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Structural origin of coiling in coiled carbon nanotubes

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Abstract

The statistical distribution of a large number of helically coiled carbon nanotubes was analyzed in a cross-correlated way in their geometrical configuration space defined by diameter and pitch. Stability islands were identified, in which the number of coils exceeds about 15–10 times the value corresponding to a uniform distribution. When comparing our data with data from literature, a good agreement is found. The statistical findings are interpreted as indirect evidence that the geometric configuration of coiled carbon nanotubes is rather decided by the atomic structure of carbon layers building up the coils than by the external parameters which on the other hand may induce the particular conditions under which coiling occurs. The possible effect of impurities like N and S on the incorporation of non-hexagonal rings and tubular growth is pointed out.

Keywords: Carbon nanotubes; Chemical vapor deposition; Transmission electron microscopy; Modeling; Defects

1. Introduction

Recently more and more experimental efforts are focused on the controlled synthesis of regularly coiled carbon nanotubes (CCNTs), predicted by Dunlap [1] in 1992, just one year after the discovery of straight carbon nanotubes [2], and first observed experimentally 10 years ago by Amelinckx et al. [3]. This increase in interest is perfectly justified by the specific properties of these carbon nanostructures. As certain types of coiled carbon nanotubes may have comparable mechanical properties with catalytically grown (CVD) multiwall carbon nanotubes (MWCNTs) [4], the coiled shape could solve one of the most crucial problems of reinforcement by carbon nanotubes (CNTs) [5]: a coil provides excellent load transfer, without the need to damage the graphitic network of the CNT by covalent functionalization. To fully exploit this advantage the entangling of coils has to be avoided and a good dispersion in the matrix has to be achieved. Novel devices and sensors can be built using CCNTs, which can have sensitivity as high as femtograms [6]. Also, CCNTs may find several applications in nanoelectromechanical systems (NEMS) and when the patterned growth of CCNTs will be realized, this may constitute the basis for very high sensitivity and high resolution tactile sensors.

In order to be able to understand the best ways of mass producing the CCNTs to be able to fully exploit their potential benefits, it is of utmost importance to understand the relation between the structure and growth mechanism of these nanostructures. One very important question to be decided is: has the coiling a structural origin, i.e., are coiled carbon nanotubes a class of structures distinct from the straight carbon nanotubes, or is coiling the result of a faulted shape that straight carbon nanotubes adopt due to certain external conditions, like the different extrusion velocities of

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carbon on different facets of the catalytic particle [3], hindered growth [7], or else.

The early structural models of CCNTs [1,8] were based on a very specific arrangement of isolated defects, pentagons (P) and heptagons (H) in a perfect hexagonal (Hx) lattice. If the regular arrangement is perturbed by misplacing one single non-hexagonal (n-Hex) ring, the structure will not be any more a regular coil [9]. Recently we proposed a novel class of models in which the n-Hex rings are not considered as defects, but regular building blocks of a structure [10–12], leading to haeckelite sheets, similar to graphene [13]. The coiling arises as an intrinsic property of the structure due to the existence of so called "stressors" [11]. The coiled tubes rolled from haeckelite sheets are defect tolerant [10]. Coiled and "necklace type" [14,15], tubular nanostructures may be rolled from haeckelite in a similar way like the straight carbon nanotubes are rolled from graphene [11,14]. Another class of models was proposed recently by László and Rassat [16] based on a topological approach. In their tiling patterns the distribution of n-Hex rings is an intermediate of the two previously discussed cases: rows of connected heptagons separate stripes of hexagons in which isolated pentagons are incorporated.

A very wide variety of experimental conditions were used for the synthesis of CCNTs, it is not within the scope of the present paper to give an overview of the field. However, some general characteristics may be pointed out: (i) in all experiments when CCNTs were produced some kind of catalyst was used; (ii) to our knowledge no CCNTs were produced by the so called high temperature methods, operating in the range of 2000 °C, or above; (iii) not always, but in the great majority of the experiments N_2 was used as neutral carrier gas.

Given the great variety of experimental conditions, it is worth to carry out a statistical analysis of the characteristic parameters of the produced coils. These parameters are: coil diameter and pitch [17,18]. If the way in which coiling takes place is decided by external parameters like the shape of the catalyst particle, the non-homogeneity of the extrusion velocity of carbon on different facets, geometric hindrance in growth, or else, there will be no reasons to find any systematic relation in coil diameters and pitches. On the contrary, if the coiling is decided by intrinsic structure and energetic stability, such as minimizing the stress to which the sheet used for constructing the coil (graphene or haeckelite) is subjected, some correlation should be present between diameter and pitch. This statistical study is the purpose of the present paper.

2. Experimental

Carbon nanotubes were grown by CVD at ambient pressure with several catalysts, using acetylene as carbon source and N_2 as carrier gas as described earlier [19]. Various catalysts were used: Co/SiO_2 and Co–Pr/SiO_2. The pure Co/SiO_2 catalysts were prepared by ion-adsorption precipitation (IAP) and sol–gel (SG) method, too, with different concentration of active metal particles (5–12.5 wt% of Co for the first mentioned method IAP and 1–12 wt% of Co for SG). While the IAP catalyst were prepared under basic condition, for the SG acidic environment was used. Further details of the preparation are given elsewhere [19,20]. A total of 12 different experimental runs were completed: one IAP in which Co–Pr was used, four IAP with only Co, and seven SG, with Co only. The product of each experiment was investigated by TEM, 200 coil diameter and pitch pairs were collected from all of the experiments.

3. Statistics

The coil diameter and pitch values (as defined in Refs. [17,18]) obtained from the TEM images were evaluated in a *correlated* way, i.e., opposite to the procedure of Hernádi et al. [17] and Lu et al. [18], who used 2D plots for representing either number vs. pitch, or number vs. diameter, a 3D plot was used to plot the number of coils exhibiting a certain pair of coil diameter and pitch value. The result is shown in Fig. 1.

One can clearly remark that there are some regions, which will be called "stability islands", where the number of coils is significantly higher than in the neighboring regions. The first stability island (taken as a compact region) is delineated by the crossing of the region of 50–70 nm pitch and 20–60 nm diameter. More precisely, the three most stable configurations are the ones detailed in Table 1, a less pronounced stability region is found between pitch 30–50 nm and the same diameters, the parameter combinations are given in Table 2.

A fraction of 24.5% of the total number of coils is found in the two stability regions, which has to be compared with 2% that would correspond to the same area if a uniform distribution of coils over the entire area of the plot would be found. The analysis of the coil diameter distribution of Fig. 1 shows that half of the coils are found in the range of 50–70 nm, while again, half of the coils have a pitch in the range of 30–80 nm. As a further check, the histograms of Hernádi et al. [17] and Lu et al. [18] were used to compare them with the data of present work. As from their histograms one cannot find the correlation of coil diameters and pitches, only 2D comparison was possible, Fig. 2a and b. The three data groups of Hernádi et al. [17] and Lu et al. [18], together with those of present work contain 345 coils, which we believe is a sufficient number to allow for some safe conclusions. As one can observe from Fig. 2, the data show coincident stability regions. Taking into account that the

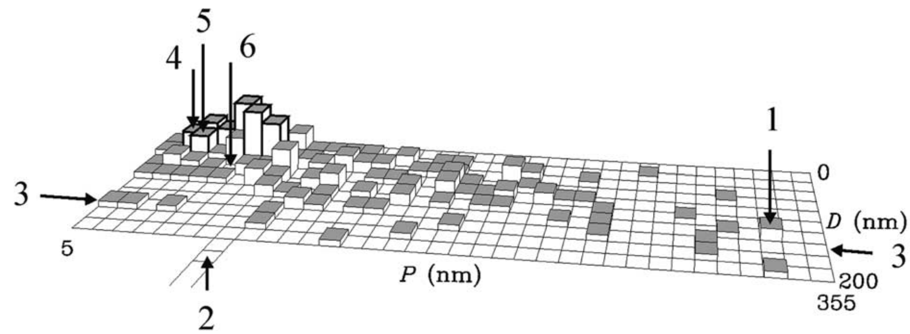

Fig. 1. Cross-correlated 3D plot of number of coils vs. coil diameter (*D*) and pitch (*P*) values for coiled nanotubes grown by CVD. The two stability islands mentioned in the text are highlighted in bold lines. Labeled arrows indicate the position of the coils mentioned in the text: 1 and 2 [22], 3 [23], 4blank;[24], 5 and 6 [20].

Table 1
The three most frequent coil configurations found within the first stability island

Type	*P* (nm)	*D* (nm)	Average *d* (nm)	*P*/*R*	Fraction (%)
Type 1.1	50	30	12	5.6	5
Type 1.2	60	50	13	3.2	5
Type 1.3	70	50	15	4.0	4

In the case of uniform distribution in one column of the 3D plot one should find 0.28% of the coils.

Table 2
The coil configurations of the second stability region

Type	*P* (nm)	*D* (nm)	Average *d* (nm)	*P*/*R*	Fraction (%)
Type 2.1	30	30	10	3.0	3
Type 2.2	30	50	12	1.5	2.5
Type 2.3	40	30	12	4.5	2.5
Type 2.4	50	50	15	2.8	2.5

data come from three different laboratories and from a number of at least 15 experimental cycles, the chance of accidental coincidences is rather low. Therefore we believe: these data are an indirect proof that the way in which carbon nanotubes are coiled has an intrinsic, structural origin and it is not decided by external factors. However, the external factors may contribute in creating those specific growth conditions which make that the coiled structure is more stable than the straight tube. As the degree of stability is a characteristic of a certain structure, the most stable structures may be "selected" under various external conditions. Although these indirect data do not allow to unambiguously decide which structural model is best describing the atomic structure of the CCNTs, due to the fact that in the models with isolated n-Hex rings one can increase at will the length of tube segments between the isolated n-Hex rings (which may increase both the coil diameter and the pitch), these models are less likely to explain satisfactorily why the same coil configurations are found to be characteristic for different experiments and different laboratories.

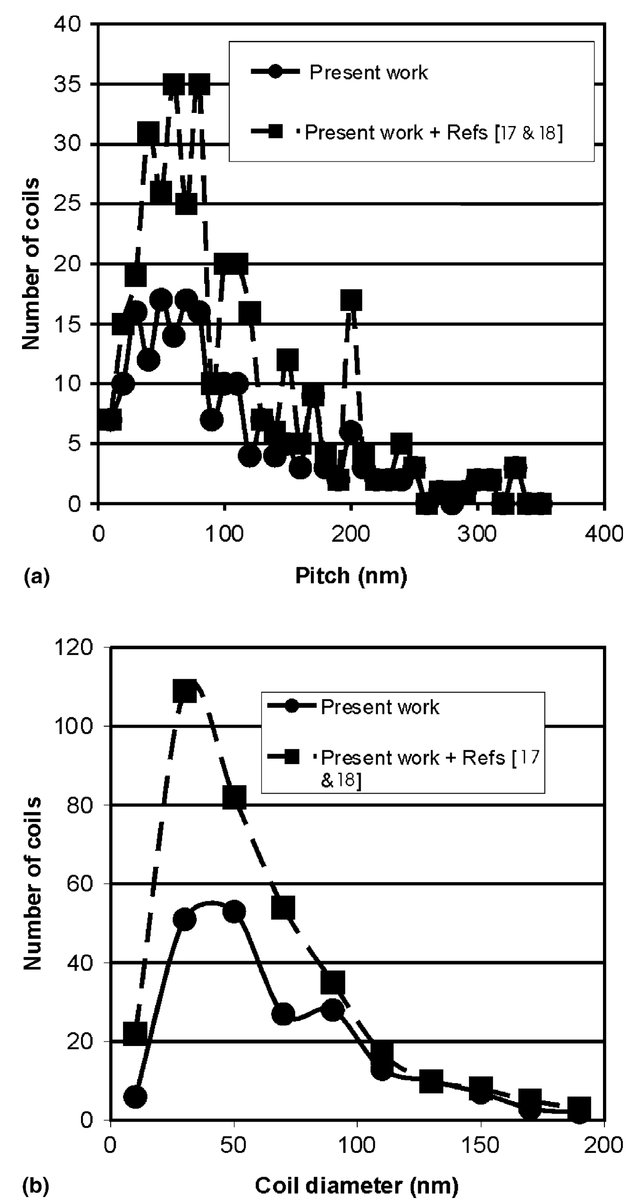

Fig. 2. Comparative data of 2D coil distributions of present work and data of Refs. [17,18]. (a) Number of coils vs. pitch, *P*; (b) number of coils vs. diameter, *D*.

A further point which may be worth emphasizing is the question of the typical size of the catalyst particles. In order to produce enough stress for the generation of n-Hex ring kinetically, the size of the catalyst particle should be larger than the typical tube diameter in order to allow different extrusion velocities of the carbon on differently oriented crystalline faces [21]. Gao et al. carried out a study targeted to elucidate this issue. They found that the statistical distribution of the inner diameter of nanotubes is coincident with the size distribution of the catalytic particles. This finding strongly questions the validity of the growth model based on the different extrusion velocities of carbon on different crystalline planes [21].

High resolution transmission electron microscopy (HRTEM) was used by several groups to investigate in more detail the structure of CCNTs. Bernaerts et al. [22] and Zhang and Zhang [23] report on coils composed of straight segments, the diameter and pitch values ($D_1 = 330$ nm, $P_1 = 110$ nm; $D_2 = 214$ nm, $P_2 = 78$ nm) of Ref. [22] and ($D_3 = 153$ nm, P_3 cannot be determined from the TEM image as the investigated object is a single spire of a coil), and of Ref. [23], respectively, place these coils in low density regions of Fig. 1. HRTEM image of a coil with $D_4 = 52$ nm and $P_4 = 35$ nm, indicating a position on the edge of stability region 2 of Fig. 1, was recently reported by Saveliev et al. [24]. This coil shows continuous curvature of the graphene layers [24]. In a recent work [20] we compared HRTEM images of continuously-curved CCNTs and coils composed of straight segments. The diameter $D_5 = 27$ nm and pitch $P_5 = 21$ nm place the coil constituted of continuously-curved sheets in stability region 1 of Fig. 1. The diameter of the coil constituted form straight segments cannot be determined accurately from the HRTEM image, a value in the 60 nm range can be estimated, with a pitch $P_6 = 53$ nm which places it on the edge of a low density region of Fig. 1. From a purely geometric point of view, the coils of the two stability regions in Fig. 1 have diameter and pitch values close to each other, or smaller pitch than diameter, Fig. 3. Although the scarcity of the HRTEM data for CCNTs does not allow us to decide if it is more frequently found that coils are continuously curved or composed from straight segments, the available HRTEM data do not contradict the results of the statistical analysis.

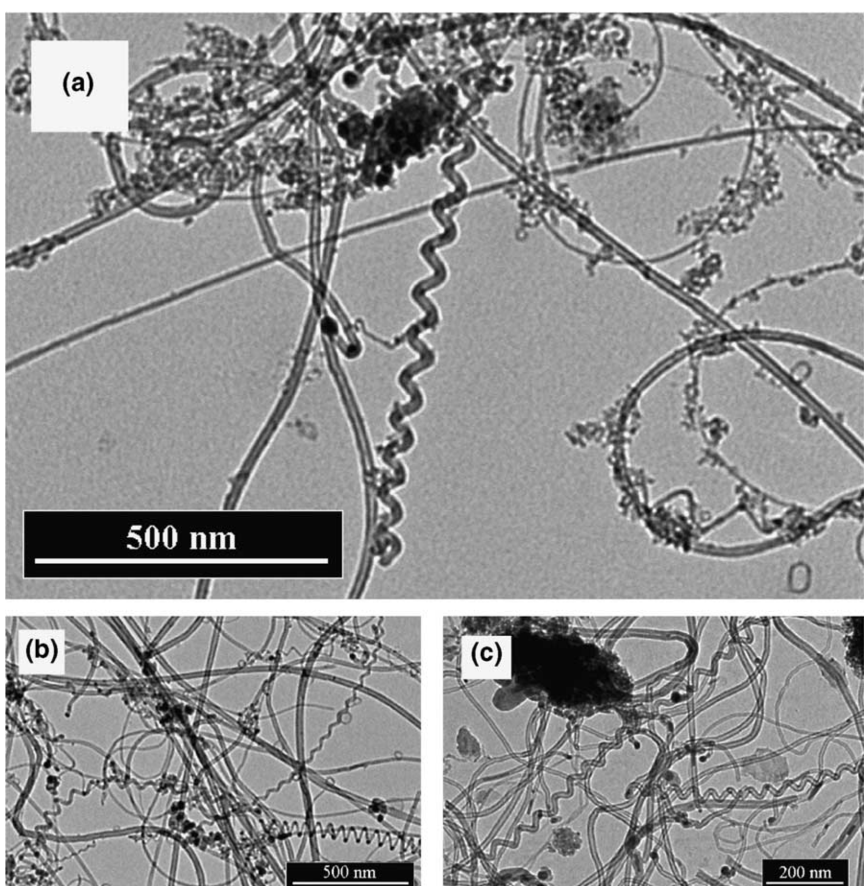

Fig. 3. TEM images of coils from the stability islands (see Tables 1 and 2). (a) A 1.3 type coil; (b) from left to right: 1.3, 1.2 and 2.4 coils; (c) from left to right 1.2 and 1.1 coils.

4. Coils with defects

The detailed HRTEM investigation of coiled carbon nanotubes revealed that visible defects may be present in the structure and arrangement of the carbon layers, but the overall, regular coiling aspect may be conserved [17]. Topographic STM data confirm that after a region with structural alterations, the regular helical structure may be continued [10,25]. Such a behavior is less likely when the way in which coiling occurs is decided by isolated n-Hex rings as the local alteration of the structure clearly indicates that the regular arrangement of these rings was perturbed and there are no apparent reasons why after a while the very same arrangement would be restored. On the other hand in a haeckelite type model, the coiling is the result of the collective behavior of the rings constituting the haeckelite sheet [11] which can make that after the local perturbation the structure comes back to the same status of equilibrium as before the perturbation.

5. Continuum mechanics analysis

If the data of Fig. 1 are converted into values of curvature radius for the coil, defined as

$$\rho = \frac{R^2 + (P/2\pi)^2}{R} \qquad (1)$$

$$R = \frac{D - d}{2} \qquad (2)$$

where ρ is the curvature radius of the coil, R is the radius of the helix as drawn by the axis of the coiled nanotube, d is the diameter of the nanotube, P is the pitch, D is the coil diameter, one finds as the most frequent curvature value 25 nm. This value of curvature, if achieved starting from a straight MWCNT, i.e., one built only of hexagons, would mean a relatively high value of stress. The analysis of the pitch angle values (defined as the angle between the tangent to the helix and its axis) calculated from the data used to build Fig. 1, shows that the most frequent pitch angles are in the range of 55–75°. These data are characteristic for coils as shown in Fig. 3. One should point out that some subjectivity in the selection of the objects which are included in the TEM image, and in the selection of the CCNTs, for which the diameter and pitch is measured may not be fully excluded. For low values of pitch angle it may not be straightforward to make the difference between a large pitch small diameter coil and a curved MWCNT, characteristic for CVD growth.

In Ref. [26], the shape of a nanotube was determined by continuum elasticity, taking into account the curvature elastic energy of the graphitic layers, the van der Waals attraction between the layers, and the surface energy. It was shown that a circular helix is a stable solution of the equilibrium shape equation of the tube axis, provided the ratio between its pitch P and its radius R be exactly 2π. One finds P/R values as listed in Tables 1 and 2. All these values deviate significantly from the optimum. In fact, assuming an average tube diameter of 15 nm for all the coils represented in Fig. 1, 68% of them turn out to have $P/R < 6.0$ and 28% have $P/R > 6.6$. It was found by Bai [27], too, that the pitch/radius is far from the optimum value 2π. The curvature $1/\rho$ of the coils that belong to the stability islands of Fig. 1 is so large that the van der Waals energy cannot compensate for the curvature elastic energy of the graphitic sheet. Indeed, bending a tube of diameter $d = 10$ nm for instance on an arc of radius $\rho = 25$ nm, would induce a strain $d/2\rho = 20\%$ on the inner and outer sides of the bent tube. These are enormous strains, and the tube will buckle on its compressed side at a much smaller curvature [28]. Consequently, the coils are not elastically bent nanotubes driven by the van der Waals adhesion of the layers. Their helical shape is imposed by their atomic structure, either through a regular incorporation of pentagons and heptagons, for those coils which present sharp bends between straight portions, or possibly by a Haeckelite type atomic structure for those coils which present a continuous curvature. To some point, the situation is the same in carbon onions where continuously-curved graphitic spherical sheets have been observed with a radius of the order of 10 nm [29]. This continuous curvature can be achieved if a large proportion of pentagons and heptagons are incorporated in the graphitic networks like in the haeckelite nanotubes, possibly through Stone–Wales transformations [30].

6. Nitrogen and sulfur

As already mentioned, the great majority of the experiments which resulted in coiled carbon nanotubes were carried out using nitrogen as inert carrier gas. The truly inert behavior of nitrogen may be worth investigated in some more detail. As recently proposed by Zhong et al. [31], N may contribute to the coiling, possibly by favoring the formation of pentagons [32]. Moreover, in a recent work Kovács et al. [33] showed that during CN_x deposition, the presence of transition metals like Ni, enhance the formation of fullerenic closed shells which exactly follow the surface of the transition metal nanoparticles (see Fig. 3 of Ref. [33]). This finding is in agreement with the mechanism based on the selection of a particular haeckelite surface, which is best encapsulating a transition metal particle of given radius [11].

On the other hand coiled carbon nano-objects have been produced in some experiments in which no nitrogen was, used [34–36]. Except Ref. [36], where hydrogen was bubbled through thiophene the coiled structures were not tubular. So, it cannot be excluded that impurities like N or S may promote formation of coiled carbon nanotubes, while in their absence the coiled structures are amorphous or non-tubular. In the case of nitrogen there exists an extensive literature originating from the CN_x research, conclusively showing that N may be incorporated in carbonaceous materials [32,33,37]. On the other hand, sulfur seems to be useful for enhancing the production of Y-branched carbon nanotubes [38], in which n-Hex rings also have to be incorporated to make possible the branching.

7. Conclusions

We analyzed the shape of more than 300 coiled carbon nanotubes. The statistical, HRTEM and continuum elasticity investigations concordantly show that the coiling of carbon nanotubes has structural origin while various external factors may create the specific conditions which make that the coiled shape is more favorable than the straight one. On the basis of the analysis one can conclude that the most frequently found coiled carbon nanotubes are grouped in certain stability "islands" in their geometrical configuration space, which are reproduced in different experiments and different laboratories. We interpret this as indirect evidence that the way in which carbon nanotubes are coiled has an intrinsic, structural origin and it is not decided by external factors. The possible role of impurities like nitrogen and sulfur in promoting the production of coiled carbon nanotubes is pointed out.

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