low viscosity. The high filling efficiency is attributed to the combination of capillary forces,⁵⁴ possibly added with the effect of the concomitant fluid evaporation,⁵³ the latter being assumed to drive a continuous flow of fresh suspension from the outside to the inside of the tube.

The method is interesting because it is quite simple (two steps, opening and filling) and efficient, but it comes with severe limitations related to geometrical constraints and the morphology of the filling material feedstock. Indeed, nanotubes to be filled will be limited to MWNTs, unless less than 1-nm-large clusters are considered in the future to tentatively fill SWNTs. One related example has actually been reported already in which nanohorns (nanohorns are single-graphene nano-sized capsules⁵⁵ that can be considered failed SWNTs)

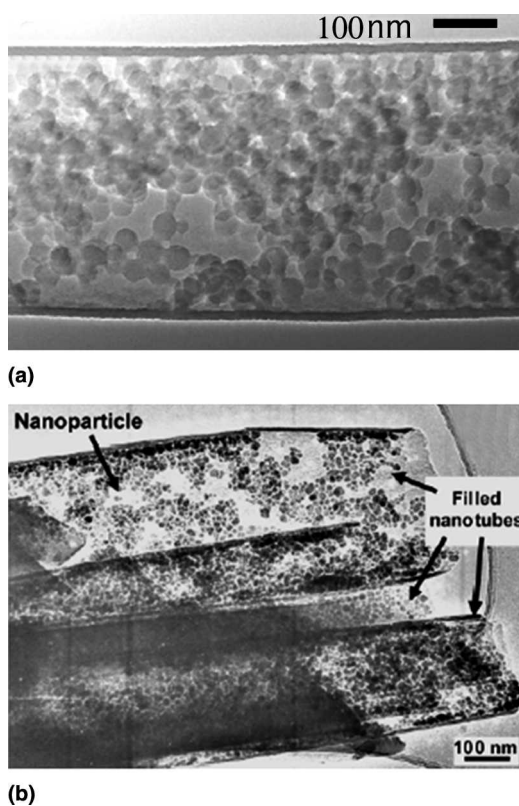


FIG. 5. Examples of MWNTs filled with nanoparticles via the suspension method (liquid route), taken from pioneering works. (a) Polystyrene nanobeads initially suspended in ethylene glycol.⁵³ (b) Fe₃O₄ nanoparticles initially suspended in water- or organic-based “ferrofluids.”⁵⁴ Reprinted with permission of American Chemical Society.

were partially filled with 1 nm or less Gd-containing clusters.⁵⁶ On the other hand, obtaining encapsulated nanowires this way appears somehow impossible. Generally speaking, the trickiest part of the procedure is the need to be able to prepare nanoparticles of the desired materials before the filling step. This is not of common knowledge. However, some are now commercially available (e.g., Sigma-Aldrich), even as a ready-to-use suspension (e.g., “ferrofluids” supplied by Ferrotec Corporation, Japan). At any rate, this field is just starting, and interesting developments are expected. Smaller diameter MWNTs or large-diameter SWNTs should be able to be used, annealing post-treatments should possibly be able to transform the packed nanoparticles into single nanorods in MWNTs with narrow inner cavity, etc.

The solution method is quite similar to the latter, and consists in putting into contact a concentrated solution of the desired materials with the previously opened nanotubes. This generally requires considering soluble derivatives of the materials ultimately wanted to fill the nanotubes (MWNT or SWNT), such as salts (halides or nitrates, usually). It is the compulsory method to use when the desired filling material does not present the appropriate physical constants for inserting itself via the gas route (see above) or the melting method (see below), both of which should be preferred for their higher filling efficiency and fewer number of steps. Examples where the desired filling material is directly inserted into nanotubes via the solution method are actually seldom, and post-treatments (most often calcination as in Ref. 57 or reduction as in Refs. 22, 42, and 58, but also other treatments such as photolysis or electron irradiation, as in Ref. 59) are most often necessary to obtain the hybrid nanotube with the desired chemical composition (Fig. 6). This method was actually the very first one used to deliberately fill SWNTs [with Ru from RuCl₃, see Fig. 1(b)],²² and has been widely used since then.

An interesting feature of the solution method is that it is usually operated at room or mild temperature. This allows nanotubes to be filled with thermally unstable materials such as fullerenes grafted with organic functions⁶⁰ or peculiar endofullerenes, e.g., N@C₆₀.⁶¹ A valuable alternative is to keep operating at mild temperature conditions (~50 °C) but use high pressure (~150 bars) to be able to replace regular solvents (water, acids, chloroform, toluene, etc.) with supercritical CO₂.^{62,63} The latter is a very powerful solvent and exhibits a high penetrability in nanopores from a very low viscosity and low surface tension. Although operating times as long as several days might be necessary,⁶² the method is quite promising for being applicable to a large range of compounds.

Finally, although the solution method is intrinsically multistep to generally account for opening, filling, and post-treating the nanotubes, it could also be made

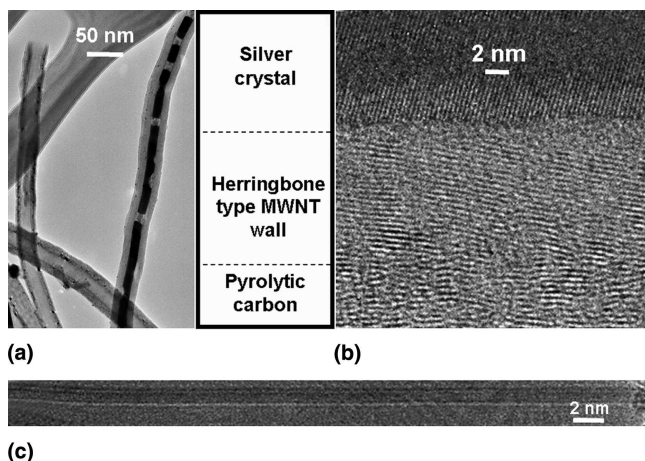


FIG. 6. Examples of nanotubes filled with Ag via the solution method (liquid route): nanotubes were soaked in a water solution of silver nitrate upon stirring for 48 h at room temperature, and then calcined at 300 °C in vacuum. (a) CCVD MWNTs, partially filled. (b) High-resolution detailed portion of the nanotube filled in (a), showing that Ag is a single crystal. Incidentally, the nanotube wall is showed to be bilayered, with two different orientations of graphenes with respect to MWNT axis. (c) Electric arc SWNT, filled over a length higher than 60 nm.

into a single step in some specific cases,⁶⁴ i.e., raw nanotubes are opened and then filled while soaking in a single solution. This requires the solution to be able to contain the dissolved filling material as well as to be oxidizing toward the nanotubes. In Ref. 64, this was achieved by soaking raw SWNTs from arc within a supersaturated solution of CrO_3 in concentrated HCl. Both reacted to form CrO_2Cl_2 , which is known for being highly oxidizing for polyaromatic carbon, including graphite,⁶⁵ hence resulting in opening the SWNTs. The excess CrO_3 was then able to enter the SWNT cavity, thereby forming CrO_x @SWNT hybrid nanotubes.

To summarize, the solution method is quite useful as an alternative when other routes (gas route and melting method) are not possible because of the inappropriate physical properties of the desired filling materials. Thanks to the large variety of compounds that can be found soluble in some solvent, the method appears widely applicable. Except for very specific cases, the method has to be multisteped (three steps), which can be a drawback. Nevertheless, the main limitation lies in the concomitant filling with the solvent molecules (along with the dissolved desired material), which cannot be avoided. As a common observation (see Refs. 64 and 66), this prevents high filling rates from being achieved.

As opposed to the solution method, the melting method allows high filling rates to be achieved and was among the first methods used to fill MWNTs (with PbO^{17}), and was subsequently demonstrated to be highly successful even for SWNTs (Fig. 7). For instance, SWNT filling rates as high as $\sim 70\%$ were reported for PbO ,⁶⁷ although cumulating filling cycles were

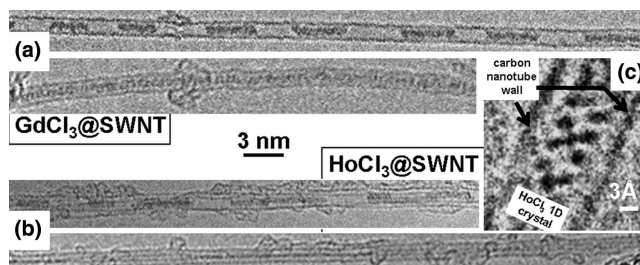


FIG. 7. Examples of SWNTs filled with lanthanide chlorides via the melting method (liquid route): nanotubes were sealed under vacuum in a quartz ampoule along with the ground material to fill them with, and were then heat treated for 24 h. (a) GdCl_3 @SWNTs obtained at 700 °C. (b) and (c) HoCl_3 @SWNTs obtained at 820 °C. Filling materials can form continuous nanowires [bottom image in (a) and (b)] or, as a common observation, short segments somewhat periodically displayed [top image in (a) and (b)]. (c) Both wires and segments are truly one-dimensional crystals.

necessary to achieve it. This makes the method almost as efficient as the gas phase route obviously because for both methods, only the desired filling material is entering the nanotube cavity.

The procedure is similar to that for the solution method of the gas phase route, i.e., putting together the previously opened (or not, see next paragraph) nanotubes and the material to fill the latter within a quartz vessel sealed under vacuum, and then heating up the whole. The temperature has of course to be above (~ 30 °C–100 °C higher) the melting temperature of the filling material and maintained for long times, in the range of 1–3 days (see Refs. 15, 66, and 67 among others). Such long times are necessary to account for the high viscosity that the molten materials may exhibit and that slows down the filling kinetics (specifically within SWNTs), and also to account for cycling. Cycling does not require repeating the whole procedure and, provided a sufficient amount of the material to fill is provided as a feedstock in the starting sealed ampoule, repeatedly operating within a limited temperature range (e.g., ± 30 °C) bracketing the filling material melting temperature was shown to be enough.⁶⁷ Again, when high-melting-temperature materials, e.g., metals, lanthanides, etc., are the ultimate filling materials envisaged, compounds such as salts or oxides are the preferred materials for the filling steps because they usually exhibit lower melting points. Hence, post-treatments for reducing the intermediate compounds into the desired filling materials are needed. However, interesting observations regarding the behavior of one-dimensional crystals were already possible on such intermediate hybrid materials (see Sec. III. A).

A valuable alternative proposed by the Oxford Group as early as in 1999⁵⁹ and thoroughly used since then in most of their filling experiments is to use the chemical activity of the halides toward polyaromatic carbon (at least at defective sites as for other oxidation reactions; see Sec. II. C. 3. a.) to get the nanotubes opened within

the filling step, thereby making needless a preliminary, separate nanotube-opening step. However, this is mainly valid for SWNTs only (and DWNTs), for the reasons related to the number of walls already discussed in Sec. II. C. 3. a. By the way, it is a pity that Grigorian et al.,⁶⁸ in their early attempt to dope SWNT bundles with iodine using the melting method, did not realize this ability of molten iodine to open SWNTs. Had they demonstrated in their first paper that iodine was actually partly filling the SWNT cavities as they demonstrated it 2 years later,⁶⁹ their work would have been cited among the pioneering ones regarding the demonstration of the ability of SWNTs to be filled with foreign materials.

To summarize, the melting method is the second method to be preferred for filling nanotubes because of the possibilities for high filling rates, simplicity (one to three steps, depending on the goal and the material to fill), and versatility. Its main limitation is its requirement for selecting the materials to fill (or their compounds) among those exhibiting the convenient surface tension (i.e., $<130\text{--}170\text{ mN/m}^{30}$) when molten at the filling temperature.

Finally, the assisted filling methods are worth being considered because they correspond to attempts to develop original and/or simpler and/or more efficient, etc., ways to synthesize hybrid nanotubes. Two examples have been reported. One by us,^{70,71} who proposed to use solutions of halides (FeCl_3 , MoCl_5 , and I) in chloroform subsequently irradiated with UV at room temperature. Chlorine moieties are thereby created that are able to attack the SWNTs, allowing the filling to proceed from the dissolved material. Filling rates were actually low, but the procedure was not optimized and might have included cycling for instance. The method should be applicable to, but also limited to, any compound soluble in chloroform. The method is dedicated to filling SWNTs (and possibly DWNTs) only, for the same reasons as developed above for the opening by molten halides.

The other example was proposed by a Japanese consortium and consists of using collisions of accelerated atoms from a plasma generated between a grounded electrode and a stainless steel plate on which SWNTs were previously deposited. Hybrid nanotubes inserted with fullerenes^{72,73} and Cs⁷³ were formed this way. Oxidized, and therefore opened, SWNTs were used for purity purposes only, and the method should work with raw (closed) SWNTs as well. Kinetic energies involved are in the range of $\sim 150\text{ eV}$ (for alkali metals) and filling rates can be fairly high ($\sim 50\%$ for C_{60} @SWNTs) with respect to the short duration of the run ($\sim 1\text{ h}$). However, damage to the nanotubes by the energetic bombardment was suspected, yet the extent of it was not estimated. This method is likely to be dedicated to filling SWNTs only, considering the tremendous energy that would be needed to enter a nanotube through a multi-graphene wall.

D. Filling materials

Every type of material (i.e., atoms, molecules, and compounds) has now been experimentally inserted into SWNT cavities. This section will provide a thorough listing of the various hybrid nanotubes whose preparation was reported in the literature, not mentioning virtual fillings via modeling whose related references will not be provided here. Whether the filling claimed in the papers cited was actual will not be discussed. Direct evidence for filling, such as TEM imaging, was not always provided, and the successful synthesis of hybrid nanotubes was sometimes reported on the mere basis of spectroscopic investigations, which may be mistaken. Because the literature has become abundant regarding a given topic (for instance, regarding peapods), citing all of the related papers was impossible and citing selected references (e.g., the pioneering works) was preferred.

1. Atoms (isolated or as chains)

Encapsulating atoms so that they remain isolated is quite difficult because corresponding to a highly unstable situation and demonstrating the presence of such isolated atoms in SWNTs is an experimental challenge. When not forming elongated crystals as nanowires (see Sec. II. D. 3), encapsulated atoms tend to gather as single-atom-wide chains. However, examples for such chains are scarce. The first one ever was iodine,⁶⁹ which was convincingly demonstrated to be able to adopt a beautiful double helical chain structure (Fig. 8), presumably from commensurability situations between the I-I distance in the chain and some peculiar periodicities of the graphene lattice.⁶⁹ Based on this pioneering work, a similar structure was assumed for encapsulated cesium chains prepared later.⁷³ However, the formation of chains may be prevented and Cs atoms may remain as isolated, observ-

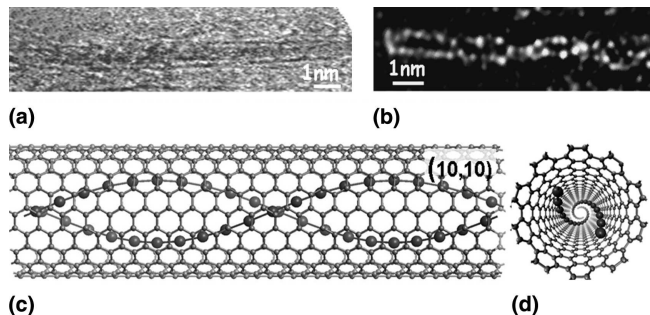


FIG. 8. Examples of SWNTs filled with a double-helix chain of iodine atoms. (a) High-magnification but low-resolution TEM image of a filled SWNT within a bundle: the filling material is hardly seen other than as a dark contrast. (b) High-resolution Z contrast image of a filled SWNT similar to that in (a): the double-helix configuration is revealed. (c) and (d) Side and top views, respectively, of a model of the latter, considering a (10,10) SWNT. All of the images appear in Ref. 69 with permission from American Physical Society.

able atoms if the latter are encapsulated along with large and low-reactivity molecules such as fullerenes, which somehow obstruct the pathway on the one hand, and do not favor the bonding or adsorption of the Cs atoms to their surface on the other hand.⁷⁴

2. Molecules

Except for some rare examples whose motivation was more related to typology issues (e.g., filling BN- or C-MWNTs with fullerenes^{51,52}), filling nanotubes with molecules was and still does systematically involve SWNTs. For most of the following filling materials, the goal was generally to introduce electron donor or acceptor molecules, and thereby to tentatively modify the electronic structure of the subsequent hybrid nanotubes to obtain peculiar electronic behaviors via band gap modulations. The first molecules ever inserted into SWNTs were C₆₀ fullerenes^{21,47} thereby forming the so-called nanopeapods [Figs. 1(a) and 4(a)]. Many fullerene-related filling materials have followed since then, including high fullerenes (namely C₇₀, the most popular one,⁷⁵) C₈₀, C₈₄,⁷⁶ C₇₈, C₉₀,⁷⁷ endohedral fullerenes (such as N@C₆₀,⁶¹ La₂@C₈₀,⁷⁸ Sc₃N@C₈₀,⁷⁹ Er_xSc_{3-x}N@C₈₀,⁷⁹ Dy₃N@C₈₀,⁸⁰ Gd@C₈₂,^{77,81,82} La@C₈₂,⁸³ La₂@C₈₂,⁸³ Dy@C₈₂,^{77,84} Sm@C₈₂,^{85,86} Sc₂@C₈₄,^{76,87} and Gd₂@C₉₂⁸⁸); doped fullerenes, where fullerenes are combined with elements (e.g., Cs⁷⁴ and K^{89,90}) or compounds (e.g., FeCl₃⁸⁹); functionalized fullerenes [cyclopropa-C₆₀-dicarboxylic acid diethyl ester, abbreviated as C₆₁(COOEt)₂@SWNT,⁶² and 4(pyrrolidin-1-yl)phenol.⁶⁰

Regarding the former category (high fullerenes), C₉₂ is the largest fullerene inserted so far, yet as endohedral fullerenes since C₉₂ was meanwhile encapsulating gadolinium atoms in the work cited.⁸⁸ Of course, elongated capsules obtained from the in situ coalescence of encapsulated C₆₀ upon electron irradiation,^{21,91} laser irradiation,⁹² thermal treatment,^{47,93,94} and both electron irradiation and thermal annealing combined^{95,96} may also be considered high fullerenes (e.g., C₁₂₀ is obtained from the coalescence of two C₆₀). In this regard, the ultimate high fullerene possibly encapsulated is an inner SWNT, thereby making the whole become a DWNT that could also be abbreviated as SWNT@SWNT! DWNT may actually be synthesized in a single step via CCVD processes⁹⁷ and arc plasma processes,^{98,99} in addition to the coalescence treatment aforementioned. The synthesis and use of DWNTs is a fast-growing topic that could be worth writing a review article about, and the related aspects will not be further developed here. For the two middle categories (endohedral and doped) of the fullerene-related materials listed in the previous paragraph, the main motivation was the usual modification of electronic structure and behavior, ultimately aiming to high critical temperature superconductivity based on the

previous results obtained with doping fullerite with lanthanides and other materials.¹⁰⁰ For the latter category (functionalized), one goal was to demonstrate the feasibility of inserting thermally unstable molecules, ultimately aiming to allow the filling of SWNTs with molecules wearing chemically or electronically active functionalities likely to be useful for a variety of applications.

Although fullerenoids are the most popular filling molecules, several other organic molecules have been recently inserted in SWNTs: metallocenes,^{79,101,102} ortho-carborane,¹⁰³ fulvalenes,¹⁰⁴ Zn-diphenylporphyrin,^{105,106} Pt-porphyrin, rhodamin-6G, and chlorophyll.¹⁰⁶

In addition, some of the works deal with filling SWNTs with molecules that are gaseous at room temperature, as opposed to the aforelisted ones, which are solid or liquid. However, except for hydrogen, whose adsorption by SWNTs, MWNTs, and carbon nanofibers was extensively investigated for reasons related to the perspective of a new era based on hydrogen economy,¹⁰⁷ gaseous molecules investigated are still scarce: xenon,¹⁰⁸ oxygen, nitrogen,¹⁰⁹ etc. Even more critically than for any other filling material, filling SWNTs (or MWNTs) with gaseous molecules whose physisorption is the main interaction mechanism with the nanotubes makes highly questionable the actual location of the adsorbed molecules. Considering SWNT bundles, the inner nanotube cavity is only one of four distinct adsorption sites identified from their various adsorption energy potential.¹¹⁰ In addition, the demonstration of the actual adsorption of some gaseous molecule onto or within any material, including CNT, is generally indirect, via so-called gravimetric or volumic methods, with which the only evidence for gas adsorption is obtained from the weight gain of the nanotube sample or the measured consumption of a known volume of feedstock gas, respectively. This opens wide the door for misinterpretations from various sources or errors independent from the tested material (e.g., leaks, H₂O traces, impurities, buoyancy effects, etc.), which are likely to contribute significantly (or even prevalently) to the demonstration of an adsorption phenomenon onto nanotubes. That is why the supposedly ~7 wt% filling of gaseous H₂ in SWNTs reported as early as 1997,¹¹¹ i.e., before the two 1998 papers by Smith et al.²¹ and Sloan et al.²² cited in Sec. II. A, cannot be opposed to the latter as the first demonstration of the effective filling of SWNTs. For instance, such a kind of misinterpretation regarding the work reported in Ref. 111 was revealed later on in Ref. 112. Therefore, the adsorption of permanent gases in nanotubes will not be considered further in this review.

3. Elements (as wires and/or crystals)

As opposed to encapsulated iodine or cesium atoms, which were demonstrated to gather as monoatomic

chains (see Sec. II. D. 1), other elements may form wires when encapsulated in SWNTs, most often crystallized [e.g., Fig. 4(b)]. SWNT-encapsulated elements include Bi⁴² and Se⁴⁹ on the one hand, and Ru,²² Bi,⁴² Ag,^{57–59,113,114} Au,⁵⁸ Pt,⁵⁸ Pd,⁵⁸ and Fe¹¹⁵ on the other hand. The former (Bi and Se) are distinct from the latter because they were inserted as a liquid (molten) or a vapor, whereas the latter were inserted as salts in a first step, and then formed in situ from the salts via post-treatments (e.g., thermal treatment and/or hydrogenation). Reasons why, upon encapsulation in SWNTs, some atoms such as Bi and Se form several-atom-large nanowires while other atoms such as I and Cs form single-atom chains have not been discussed. The reasons do not lie in discrepancies in the average diameters of SWNTs, because the latter mainly originate from the regular electric arc method that provides SWNT diameter distributions in the 1- to 2-nm range and commonly centered on 1.4 nm. Reasons neither lie in the respective filling processes because that used for I (molten state filling⁶⁸) is very different from that used for Cs (ion bombardment⁷³), whereas the former is similar to that used for Bi⁴² and Se.⁴⁹ The explanation may relate to the existence of some commensurability between the atom chain periodicities and the surrounding graphene lattice as investigated and proposed in Ref. 69. Unfortunately, the latter aspect was not investigated for Cs chains, and the commensurability-related explanation should therefore be reasonably considered as a mere possibility.

4. Compounds (as nanowires or nanoparticles)

Filling SWNTs with compounds is a very important topic likely to provide successful alternatives when filling with chemical elements is not possible, typically because of too high a melting point and/or surface tension of the considered elements at the molten state (see Table I). Considering compounds may also give access to filling via solutions, as an alternative when a low-temperature filling process is needed or when the elements considered are poorly soluble. Compounds are typically salts, among which halides are the most popular, for the several advantages they offer such as high versatility (many types of halides are possible, i.e., involving Cl, I, Br, or F, thereby offering a wide range of melting temperatures and solubilities); suitable range (i.e., not too high, e.g., <1000 °C) of melting points in many cases; good solubility in usual solvents (chloroform, water, etc.); and high chemical reactivity toward carbon that allows the nanotube to be opened and then filled by the molten halides all at once.

Oxford University, sometimes associated with Cambridge, is undoubtedly the most active group in the field. First, based on their previous works on filling MWNTs, they have filled SWNTs with many kinds of halides since 1998,²² mainly using the melting method, but also using

TABLE I. Surface tensions of some elements and compounds (halides and oxides) that have been investigated in the literature dealing with filling or wetting carbon nanotubes with molten materials.

Material	Surface tension (mN/m)	Melting temperature (°C)	Filling temperature (°C)	Source (reference)
AgCl	113–173	560	660–560	15, 59
AgBr	151	432	532–590	15, 59
AgI	171	455	555	15
Al	860	660		30
BaI ₂	130	740	840	15
Bi ₂ O ₃	200	825		117
CaI ₂	83	784	884	15
Cs	67	29		29
CsI	69	627	727	15
Ga	710	30		29
GdCl ₃	92	609	659	116
Hg	490	–38		29
K	117	336		30
KCl	93	771	870	59
KI	70	681	781	15
LaCl ₃	109	860	910	116
LiI	94	449	549	15
NaI	81	661	761	15
NdCl ₃	102	784	834	116
Pb	470	327		29
PbO	132	886		117
Rb	77	39		29
RbI	70	647	747	15
S	61	112		29
Se	97	217		29
Te	190	450		29
UCl ₄	27	590	690	59
V ₂ O ₅	80	690		31, 117
ZrCl ₄	1.3	437	487	15
HF	117			30
HNO ₃	43			117

Surface tension values are given at the filling temperature when provided in the related references, otherwise they are given at melting temperature.

the solution method, and in few instances, the gas route. The following list corresponds to the materials inserted by the Oxford Group,^{23,24,118} yet includes some materials inserted by other groups as well. The list is probably not complete, but provides an idea of the extensive work carried out in the field: HgTe,¹²⁵ (Na/Tl/Cs)Cl,^{23,117,120} (Cd/Fe/Co/Pd)Cl₂,^{58,121} [Ln(La to Lu)Tb/Ru/Ho/Gd/Au/Y/Fe]Cl₃,^{22,58,66,70,115,117,121} Al₂Cl₆,²³ (Hf/Th/Zr/Pt)Cl₄,^{48,58,118,121} MoCl₅,⁷⁰ WCl₆,²³ (KCl)_x(UCl₄)_y,^{15,59} CsBr,²³ AgCl_xBr_yI_z,^{15,26,59,122} (Li/Na/Cs/K/Rb/Ag)I^{15,24,123–125} (Ca/Cd/Co/Sr/Ba/Pb/Hg)I₂,^{15,118,120,126–128} (Te/Sn)I₄,^{121,123} and Al₂I₆.¹²¹

From 2001, oxides were also directly inserted into SWNTs, starting with CrO₃^{64,113} and Sb₂O₃^{129,130} and then followed by others such as PbO,⁶⁷ Re_xO_y,⁵⁰ and UO₂¹⁶ (although the latter was obtained from the primary filling with uranyl salts), sometimes with a fairly high filling rate (e.g., 80%–90% for PbO). Although oxides can be interesting alternatives as intermediate compounds or can exhibit interesting intrinsic properties on

their own (e.g., CrO_3 is electrically conductive), they will never become as popular as halides because oxides with high solubility in harmless solvents or reasonable melting temperatures are not many.

Other compounds that were attempted for filling SWNTs are typically nitrates (specifically silver nitrate,^{58,113,114} but also bismuth nitrate,⁴² uranyl nitrate,¹⁶ etc.), acetate (uranyl acetate¹⁶), and hydroxides (KOH and CsOH ¹⁶).

Figures 6 and 7 provide examples of filling achieved with or via such compounds, respectively, Ag initially introduced as nitrate dissolved in water, and GdCl_3 and HoCl_3 inserted in a molten state.

III. PECULIAR PHYSICAL ASPECTS RELATED TO X@CNTS

The synthesis of X@CNTs, specifically involving SWNTs, has a quite young history, and examples of experimental measurements showing peculiar properties of hybrid SWNTs are quite seldom. Likewise, little theoretical work to tentatively predict the electronic properties of X@CNTs (but peapods) has been carried out thus far, and expectations are mainly based on the anticipated possibility to modulate the band gap thanks to the filling material, or to modulate the band gap of the latter thanks to the enforced structural deformations. Published theoretical works mostly concern magnetism,^{131–134} and involve types of X@CNTs that have unfortunately not been able to be prepared yet (namely, Cu@SWNT and Fe@SWNT). Hence, most of the observations have dealt with the chemical and structural behavior of the encapsulated materials thus far (see Sec. III. A). However, measuring hybrid SWNT properties (see Sec. III. B) is an exciting and fast-growing topic, and many articles dealing with such experimental measurements should be released in the near future.

A. Specific behavior in hybrid SWNTs

Two major examples have been reported regarding specific behaviors of materials encapsulated in SWNTs. The first one deals with fullerenes, which have shown a series of peculiar behaviors including dimerization, coalescence, and diffusion. The early observations of the latter behaviors were already reviewed in Ref. 45 and will therefore not be detailed here. Briefly, they originated from the dynamic TEM observation of encapsulated fullerenes upon electron irradiation in the microscope. When they are densely packed into SWNTs, irradiated fullerenes (100 kV) were found to first get closer to each other in pairs, assuming dimerization,^{21,93} and then to coalesce into elongated, somewhat distorted capsules (actually higher, elongated fullerenes).^{21,91} Coalescence may also occur upon thermal treatment (in the

range of 1200 °C for 1–2 days, typically). In that case, the coalescence may proceed up to forming an inner tube with apparently perfect walls, thereby forming a DWNT.^{21,47,93} Coalescing encapsulated fullerenes into DWNTs at lower temperature (<700 °C) is possible if annealing is combined with electron irradiation (150–300 kV).^{95,96} Interestingly, the latter experiments revealed that the inner tube diameter value is linearly related to that of the outer tube diameter in a manner that results from compromising between the need for the intertube distance to respect the van der Waals gap (~0.34 nm) and the need for the innertube diameter to maintain the initial C_{60} -fullerene diameter (~0.7 nm).⁹⁶ On the other hand, when encapsulated fullerenes are not packed, electron irradiation was shown to induce a random ionization of the contained molecules that were subsequently able to repulse or attract each other, thereby randomly generating back and forth diffusion movements of individual fullerenes or fullerene trains within the nanotube cavity over several nanometers.⁹³ Obviously, such behaviors were specifically permitted by the encapsulated situation of the fullerenes because no such behavior was observed for fullerenes in bulk fullerite (i.e., nonencapsulated) when electron irradiated.

Related dynamic behaviors upon electron irradiation were also reported for other materials encapsulated in SWNTs such as clusterization of ZrCl_4 crystals⁴⁸ and steady rotation of Re_xO_y clusters.⁵⁰

In addition, the mere fact that encapsulating crystals in SWNTs enforces a nanowire morphology that is generally unusual for most of the filling materials tested thus far is intrinsically a peculiar behavior, as demonstrated by attempts to remove the carbon sheath, which resulted in the loss of the nanowire morphology for several halide crystals.²⁶ Moreover, a second major behavior that is specific of the encapsulation in SWNTs is to frequently generate structural discrepancies with respect to the same materials in bulk state. Structural peculiarities actually include preferred orientation with respect to the nanowire elongation axis, reduced coordination, lattice expansion and/or contraction, and new structures. Preferred orientation may originate from the need to maintain the stoichiometry as far as possible.²⁴ Reduced coordination is obviously the consequence of the limited space in which the encapsulated crystals have to grow, which may be the cause for the lattice expansion in the radial direction as observed for CrO_x ⁶⁴ and KI.¹²⁴ Lattice distances along the wire axis are less likely to overcome distortions because the confinement is relatively nil in this specific direction, but numerous examples of a lattice contraction in this specific direction can be found, e.g., for Ag,¹²² Sb_2O_3 ,¹²⁹ KI,¹²⁴ and even fullerenes because the 1-nm C_{60} - C_{60} distance in fullerite was found to become 0.97 nm for C_{60} chains in peapods.¹³⁵ Such lattice contraction behaviors correspond to the Poisson effect,

which is well known in bulk material mechanics. Such lattice distortions are significant, and may reach 14% or more. Despite the crystallization of binary halides may adopt different structures (three dimensional, layered, chain, and molecular in bulk state),¹³⁶ it is clear that the limited space available in SWNTs (and DWNTs) will not allow all of them to develop (specifically for the three dimensional and the layered structures), depending on the radius of the atoms involved [Figs. 9(a)–9(d)].

Furthermore, for a given compound (e.g., PbI_2), the structure type may change with respect to the available inner space within the nanotube capillaries.^{120,128} Ultimately, structural constraints can be such that new structures are created, e.g., for NdCl_3 ,¹¹⁶ CrO_3 ,⁶⁴ CoI_2 ,¹¹⁷ or BaI_2 ,¹²⁶ giving rise to peculiar features such as unusual symmetry [Figs. 9(e) and 9(f)]. Finally, it was observed that the ability of the filling material to crystallize may depend on the available inner space on the one hand, and on the deformability of the tube wall on the other hand. Indeed, small diameter hybrid SWNT walls were found to accommodate the contained crystal structure (CoI_2 ¹²⁷ or PbI_2 ¹²⁸) to such an extent that filled SWNTs exhibit oval cross-sections. Accordingly, PbI_2 was found amorphous when filling DWNTs with similar small diameter, presumably because the deformability of the tube wall is much decreased, hence not allowing the crystal structure to develop.

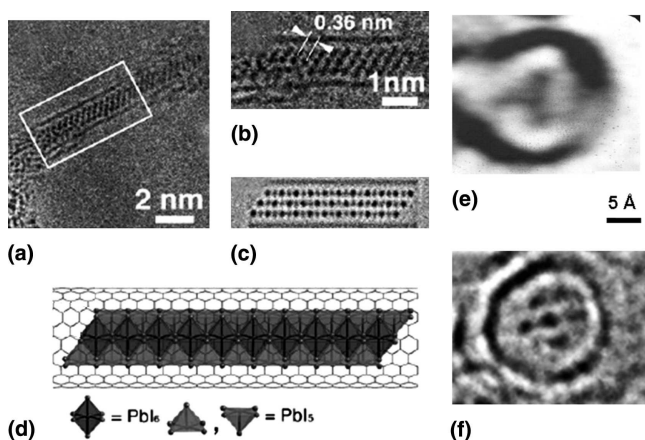


FIG. 9. (a) and (b) High-resolution TEM image of a SWNT filled with PbI_2 . (c) Corresponding calculated image, based on the model shown in (d). Although bulk PbI_2 structure is a two-dimensional-layered type, encapsulation in SWNT enforces it to become a one-dimensional polyhedral chain (modified from Ref. 128). (e) High-resolution TEM image of a cross-section of a SWNT filled with CrO_x . The filling material structure exhibits a 3-fold symmetry in which each lobe is assumed to be the projection of a chain of CrO_4 tetrahedra (from Ref. 64). (f) High-resolution TEM image of a cross-section of a SWNT filled with HoCl_3 from the same sample batch as in Figs. 7(b) and 7(c). The filling material structure exhibits a 5-fold symmetry, yet is deformed. Based on the structural similarities with NdCl_3 ,¹¹⁶ each dark spot is supposed to be the projection of a chain of HoCl_x polyhedra. Note that this projected structure seen in cross-section is hardly compatible with the longitudinally projected structure image seen in Fig. 7(c), suggesting the occurrence of several types of display for the polyhedra chains.

Many of the latter aspects were thoroughly reviewed recently in Refs. 23, 24, and 118. At any rate, such structural features are specific to encapsulating SWNTs as opposed to MWNTs, which definitely exhibit too large of an inner volume.

B. Properties of hybrid nanotubes

The structural features reported in the previous section provide high prospects that some hybrid SWNTs should exhibit quite peculiar physical properties, specifically regarding transport and magnetism. As far as properties are concerned, the distinction should be made between the peculiar behaviors of the filling materials specifically resulting from their encapsulation, the properties intrinsically from the filling materials that are naturally transferred to the whole hybrid nanotube, and the peculiar properties that may result from the nanotube/filling material interactions. Unfortunately, such examples are still very few. Probable reasons are that although high filling rates can be achieved that are suitable for structural investigation, the whole material may remain too imperfect (e.g., impurity content) to investigate them as a bulk in a reliable manner. On the other hand, investigating isolated, single X@CNT s requires nanolithography facilities and specifically designed measurement devices that are not of easy access yet. In addition to possessing the related technological know-how, explaining and understanding the phenomena observed requires one to be able to characterize the very same X@CNT tested to ascertain the extent of filling and the structural features of the encapsulating SWNT, which is definitely not routine. Therefore, all of the works published thus far deal with peapods on the one hand (because they are easy to prepare, have been studied for the longest time, and are able to present such high filling rates that ascertaining the filling extent for the X@CNT investigated is no longer an issue) and/or measurements of bulk materials on the other hand.

Thus far, however, results are a bit disappointing. For instance, thermal properties of peapods were found to show no change with respect to pristine SWNTs, presumably because the propagation of phonons from a C_{60} molecule to the neighboring one is too slow.¹³⁷ On the other hand, measurements of transport properties resulted in contradictory statements. It was actually reported that electrical resistivity of $\text{C}_{60}@\text{SWNT}$ s (at low temperature) increases with respect to pristine SWNTs,^{81,138} whereas Vavro et al.¹³⁷ reported the contrary. Similarly, no temperature dependence of $\text{Dy@C}_{82}@\text{SWNT}$ -based field emission transistor characteristics was observed,⁷⁷ whereas the opposite was stated in other experiments.^{84,139} However, a consensus seems to be reached regarding the effective charge transfer from the contained fullerenes or metallofullerenes to the encapsulating SWNT, to an extent that is variable

according to the SWNT diameter.^{78,140,141} This is consistent with the observation that indirect tunneling between inserted C_{60} through the SWNT wall is preferred, instead of direct tunneling from C_{60} to C_{60} .^{77,137,142}

However, some results were published regarding hybrid SWNTs other than peapods. As early as in 1998, the electrical resistivity of I@SWNT was found to be significantly decreased with respect to pristine SWNTs, with some evidence for charge transfer.⁶⁸ However, it is difficult to ascertain that this result accounted for the contribution of encapsulated iodine, because iodine doping (i.e., intercalation of I atoms between bundles and between SWNTs within bundles) certainly occurred as well (doping was actually the only association envisaged in the early work because iodine encapsulation was revealed only 2 years later⁶⁹). It is not trivial to question whether I in doping and filling positions contribute similarly or not because both sites do not see the same graphene curvature, anticipating different electronic interactions. At this early stage of understanding X@CNT properties, we need to know. In this regard, modeling should certainly help, and the recently reported calculation demonstrating the change from semimetal to semiconductor of a HgTe crystal upon its encapsulation in SWNTs, with little interaction with the tube wall,¹¹⁹ is a good example of the kind of work that is going to be necessary to understand hybrid SWNTs well and to support experimental measurements. Such a consistency is claimed for Ag- or CrO_3 -filled SWNTs, whose modeling confirms to the donor and acceptor roles, respectively, of the filling materials toward the containing SWNTs in agreement with the resonant Raman data.¹⁴³ Electron transfer was also found in bulk ferrocene@SWNT material upon photoexcitation.¹⁰¹ However, the recent work by Carter et al.¹¹⁹ can be considered the first full demonstration of modification of the electronic behavior (namely, the change from semimetal to semiconductor) from the geometric constraints imposed on the encapsulated crystal in a HgTe@SWNT material.

On the other hand, investigating the magnetic behavior of hybrid SWNTs is also a fast-growing topic, although theoretical works^{131–134} are still more numerous than experimental ones.¹¹⁵ The latter show that the ferromagnetism of iron is maintained in spite of its nanowire morphology with a nanometer-sized diameter, as the only example so far of an intrinsic property of the encapsulated material that has been transferred to the whole hybrid material. Likewise, it is also worth noting the first proposed application for hybrid SWNTs (CrO_x @SWNT) as a material to build electrodes for symmetric supercapacitor devices capable of unprecedented charging speeds, thanks to faradaic reactions that occur between the nanosized CrO_x crystals and the acidic electrolyte.¹⁴⁴

IV. FILLING, WETTING, AND CAPILLARITY

Data regarding physical properties of hybrid SWNTs have now started being reported, which is probably the most exciting part of this research field. This should not suggest that synthesis mechanisms are well understood yet, specifically regarding filling via liquid routes. Of course, from the work by Dujardin et al.,^{29,30} the surface tension of the liquids to fill the nanotubes with was acknowledged as a key parameter for successful filling. However, because the pressure difference that makes a liquid enter and proceed within a tube is proportional to the liquid surface tension and inversely proportional to the tube diameter, according to a relation obtained by combining the Young-Laplace's laws and the Jurin's law,¹⁴⁵ narrow tubes should fill over a longer length range than large tubes, meaning higher filling efficiency. However, this is not consistent with the conclusions from early works dealing with filling nanotubes with liquids, while comparing MWNTs with narrow and wide inner cavity, respectively. Indeed, until 1999, the filling of SWNTs was estimated to be inefficient,^{30,146} and Ugarte et al.²⁸ actually stated that "there appears to be a preference for the wider cavities to fill compared with the narrower cavities." This suggested that the laws (such as Young-Laplace's laws) driving regular wetting phenomena that were established for submillimeter capillaries (so-called "macrowetting" in the following), could not apply to capillaries in the nanometer range (so-called "nanowetting" in the following). This was further supported by early predictions by Pederson and Broughton,¹⁴⁷ who calculated that increasing the tubule radius decreases the incarceration energy and the overlap repulsion activation barrier at the mouth of the tube, from which they deduced that material encapsulation in narrow SWNTs via liquid or gas route should be disfavored with respect to larger MWNTs.

However, actual experiments carried out on SWNTs were found to contradict such early statements based on MWNTs. We did observe that filling efficiency appeared often better for regular SWNTs (inner cavity ~ 1.4 nm in the average) than for MWNTs (inner cavity ~ 30 – 40 nm in the average, herringbone type) for molten materials such as $GdCl_3$ and CoI_2 . Likewise, condensation of Se was found to occur first in the narrowest nanotubes,⁴⁹ and filling with Bi via the gas and liquid routes was found to be more efficient in SWNTs than in MWNTs "as a result from stronger capillary forces."⁴² Generally speaking, SWNT filling rates as high as $\sim 70\%$ (for PbI_2 ¹²⁸) or even 80% – 90% (for PbO ⁶⁷) were observed. Therefore, nanowetting is a reality.

However, chances are high that discrepancies may occur in nanowetting with respect to regular macrowetting. For instance, it is reasonable to admit that there should be a minimal tube diameter below which filling is no longer

possible, although such a threshold value cannot be given because it depends on the surface tension of the liquid material used to fill the nanotubes, e.g., 4 nm for Al_2O_3 and 0.7 nm for V_2O_5 ³¹ (see Sec. II. C. 1). This might explain why extensive filling studies on SWNTs have demonstrated that there is no direct relation between surface tension and filling efficiency.¹⁵ Also, as opposed to macrowetting, gravity is certainly not to consider in nanowetting because of the tiny volumes of liquid involved that make related weights negligible with respect to capillary forces. On the contrary, the role of viscosity, which is independent from surface tension (e.g., Hg provides a good example of a low viscosity liquid, 1.53 cP, with high surface tension of 490 mN/m), is likely to be enhanced in nanowetting. In macrowetting, viscosity is considered to only affect the wetting dynamics. The reason is, whatever the tube diameter, friction forces increasingly oppose the wetting forces because the tube/liquid contact surface where the friction forces take place increases as the liquid proceeds in the tube, while the gas/liquid/solid contact line where the capillary forces take place remains constant. This may ultimately cause the liquid progression to stop. In macrowetting, molecules from the liquid located at the liquid/solid interface go slower than molecules from the liquid core, somehow inducing a convection-like effect at the progression front where friction-affected molecules are continuously replaced by nonaffected molecules, which thereby feed the liquid/solid interface as the liquid progresses within the tube. In nanowetting, there should be a nanotube diameter below which the friction forces may affect all the molecules of the liquid because they all can be considered surface molecules, thereby preventing the convection-like effect from occurring, and subsequently hindering the filling event.

On the other hand, it is likely that viscosity is not the only additional key to consider for controlling the filling of nanotubes. The size of the atoms or molecules in the liquid, for instance, certainly matters for nanotube cavities below ~ 1 nm. Also, the intrinsic saturating vapor pressure value of the desired filling materials is likely to be important when using the melting method. Despite the filling temperature being maintained below the vaporization temperature of the filling material, some vapor pressure actually develops in the sealed ampoule. This pressure is likely to help the molten material to enter the SWNT cavity, with the consequence that materials with higher saturating vapor pressure should provide higher filling rates (considering that other parameters are equal). Such an aspect has not yet been investigated. Finally, local conditions may play an important role as well, as probably the only reason why, within the same filling experiment, some nanotubes are found extensively filled, whereas neighboring ones are found empty, yet obviously wide open [Fig. 6(a)].

V. CONCLUSIONS

In contrast with pessimistic early predictions, the narrow cavity of SWNTs can be filled with liquid and gaseous materials with high filling rate efficiency. For filling methods involving liquids, this means that, in first approximation, wetting nanosized capillaries obeys the same laws (such as Laplace-Young's laws) as wetting of submillimeter capillaries. However, it is now ascertained that the surface tension of the filling materials at liquid state is not the only relevant parameter to consider in nanowetting when the latter involves narrow (~ 1 nm and below) nanotubes. A large panel of methods is now available to fill SWNTs with a large variety of materials (elements or compounds) with an efficiency that unfortunately still largely depends on empirically determined filling conditions. Resulting hybrid SWNTs are expected to exhibit peculiar physical properties that are now being tested, and related results have just started to be released, with the reasonable hope that breakthrough reports, e.g., regarding transport or magnetic behaviors, may be anticipated in the close future. X@CNTs are part of a whole family of a new generation of CNT that can be named "meta-nanotubes," which result from the chemical modification (via filling, doping, grafting, coating, etc.) of nanotubes. In addition to their potential in exhibiting new properties, meta-nanotubes are likely to represent the actual economical future of nanotubes in many instances because they are much more suitable than pristine nanotubes for incorporation into complex materials (e.g., composites) and devices. Hence, with respect to the first 10 years of the nanotube saga that started in 1991 during which physicists have been authoring most of the published works thanks to the ease with which pristine nanotubes were able to be prepared, chemistry is now back in first place on the stage.

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