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Synthesis, Model and Stability of Helically Coiled Carbon Nanotubes

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Structural model of helically coiled carbon nanotubes is proposed. It is constructed by means of topological coordinate method. Relaxation and cohesive energy calculation are performed by molecular mechanics, using second-generation bond order potential for hydrocarbons introduced by D. W. Brenner. Our experiments focused on the production and development of catalysts for the synthesis of helically coiled CNTs (carbon nanotubes). The catalysts were tested in the decomposition of acetylene by CCVD (Catalytic Chemical Vapor Deposition) method. The carbon deposit was imaged by TEM (Transmission Electron Microscopy), HRTEM (High Resolution Transmission Electron Microscopy).

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The existence of helically coiled carbon nanotubes was first predicted by Ihara et al.¹ and Dunlap² in the early nineties and a few years later a Belgian research group reported their experimental observation.³ Recently, we reviewed⁴ regularly coiled carbon nanotubes, their synthesis, their structure, formation mechanism, and theoretical aspects, giving an up-to-date summary of scientific results accumulated until now on this field.

Here we present a technique of construction of atomistic models of helically coiled carbon nanotubes (HCCNTs) based on the topological coordinate method which uses triple connected graphs of pentagons, hexagons and heptagons^{5,6} as well as the synthesis and characterization of coiled carbon nanotubes. This technique overcomes the shortcomings of the previously proposed methods in which the coils are built out of particular fullerene¹ or out of particular straight single-wall CNT,^{2,7} getting thus only a few different tubes helical diameter of which reaches two nanometers at most (i.e. several orders of magnitude less than the average coil diameter of the CCVD grown tubes).

Stability of the obtained models of the helically coiled CNTs is verified: their cohesive energy is calculated after performing molecular dynamic relaxation based on the second-generation reactive empirical bond order Brenner potential for solid carbon structures.⁸

We investigated the effect of the pH during the wet milling catalyst preparation process, we calculated the carbon yield of the catalysts, and characterized the coil structures more in detail by measuring the dimensions of these coils after catalytic carbon nanotube synthesis. We observed the morphology of helically coiled carbon nanotubes by TEM and HRTEM.

Modeling

SWCNTs (Single Walled Carbon Nanotubes) can be obtained by identifying a pair of the opposite edges of a parallelogram cut out from a graphene sheet. Positive and negative Gaussian curvatures in the carbon structures arise from substitution of some hexagons by pentagons and heptagons, respectively. Thus, in order to construct helical nanotube structure we start with three-coordinated periodical stylized tiling of the plane by heptagons, hexagons and pentagons and apply the procedure of building up a helical tubular structure, based on the topological coordinate method.⁵ After getting three-dimensional coordinates of the carbon atoms of a helically coiled CNT we proceed with relaxation. Final relaxed structure depends on the tiling and on the super-cell position. Hence, we start with particular tiling and super-cell and construct series of graphs and super-cells by further insertion of horizontal and vertical stripes of hexagons, between the

pentagons and heptagons or between the twin columns of heptagons in order to enlarge tubular diameter and indirectly, through process of relaxation, enlarging also diameter of a coil and changing helical angle and helical step as well.⁶

Helically coiled CNT is constructed from the graph defined as follows (more detailed description of the model is given in Ref. 6): $(n_6, n_r, n_7, n_5, (\mathbf{b}_1, \mathbf{b}_2))$, where $\mathbf{b}_1$ and $\mathbf{b}_2$ are the super-cell vectors, n_r is number of rows of hexagons added above a single LR (Laszlo-Rassat)⁵ cell $(n_6, (1, 0), (0, 1))$, n_7 and n_5 are numbers of columns of hexagons inserted between the columns of heptagons and pentagons, respectively (Figure 1). Three series of helically coiled CNTs defined by the n_5 parameter are shown in Figure 2. This parameter defines radial position of pentagons, i.e. their distance from the helical axis. Helical diameter increases and helical step decreases with n_5 , when n_6 and n_r are fixed. Within each of the series particular tubes are defined by parameters n_6 and n_r which are here set equal and are taking the values 1, 3, 5, 7 and 9. The super-cell vectors are $\mathbf{b}_1 = (1, 0)$ and $\mathbf{b}_2 = (0, 5)$ and there is no separation of the columns of heptagons of the original LR cell (i.e. $n_7 = 0$). Within each of the series tubular and helical diameter increase linearly with $n_6 = n_r$, as well as the monomer length a .

However, if $n_6 \neq n_r$ and the value of n_6 is fixed, the helically coiled CNTs constructed out of such graphs mutually differ by the size of the helical diameter and helical step (the both increase with n_r) while tubular diameters of these coils do not differ appreciably. Oppositely, if n_r is fixed, helical and tubular diameter increase with n_6 while the inclination decreases.

Different choices of the super-cell, within the same tiling, have considerable impact on the overall structure of the helically coiled tube. Particular choice of the super-cell defines orientation of the polygons relative to the nanotube axis while concentration of pentagons and heptagons is determined by the tiling only. However, fine tuning of the geometrical parameters of the coiled nanotube cannot be achieved by taking different super-cell vectors on the same tiling. Engineering of the structural features of the helically coiled CNTs is easier to control when the type of the super-cell remains the same while the tiling is changed gradually. Characteristic structural data of the ensemble of 218 modeled helically coiled CNTs is summarized in Table I.

Experimental

Preparation of the catalysts for the synthesis of coiled carbon nanotubes.— Here we apply wet milling with distilled water and with ammonia solution, they provide slightly acid and basic environment, respectively. During the wet milling process 0.2469 g of the precursor $(\text{Co}(\text{NO}_3)_2(\text{H}_2\text{O})_6$, Sigma-Aldrich), 0.95 g of the support (13X

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Figure 1. (Color online) Graph $(n_6, n_r, n_7, n_5, (b_1, b_2)) = (1, 1, 2, 2, ((2, 2), (1, 3)))$: tiling of the plane by heptagons, pentagons and hexagons where one row of hexagons is added at the top of the original LR cell and columns of heptagons and pentagons are separated by two stripes of hexagons, each. Super-cell vectors b_1 and b_2 are represented by the arrows and the unit cell by the rectangle.

zeolite, UOP Fluka) and 2 mL distilled water or 25% NH_4OH were mixed mechanically in a Pulverisette 6 type planetary ball mill (in air), equipped with a 250 mL grinding bowl. As-prepared catalysts contained 5% metal. Each time 8 balls of 20 mm size were used for homogenization. The rotational speed was 450 rpm, the respective treatment times of planetary ball milling were 60 minutes.

CCVD Synthesis of helically coiled carbon nanotubes.— Carbon nanotubes were grown catalytically by acetylene decomposition at 720°C for 30 min in a fixed-bed flow reactor using gas feed of nitrogen (500 mL/min) and acetylene (10 mL/min). In order to give some quantitative characterization of the catalytic decomposition of acetylene, carbon yield was calculated as follows:

$$\text{Carbon yield}(\%) = 100(m_{\text{tot}} - m_{\text{cat}})/m_{\text{corr.cat}}$$

Figure 2. Within each of the three series (defined by the value of $n_5 = 0, 2$ and 4) of helically coiled CNTs $n_6 = n_r$ dependence of the helical radius R (a) and helical diameter D and step p (b) are shown. Inset of (a) gives n_r -dependence of the helical R and tubular r radii ratio (for the series defined by $n_5 = 4$).

Table I. Range of diameters, inclination angles and length data of the ensemble of 218 modeled helically coiled carbon nanotubes.

	Characteristic data
Helix diameter D	1.2 nm–44.0 nm
Coil pitch p	0.3 nm–14.9 nm
Tube diameter d	0.4 nm–3.4 nm
Tube length	Infinite
Inclination angle χ	$5^\circ - 64^\circ$
Monomer length a	0.8 nm–10.8 nm
D/d	0.9–31

where, m_{cat} is the initial mass of the catalyst immediately before the reaction, m_{tot} is the total weight of the sample after reaction, $m_{\text{corr.cat}}$ is the corrected mass of the catalyst after weight loss at the temperature of CCVD reaction (720°C). We calculated carbon yield instead of CNT yield because oxidative purification could be carried out, however, it would result in the complete elimination of coiled carbon nanotubes.⁹ Additionally the essence of CCVD method is the selective production of CNTs, so only small amount of amorphous carbon can be formed during the synthesis.

Experimental Results

Nanosized particles generated from the solid surface during grinding tend to form agglomerate instantaneously and become stable, coarser particles. In this way, it is very difficult to produce stable nanosized particles by dry grinding method, since active nanoparticles from fresh agglomerates as soon as they contact each other. Therefore, the grinding has to be carried out in a liquid (wet milling). In the wet milling process, as the surface of the generated particle is surrounded by a solvent instantaneously, it is possible to control the agglomeration of particles much better than in the dry milling,¹⁰ furthermore the pH (or the organic nitrogen content) of the solution during catalyst preparation has a significant role on the resulted structure. Figure 3a shows the result of the wet milling with distilled water, the as-prepared sample consist of irregular nanotubes, while Figure 3b represents the coiled carbon nanotubes prepared by using wet milling with ammonia solution. The calculated carbon yield was 30.09% in case of preparing the catalyst with distilled water, and 39.1% with ammonia solution. Figure 4 summarizes the outer diameter distribution of the as-prepared helically coiled carbon nanotubes, mainly they are in the range of 10–20 nm. To compare the characteristic data with the theoretical ones, we characterized the helix diameter, coil pitch, tube diameter and tube length of the coiled carbon nanotubes (Table II), quantitatively most of the characteristic parameters are nearly close to the dimensions of the modeled helically coiled carbon nanotubes. The helix diameter is overlapping, but the modeled coil pitch and tube

Figure 3. Figure 3(a) shows the result of the wet milling with distilled water, the as-prepared sample consist of irregular nanotubes, while figure 3(b) represents the coiled carbon nanotubes prepared by using wet milling process with ammonia solution. Here the dimensions of the helically coiled carbon nanotube are the follows: the helix diameter is 58 nm, the coil pitch is 55 nm, the tube diameter is 13 nm and the tube length is 1114 nm.

Figure 4. Figure 4 summarizes the outer diameter distribution of the as-prepared helically coiled carbon nanotubes, mainly they are in the range of 10–20 nm.

diameter is smaller than the synthesized ones. Our theoretical model is single-walled in contrast to the multi-walled structure of the real tubes. On one hand the cell of the model is limited by number of atoms, on the other hand, has not been reported on the synthesis of single-walled helically coiled nanotubes according to our knowledge. To bring even better agreement we should succeed in the synthesis of single-walled helically coiled CNTs.

Stability

Relaxation and cohesive energy calculations are performed by molecular mechanics based on the bond order potential for hydrocarbons developed by D. W. Brenner.⁸ Application of the symmetry made the relaxation procedure more efficient. As to the generators of the symmetry of the helically coiled CNTs,⁶ apart from the screw axis transformation, pertains also a rotation for π around the axis perpendicular to the helical axis, relaxation can be restricted just to a half of the monomer. The Hooke-Jeeves algorithm¹¹ is used, as here it proved to give the best minima and to be reasonably fast.

Within the series of helically coiled CNTs, cohesive energy increases with the tubular and helical diameter and saturates eventually. The calculated values are between 6.7 eV/atom and 7.2 eV/atom. In Figure 5, tubular and helical diameter dependence of the energies calculated for the series $(n,n,0,n_5,((1,0),(0,5)))$, $n_5 = 0, 2, 4$ and $n = 1, 2, \dots, 11$, of helically coiled CNTs are presented. Tubes of these series mutually differ by the number of stripes of hexagons n_5 inserted between the columns of pentagons, by the number of columns of hexagons $n_6 = n$ which separate pentagons from heptagons and by the number of rows of hexagons $n_r = n$ added to the initial LR cell. Pentagon and heptagon concentration *per* monomer decreases with n .

For the sake of comparison, dependence of the cohesive energy on the tubular radius of the straight single-walled CNTs has been calculated by the same method. The fitted $E(r)$ function, Figure 5a, when up shifted for 200 meV represents also a good fit of the cohesive energies of the helically coiled CNTs. Infinite radius limit of the energy of SWCNTs which according to our calculation is 7.394 eV matches the recently reported¹² value of the graphene cohesive energy, obtained by applying the same, original Brenner, potential. The values of the cohesive energy obtained by DFTB (density functional tight binding) method¹³ are generally somewhat larger than the values obtained by

Figure 5. (a) Cohesive energy E of helically coiled CNTs as a function of tubular radius r : Black triangles represent data for the series of helically coiled CNTs $(n,n,0,n_5,((1,0),(0,5)))$, where $n_5 = 0, 2, 4$ and $n = 1, 2, 3, \dots, 11$; solid line shows the data for the straight SWCNTs calculated using the same bond order potential; dashed horizontal line at -7.394 eV indicates the infinite radius limit of the cohesive energy of SWCNTs. Inset: $E(r)$ -dependence over wider tubular radii range of helically coiled CNTs. (b) Helical radius R dependence of the cohesive energy E of helically coiled CNTs. Calculated values of the above defined series of the coiled nanotubes are presented.

the method applied here. For instance, in Ref. 6, where the symmetry based DFTB calculations are performed, cohesive energy of the helically coiled CNTs is from 7.46 eV/atom to 8.00 eV/atom, while the energies of graphene and (10,10) nanotube are 9.70 eV/atom and 8.27 eV/atom, respectively.

Conclusion

By the technique presented here we are able to build helically coiled CNTs within the wide range of geometrical parameters and also within considerably large interval of the tubular-helical lateral sizes ratio (Table I). Control over the structural features of the coils is gained by picking particular tiling of the plane and by choosing appropriate super-cell vectors.

Final structural model has smooth helical profile and circular cross section, qualitatively matching the as-synthesized helically coiled CNTs. Quantitatively most of the characteristic parameters are nearly close to the dimensions of the CCVD grown carbon coils (Table II). Nevertheless, our theoretical model is single-walled in contrast to the multi-walled structure of the real tubes.

Acknowledgments

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Table II. Range of diameters, coil pitches, length data of the as-synthesized helically coiled carbon nanotubes.

	Characteristic data
Helix diameter D	30.0 nm–88.0 nm
Coil pitch p	31.0 nm–53.2 nm
Tube diameter d	9.6 nm–29.2 nm
Tube length	150 nm–700 nm
D/d	3.3–6.8