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Carbon 42 (2004) 2561–2566
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Carbon nanoarchitectures containing non-hexagonal rings: "necklaces of pearls"

L.P. Biró [a,*], G.I. Márk [a], Z.E. Horváth [a], K. Kertész [a], J. Gyulai [a], J.B. Nagy [b], Ph. Lambin [b]

[a] *Research Institute for Technical Physics and Materials Science, H-1525 Budapest, P.O. Box 49, Hungary*
[b] *Facultes Universitaires Notre-Dame de la Paix, B-5000 Namur, Rue de Bruxelles 61, Belgium*

Received 23 February 2004; accepted 24 May 2004
Available online 15 July 2004

Abstract

The structure of novel forms of carbon nanostructures (Haeckelites) is investigated combining modeling with experimental data. New arguments are given for the existence of a theoretically predicted sp^2 hybridized carbon form, with structure close to that of graphite, called Haeckelite (Terrones et al., Phys. Rev. Lett. 84 (2000) 1716). The major difference between Haeckelite and graphite is given by the regular occurrence of non-hexagonal carbon rings as building blocks of Haeckelite. It is proposed that the necklace of pearls type nanostructures investigated by SEM, TEM and HRTEM, are built of Haeckelite and a structural model which allows a graphitic interlayer spacing for multilayer Haeckelite necklaces is proposed.

Keywords: A. Carbon nanotubes; B. Chemical vapor deposition; C. Modeling; D. Micro-structure

1. Introduction

Due to its various electronic configurations carbon is an extremely versatile element. Beyond its well known allotropes graphite and diamond, new forms have been discovered, like fullerenes [1] and nanotubes [2], and some even more recent ones were found with structure depending on the preparation techniques and particular experimental conditions used. The increasing number of papers on novel, complex carbon nanotube type nanoarchitectures like multiwall [3] and singlewall Y junctions [4], simple [5] and multiple coiled nanotubes [6,7] clearly shows that the sp^2 hybridization of carbon makes possible a large variety of tubular, carbon based nanostructures.

The toroidal [8], coiled [9,10], and the Y-branched [11–13] carbon nanotubes have been predicted theoretically soon after the discovery of the straight nanotubes. All of the early structural models are based on the insertion of non-hexagonal (n-Hx) defects in the seamless hexagonal (Hx) network. In particular, the early models of the regular helical coils of CNTs are based on a very specific arrangement of pentagons (P) and heptagons (H) in a perfect Hx lattice [10,14].

In a recent paper [6], we have generalized the idea of building tori and coiled carbon nanotubes from azulenoid units [15], and the idea of straight Haeckelite nanotubes [16]. We proposed a different model for the coiled form of carbon nanotubes which allows n-Hx/Hx ratios over unity. In this model the n-Hx rings are not any more treated like isolated defects, they constitute regular building blocks of the structure. In the present work we continue this generalization by showing that the Haeckelite type nanotubes can be wrapped from a Haeckelite sheet generated by fusing together the edges of Haeckelite stripes. The wrapping procedure is similar to the way in which straight carbon nanotubes are wrapped from a graphene sheet [17], i.e., our procedure allows the systematic generation of the various forms of coiled carbon nanotubes. Experimental observations of "necklace of pearls" type tubular carbon nanotubes are compared with the theoretical model.

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[*] Corresponding author. Tel.: +36-1-3922681; fax: +36-1-3922226.
E-mail address: biro@mfa.kfki.hu (L.P. Biró).
URL: http://www.mfa.kfki.hu/int/nano.

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doi:10.1016/j.carbon.2004.05.038

2. Structure

2.1. The Haeckelite sheet

It is possible to generate a Haeckelite sheet (Fig. 1) by fusing together several stripes, like the ones proposed in our earlier paper [6]. In order to be able to represent this surface on a sheet of paper or a computer screen, one has to accept the distortions of the angles of the polygons building up the sheet. On the other hand, if the problem is not a purely geometrical one, but a structural problem, in which physical entities like atoms are placed in the nodes of the Haeckelite network, and the atoms have clearly defined interactions, then the distortion needed for the planar presentation may be eased up, when the three-dimensional structure wrapped from the Haeckelite sheet is allowed to relax. We applied the procedure of fusing the stripes to construct a Haeckelite sheet from the stripe shown in Fig. 4b of Ref. [6], the resulting sheet is shown in Fig. 1. Three Haeckelite stripes highlighted in shades of gray indicate the way in which the sheet is generated from stripes. The heavy dots indicate the stress concentrators, the so called "stressors", which will have a major role in shaping the relaxed, tubular structures [18]. Similar Haeckelite sheets can be generated from Haeckelite stripes with one, two or other numbers of hexagons [6]. Given the multitude of the possible Haeckelite stripes and sheets, the number of Haeckelite type tubes one can wrap from a sheet of given size, is much larger than the number of straight tubes which can be wrapped from a graphene sheet of similar size.

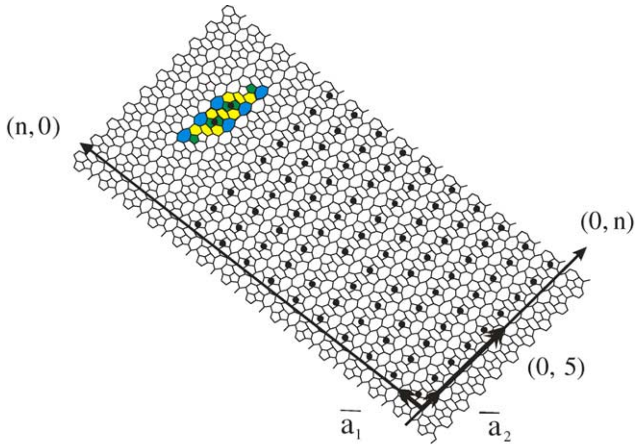

Fig. 1. Haeckelite sheet with imposed planarity. The sheet is constructed from "57–3 × 6" Haeckelite stripes [6]: three such stripes, placed side by side are highlighted in gray. Different polygons have different shade of gray. The heavy dots denote the common edge of adjacent pentagons, the "stressors" of the structure.

2.2. Necklaces of pearls

In this paper we are interested in a particular wrapping direction of the sheet shown in Fig. 1, the $(0,n)$ axis. The nanostructures generated using wrapping vectors of this type will be all "necklace of pearls" type structures as shown in Fig. 2a, the relaxed structures. These wrappings give a set of cylinders with regular circular bands of heptagons. Two examples of these are shown in Fig. 2a. During the relaxation procedure [6,18] these bands of heptagons result in negative curvature. On the other hand, the pentagons regularly arranged between the heptagon bands (the stressors) give positive curvature during the optimization. These two effects together result in a tubular nanostructure with periodic necks, a pearl-necklace like nanostructure as seen in Fig. 2a. Every nanostructure of type $(0,n)$ has necklace of pearls type shape and all $(0,n)$ nanostructures generated from the Haeckelite sheet of Fig. 1 have the "necks" separating the pearls at the same distance, which is the distance between two adjacent rows of heptagons. This opens the possibility to build multishell necklaces from $(0,n)$ nanostructures. If a second shell nucleates on the first we can assume that the second layer will have a similar Haeckelite structure like the first due to the interlayer interaction. Such a multishell construction may be performed as follows: after wrapping the Haeckelite sheet along a $\underline{C} = \underline{a}_1 m + \underline{a}_2 n$ wrapping vector the diameter of the resulting (still unrelaxed) cylinder is $d = |\underline{C}|/\pi$. This means that all of the unrelaxed $(0,n)$ cylinders have a diameter of $d_m = n|\underline{a}_2|/\pi$. Using the $|\underline{a}_2| = 0.522$ nm value from Ref. [18], the diameters for several small values of n are given in Table 1. The nanostructures for the smallest n values are unlikely to exist because of their high curvature. The $n = 5$ nanostructure, however, has already a large enough diameter to make it possible to nucleate. The unrelaxed and relaxed $(0,5)$ nanostructures are shown in Fig. 2a. The $d_{n+1} - d_n$ diameter difference is always constant 0.1662 nm for the unrelaxed nanostructures. Notice that $d_{n+4} - d_n = 0.6646$ nm for all n. This means that the intershell distance of the concentric n and $n+4$ unrelaxed cylinders is very close to the 0.335 nm equilibrium distance between the graphene sheets in graphite. Hence, it seems reasonable to attempt the construction of a multishell nanostructure from the $(0,n), (0,n+4), (0,n+2 * 4) \ldots \{0,n+(l-1) * 4\}$, nanostructures, where l is the number of layers in the structure.

Next we address the question how the relaxed $(0,n)$ necklaces can be introduced in each other. Choosing the $(0,5)$ nanostructure for the inner shell, the $(0,9)$ nanostructure is the possible candidate for the next shell. Both are shown in Fig. 2a before and after relaxation. The 5, 6, and 7 membered rings are highlighted with different shades of gray. The polygons are drawn using a simple triangularization algorithm. Fig. 2b shows the

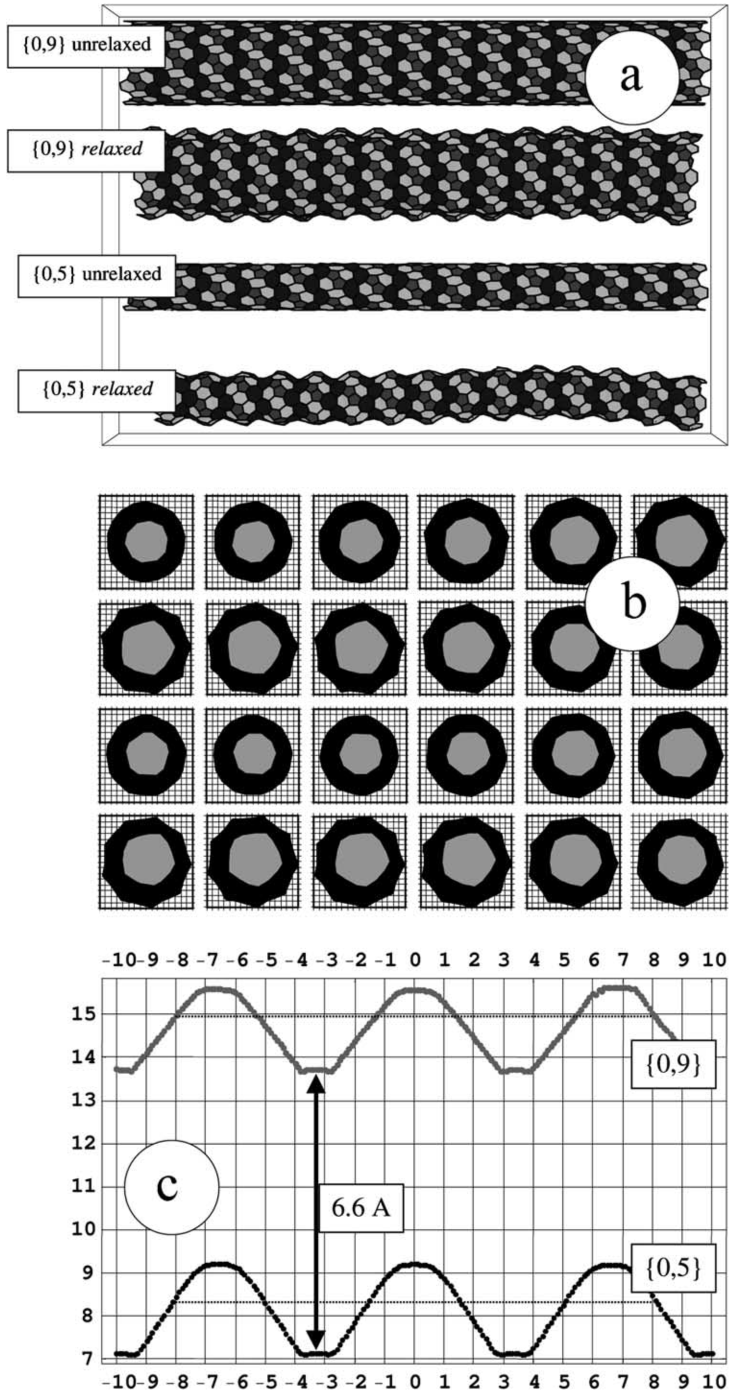

Fig. 2. Structural model of the multilayer necklace nanostructure. (a) Geometrical structures of the $(0,5)$ and $(0,9)$ necklaces. The ''unrelaxed'' nanostructures are those constructed by rolling the 57–3 × 6 Haeckelite sheet (see the text for details). The relaxed nanostructures are those optimized by the Tersoff–Brenner potential [18]. The pentagons, hexagons, and heptagons are highlighted by different shades of gray. (b) Cross-sectional analysis of the $(0,5)$ and $(0,9)$ necklaces. Cross-sections perpendicular to the axis of the polygonized models, (see (a)) are shown on a 0.16×0.16 nm grid. The outside, black (inside, gray) polygons are the cross-sections of the $(0,9)$ $(0,5)$ nanostructures, respectively. Cross-sections calculated in 0.05 nm steps along the axis of the nanostructure are shown as a ''matrix'' of images. (c) Diameters of the $(0,5)$ and $(0,9)$ necklaces along the axis. Effective diameters (see the text for details) calculated from the cross-sections along the axis of the structure. The dotted lines (at $d = 0.831$ and 1.495 nm) show the diameters of the unrelaxed $(0,5)$, and $(0,9)$ cylinders.

cross-sections of the two triangularized nanostructures at equidistant planes perpendicular to the axis of the nanostructure. One may note that the intershell distance remains nearly constant for most of the cross-sections. Fig. 2c shows d_{eff}, the effective diameters of the $(0,5)$ and $(0,9)$ necklaces along their axis. The value of d_{eff} is

Table 1
Diameter of the unrelaxed $(0, n)$ cylinders for small values of n

n	1	2	3	4	5	6	7	8	9	10
d (nm)	0.16	0.33	0.50	0.66	0.83	1.00	1.16	1.33	1.50	1.66

derived from the cross-section polygons by $d_{\mathrm{eff}} = (A_{\mathrm{cross}}/\pi)^{1/2}$ where A_{cross} is the area of the cross-section polygon. Notice that the $d_{\mathrm{eff}}(x)$ curves are very similar for the two necklaces apart from a constant shift of 0.66 nm. This means that the geometry optimization has not altered significantly the unrelaxed intershell distance. Diameters of the unrelaxed nanostructures are also shown in Fig. 2c by dotted lines.

3. Relation with experiment

So-called surface modulated spherical-layered nanotubes, having a strong necklace-of-pearl like structure, have been found in samples produced by high pressure carbon evaporation (Fig. 7 of Ref. [19]). As revealed by detailed HRTEM studies [19], the observed necklace nanostructures are assemblies of hollow, rather spherical structures (the pearls) composed of eight concentric graphitic layers, typically. A continuous, outer shell made of ~10 graphitic walls surrounds the spherical objects, which are encapsulated in this nanotube mantel.

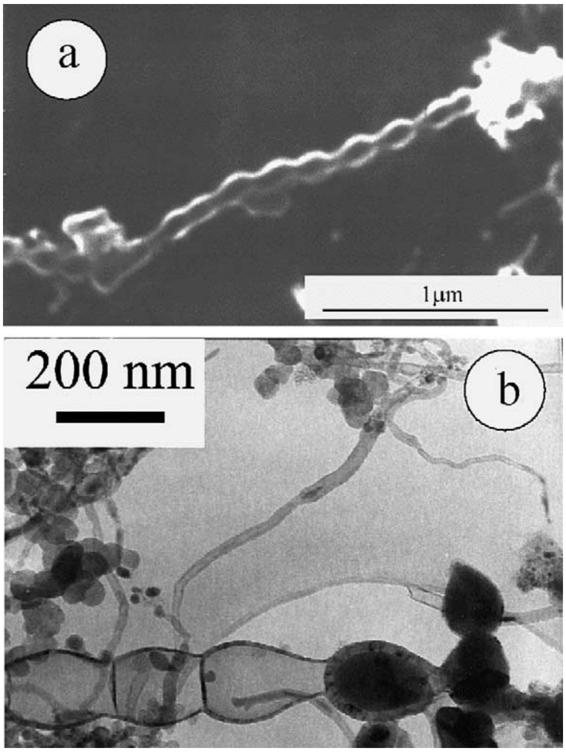

Fig. 3. Necklace of pearls in samples produced by thermal plasma [21]. (a) SEM image; (b) TEM image.

Nanotubes having a similar pearl-necklace structure have also been discovered in samples produced by a thermal plasma process [20], whose principle was described earlier [21]. The production method and an extensive structural characterization of these samples can be found in Ref. [20]. As an illustration, Fig. 3a and b are SEM and TEM pictures of such a necklace nanotube. Both the SEM and the TEM images make it clear that the necklace type nanostructures are built from a succession of ball like elements, which seem to be curved without any external constraint, except the rightmost side of the necklace in Fig. 3b, which is clearly filled and has a much thicker wall then the other pearls. The HRTEM images in Fig. 4a and b obtained from samples of the same origin [20], show the arrangement

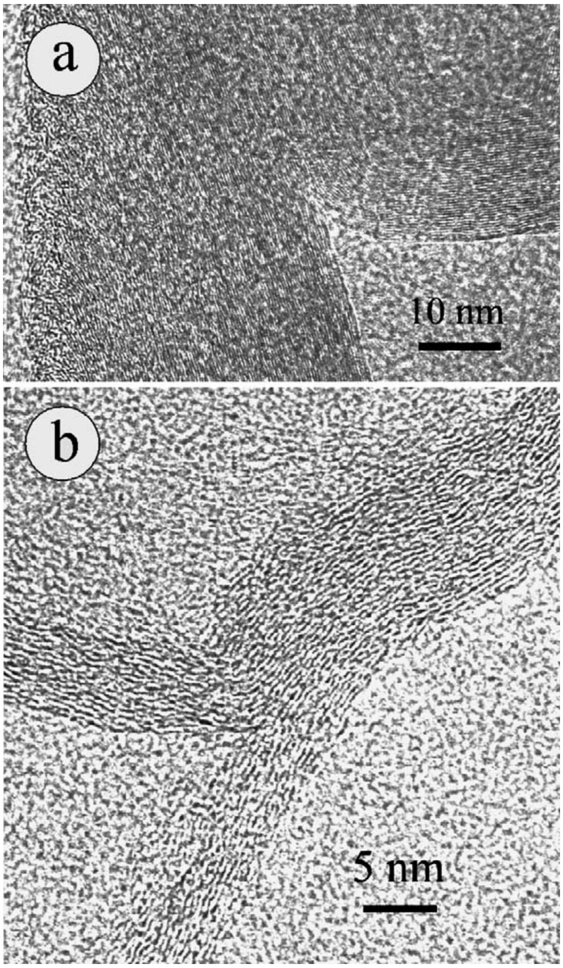

Fig. 4. HRTEM image showing the layer arrangement in two nanostructures from the same sample. (a) Straight, fish-bone nanotube; (b) Necklace of pearls.

of the graphitic layers for a straight multiwall nanotube with a fishbone structure, similar to that shown in Fig. 8 of Ref. [19]—called "conical layer nanotubes"—and for a necklace, respectively. In a similar way, like in it may be seen in Figs. 8 and 7 of Ref. [19], there is a clear difference in the arrangement of the graphitic layers. While the straight, fishbone tubes show a regular arrangement of smooth graphitic layers, in the necklaces, continuously curved and somewhat crumbled layers are seen. It is difficult to explain by accident the occurrence of these carbon nanostructures with rather different layer structure—as revealed by HRTEM—in samples produced by different methods and in different laboratories [19,20] but within the same experiment. We propose that the curvature and crumbling is the manifestation of the Haeckelite type arrangement of the carbon atoms building the necklace type nanostructures in a similar way like, it was shown through the model presented in Fig. 2, derived on the basis of the atomic arrangement shown in Fig. 1. While the fishbone type tubes are built of graphene layers.

4. Discussion

It is well known that the carbon nanotubes grown using the low temperature catalytic methods, like chemical vapor deposition (CVD) (temperatures typically in the range of 700–800 °C) exhibit random curvature, while the MWCNTs grown by the high temperature procedures, like electric arc, are usually straight, except knees and eventually branching. On the other hand, the precise atomic arrangement in the curved catalytic MWCNTs is difficult to determine. Only very few atomic resolution STM images have been reported in the literature on catalytically grown MWCNTs and those are obtained on straight segments of the CVD nanotubes [22]. A quantitative investigation by X-ray diffraction (XRD), TEM, and electron microdiffraction of the defect removal by thermal annealing up to 3000 °C of catalytically produced MWCNTs showed that the interlayer spacing of as-grown tubes may be as large as $d_{0\mathrm{NT}(200)} = 0.34235$ nm, and this spacing decreases after the highest temperature annealing to $d_{\mathrm{NT}(200)} = 0.33982$ nm [23]. HRTEM images of catalytically grown nanotubes taken in as-grown state show from mild [24] to strong [25] crumbling of the layers constituting the tube. The global morphology of the grown nanotubes is heavily influenced by the growth temperature in the range of 550–850 °C [25]. These observations may be attributed to the low probability that defects—n-Hx rings—will anneal out when low growth temperatures are used. Even in the case of single wall carbon nanotubes (SWCNT) grown in the temperature range of 2000 °C—as shown by atomic resolution STM images [26]—approximately 10% of the SWCNTs have n-Hx rings incorporated in the perfect honeycomb lattice. This is a very strong argument that the nanotubes grown at much lower temperatures can contain a much larger fraction of non-hexagonal rings.

On the basis of the above discussion it is fully justified to ask the question: are the CVD nanotubes constituted of graphene sheets or of Haeckelite sheets? A further argument can be mentioned in the favor of Haeckelite type nanostructures: in the CVD process the carbon nanotube nucleates on a catalytic particle, which in the first approximation can be regarded as having a spherical shape. This means that it is not possible to completely cover this particle with a graphene sheet. On the other hand, we showed in an earlier paper [6], that this can be very easily achieved with a piece cut from a Haeckelite sheet. The way in which the catalytic particle is covered by the growing Haeckelite sheet may depend on several factors, like the particle size and shape—which will impose a certain curvature—the local reaction conditions, etc. It may happen that under favorable conditions the particle will be fully covered using the ring arrangement corresponding to a particular Haeckelite sheet. This initial nucleus may have enough stability to preserve during the subsequent growth the particular nanostructure characteristic for a given Haeckelite sheet and it may lead to the growth of necklaces of pearls and of the regular coils [5–7].

5. Conclusions

Following the work of Terrones and co-workers [16] we bring new arguments based on structural modeling and experimental data for the existence of a theoretically predicted sp^2 hybridized carbon form, with structure close to that of graphite. The major difference between Haeckelite and graphite is given by the regular occurrence of non-hexagonal carbon rings as building blocks of Haeckelite. It is proposed that the necklace of pearls type nanostructures are built of Haeckelite and a structural model, which allows a graphitic interlayer spacing for multilayer Haeckelite necklaces, is demonstrated.

Acknowledgements

The samples used for electron microscopy examination were provided by Dr. L. Fulcheri of Ecole des Mines de Paris, Centre d'Energetique, Sophia Antipolis, France within the NANOCOMP project.

This work was supported by the EC, contract NANOCOMP, HPRT-CT-2000-00037 and EU5 Center of Excellence ICAI-CT-2000-70029, by Hungarian OTKA Grant T 043685 and by the IUAP research project P5/01 on "Quantum-size effects in nanostructured materials" of the Belgian Office for Scientific, Technical, and Cultural Affairs, LPB and GIM gratefully acknowledge financial support from FNRS in Belgium and HAS in Hungary.

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