

Regularly coiled carbon nanotubes

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ABSTRACT

Regularly coiled carbon nanotubes, their structure and formation mechanism are puzzling questions since many years. The first models were based on the very regular incorporation of a small fraction (of the order of 10%) of non-hexagonal (n-Hx) rings: (pentagons and heptagons) in a perfect hexagonal (Hx) lattice. It is difficult to understand by which mechanism takes place such a regular incorporation of isolated n-Hx rings. In the present work a new family of Haeckelite nanotubes is generated in a systematic way by rolling up a two-dimensional three-fold coordinated carbon network composed of pentagon-heptagon pairs and hexagons in proportion 2:3. In this model the n-Hx rings are treated like regular building blocks of the structure. Cohesion energy calculation shows that the stability of the generated 3D Haeckelite structures falls between that of straight carbon nanotubes and that of C₆₀. Electronic density of states of the Haeckelite computed with a tight-binding Hamiltonian that includes the C- μ orbitals only shows that the structures are semiconductor. The relation of the structures with experimental observations is discussed.

Keywords: Coiled carbon nanotube, Haeckelite tubes, non-hexagonal rings

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. Different kinds of structures have been revealed by high-resolution TEM, STM, and AFM, among which: carbon onions [3], tripods [4], helices [5], rings [6] and tori [7], disks and cones [8], nano-horns [9], and Y-branched tubes. [10 - 12]. Most of these structures can be explained if one incorporates pentagons and heptagons or larger polygons in the carbon honeycomb network [13]. Recent experiments revealed even more complex shapes of tubular type carbon nanostructures: double [14] and triple coils [15], and “necklace of pearls” type structures [16].

The toroidal [17], coiled [18, 19], and the Y-branched [20 - 22] 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 [19, 23]. If the regular arrangement is perturbed by misplacing one single n-Hx ring, the structure will not be any more a regular coil [23]. A general characteristic of the above coil models is that the ratio n-Hx to Hx is far less than unity. For example, in the case on a single Dunlap knee connecting (3, 3) to (6, 0) nanotubes with a bent of 30°, (Ref.[18], Fig. 2), when the smallest possible number of Hx rings is used, the ratio n-Hx/Hx is 0.125. A torus can be built by joining together 12 such knees. C₅₄₀ is the smallest torus made of connected (6, 0) and (3, 3) segments [18] giving n-Hx/Hx = 0.098. It is difficult to propose a viable model for the way in which these isolated n-Hx rings are

It is possible to generate a Haeckelite sheet by fusing together several stripes, like the one shown in Fig. 1. 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 easily removed, 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. 1b, the resulting sheet is shown in Fig. 2. Similar Haeckelite sheets can be generated from Haeckelite stripes with one, two [14] or other numbers of hexagons. 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.

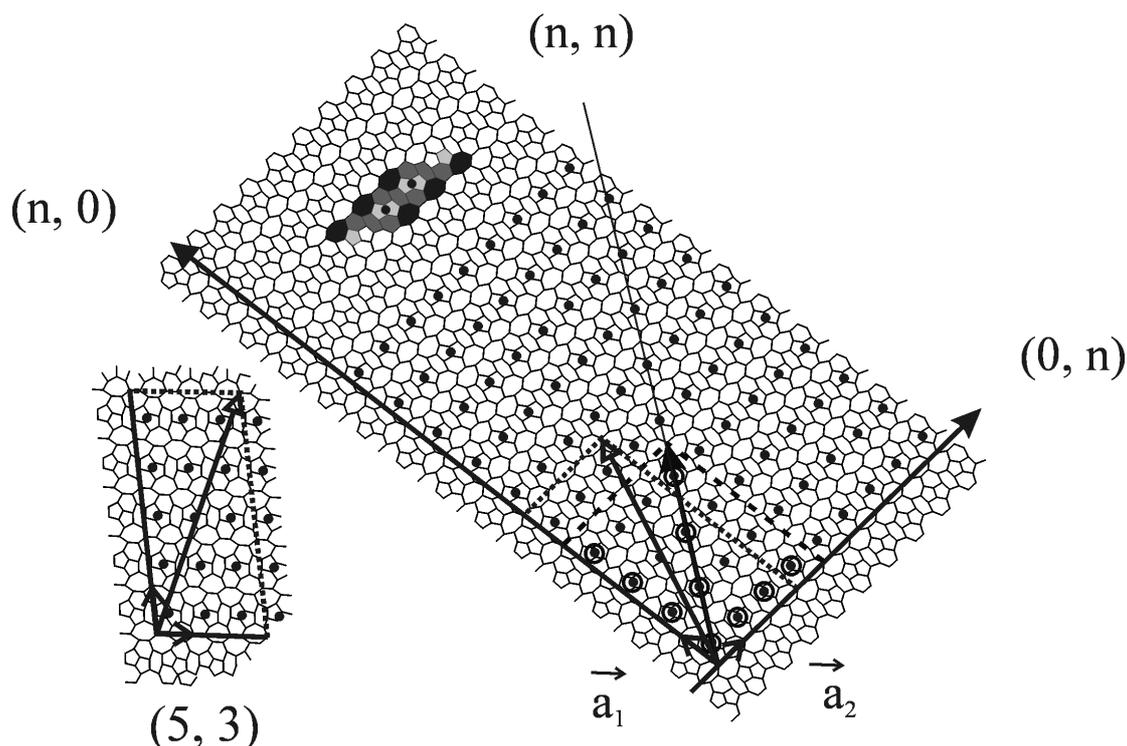


Figure 2 Haeckelite sheet constructed from fused (57 - 3 x 6) stripes, stressors are marked by heavy dots. The gray shades of the highlighted polygons are identical with those used in Fig. 1b. The two primitive vectors (the vectors \mathbf{a}_1 and \mathbf{a}_2 have length equal to 0.700 and 0.522 nm, respectively, and the angle between them is 97.8 degrees) of the sheet and three particular wrapping directions (n, 0), (n, n) and (0, n) are indicated. For these directions the stressors (highlighted by encircling) are arranged in rows which have parallel orientation with the wrapping vector. The vector with heavy head corresponds to a (4, 4) tube, while the vector with light head to a (5, 3) tube. The unit cell of the (5, 3) tube is shown on the left hand side, one may notice that the stressors have a slightly asymmetrical arrangement with respect to the wrapping vector.

3. WRAPPING THE HAECKELITE SHEET $n \times (57 - 3 \times 6)$

For a Haeckelite sheet, like the one shown in Fig. 2 one can apply the same wrapping procedure as in the case of a graphene sheet, just that due to stress relaxation the structures wrapped from a Haeckelite sheet most frequently will not be rigorously straight tubes. In the case of the particular sheet discussed here the highest stress is concentrated at the joining of the two adjacent pentagons, these joints are called “stressors”, they have a marked influence on the shape of the three dimensional nano-objects generated from the sheet. Stripes of the Haeckelite-like 2D network shown in Fig. 2 were rolled up following the usual wrapping rules used for graphitic nanotubes. In this construction, the site at the origin of the primitive vectors \mathbf{a}_1 and \mathbf{a}_2 is superimposed on the site located at $\mathbf{C}_h = n\mathbf{a}_1 + m\mathbf{a}_2$ and the tube (n, m) is

obtained. The atomic structure of the perfectly cylindrical nanotube so generated was then fully relaxed with a conjugate-gradient algorithm, using the Brenner-Tersoff potential.

One may observe from Fig. 2 that when the wrapping is done using a wrapping vector of $(n, 0)$, (n, n) or $(0, n)$ type, the stressors in the unit cell will be arranged in a particular way, in parallel rows with the wrapping vector. This means that the stressors will form circles on the surface of the tubular structure. One may expect that this will lead to particular shapes. Indeed, as seen in Fig. 3, the structures $(4, 0)$, $(4, 4)$ and $(0, 4)$ all have straight, tubular structures, i.e., neglecting the local curvature induced by the stressors, the tube axis is straight. On the other hand the asymmetric arrangement of stressors, like in the cases when only one stressor falls within the unit cell, like in the case of a $(1, 0)$ regular helical coil, or for the $(1,1)$ case, or like in the case of $(5, 3)$ where the stressors show a slightly asymmetrical distribution within the unit cell, will lead to coiled or curved nano-objects. The curvature may follow a simple rule, like in the case of the $(1, 0)$ or $(1, 1)$ structure, Fig. 4, or a more complex one, like in the $(5, 3)$ in Fig. 4, were a longer structure has to be computed for having a complete image of the kind of curvature characteristic for the nano-object.

Another particular feature of the $(4, 0)$ and of the $(5, 3)$ tubes has to be emphasized, namely they exhibit regular dips, which spiral along the circumference of the structure. In order to check if these dips may originate from a local energy minimum, we eliminated the dips, by distorting manually the structure, and started the relaxation procedure again. The dips were regenerated, therefore we conclude that they are characteristic for the structure.

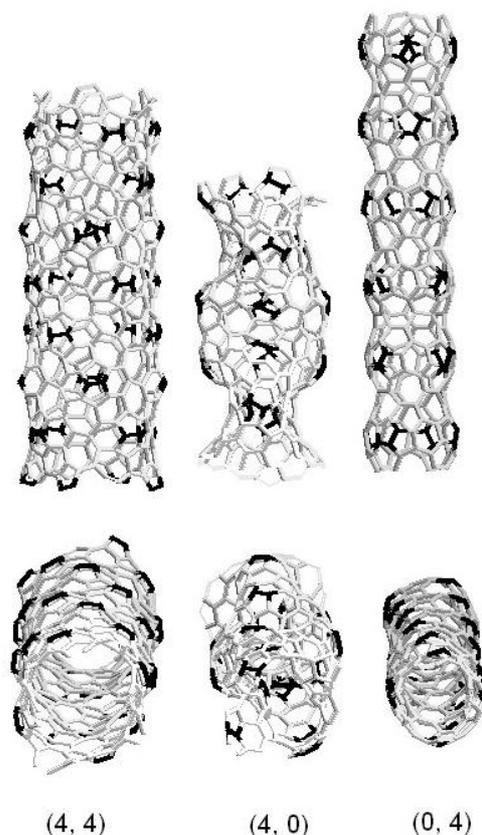


Figure 3 Tubular nanostructures generated the wrapping vectors $(4, 4)$, $(4, 0)$ and $(0, 4)$, the position of the stressors is highlighted in black, the structures are shown as viewed from a direction transversal to their axes and from a view close to axial.

Every structure of $(0, n)$ type has “necklace of pearls” type shape, moreover, all structures generated from the same Haeckelite sheet will have the “necks” separating the pearls at the same distance which is the distance between two adjacent rows of heptagons (Fig. 2). This is important because in this way multi-shell necklaces can be easily generated. If a second layer of Haeckelite nucleates on the first, it seems reasonable to assume that the second layer will be similar to the first one due to the interlayer interaction like in the case of graphite. If the first and the second layer are built from the same Haeckelite sheet, both will have necks separated by the same distance, whatever value n has in the

(0, n) wrapping vector. Therefore one may assume that a series of n values can be found for which a turbostratic like multi-shell structure can be built.

Some of the characteristic, curved tubes are shown in Fig. 4. The overall curvature of these structures arises from the asymmetrical way in which the stressors are distributed in the unit cell. The structure will tend to take a shape in which the stress is evenly distributed all over the structure. This can be achieved by compensating the stress asymmetry created by the stressors by stressing the regular bonds. Two of the three cases shown in Fig. 4 are similar in that only one stressor is found per unit cell, these are the (1, 0) and the (1, 1) tubes. While the first is a coil in the full sense of the word, the second is a “curled” tube [14], which shows a much smaller degree of curvature. This has to be related with the position of the stressor in the unit cell. For the (1, 0) tube the stressor is far from the wrapping vector, while in the (1, 1) case the single stressor is situated on the wrapping vector. It is worth mentioning that (2, 2) is a straight double coil, like the one found experimentally by STM in Ref. [14]. The (2, 0) tube will be also a straight nano-object, here again there are two stressors arranged in a way that one compensates the curvature induced by the other. The tube (5, 3) shows only a mild curvature in some sense “proportional” with the slight asymmetry of the arrangements of stressors, Fig. 2.

From the above discussion it follows that the regularly coiled structures are those ones for which a strong stress asymmetry is present, their number for a given Haeckelite sheet is much smaller than that of other less curved structures. The structures yielding less strongly curved tubular objects are much more frequent, in full agreement with experimental observation of many varieties of less curved tubes grown by the catalytic procedure.

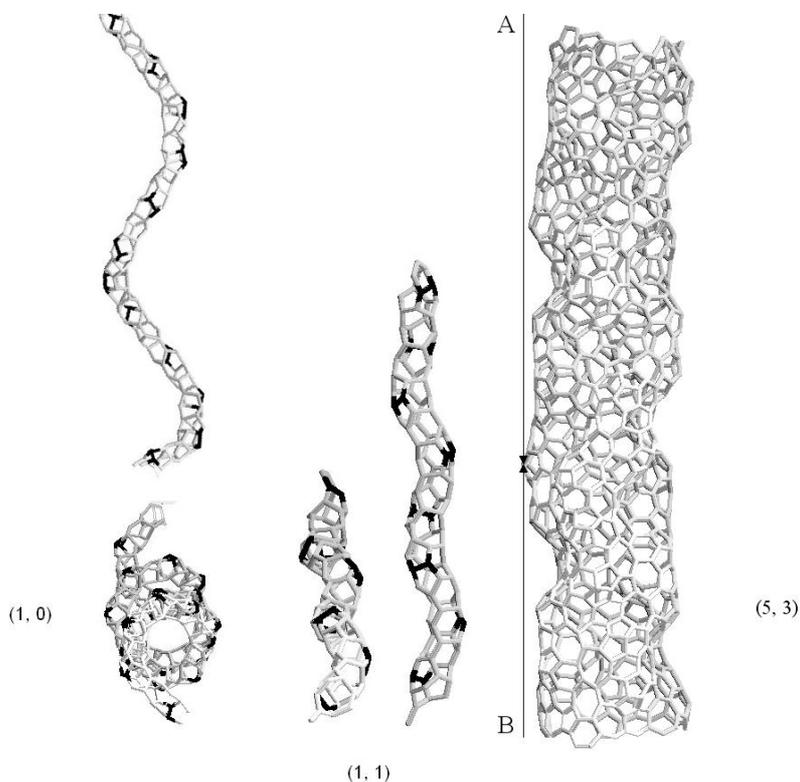


Figure 4 Curved tubular nanostructures: (1, 0) regular, helical coil; (1,0) curled tube; (5, 3) tube with mild curvature, the line AB is shown as reference for a straight object.

4. ENERGETIC STABILTY AND ELECTRONIC STRUCTURE

The atomic structure of the perfectly cylindrical nanotube generated by wrapping the Haeckelite stripe defined by the wrapping vector C_h was then fully relaxed with a conjugate-gradient algorithm, using the Brenner-Tersoff potential. The energy of the optimized structures listed in Table 1 is the average energy of the three-fold coordinated

Table 1. List of some of the Haeckelite nanotubes that were generated from the planar network shown in Fig. 2. Wrapping indices (n, m), initial diameter d, energy per atom E, width of the topological band gap E_g .

(n, m)	d (nm)	E (eV/atom)	E_g (eV)
(1, 0)	0.223	-6.38	-
(1, 1)	0.259	-6.81	-
(4, 0)	0.892	-7.00	~0.1
(4, 4)	1.038	-7.04	0.48
(0, 4)	0.665	-7.06	0.65
(5, 2)	1.119	-7.02	~0.1

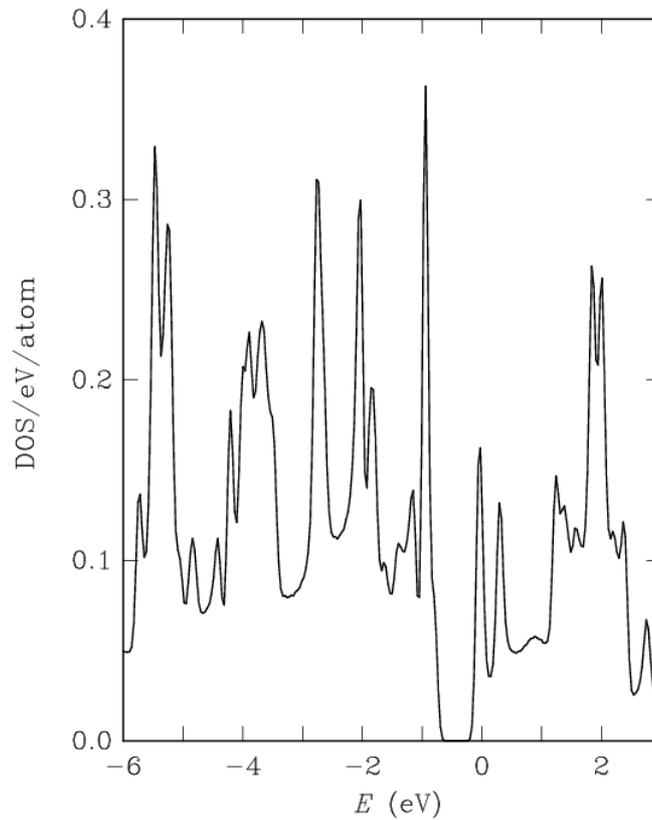


Figure 5 π -electron density of states for the (0, 4) tube calculated using a tight-binding Hamiltonian.

atoms. In such a way, the effects of the open ends are partly eliminated. The calculated energies are in the range of the values calculated for the graphene sheet -7.37 eV, and the value corresponding to the Haeckelite sheet shown in Fig. 2, -

6.83 eV. This indicates that by wrapping the Haeckelite sheet into a tubular structure, even one with a complex curvature, the energetic stability of the system increases. It is worth emphasizing that for the fullerene C₆₀ the cohesion energy per atom has the value of -6.85 eV, while most of the values calculated for the Haeckelite tubes with diameters of the order of 1 nm have a higher stability.

The electronic density of states of the Haeckelite nanotubes were computed with a tight-binding Hamiltonian that includes the C- π orbitals only. The tight-binding $pp\pi$ hopping parameter used is taken from Ref. [27]. Since all the C-C bond lengths in the relaxed structure showed very small dispersion around 0.142 nm, the hopping parameters were taken the same for all the first-neighbor pairs. These calculations aimed at exploring the effects of the topology on the electronic properties of the nanotubes; which are robust characteristics in the sense that they do not depend on the details of the structural optimization. The calculations were not carried out for nanotubes with a diameter smaller than 0.6 nm, because the tight-binding Hamiltonian may not be accurate enough for carbon nanotubes with small diameter. The calculated values of the topological gap of the nanotubes are listed in Table 1. The σ - π coupling brought about by the curvature of the structure may affect the position and magnitude of the band gap by a few tenths of an eV. Interestingly enough, all the nanotubes were found to be semiconductor. By comparison, the straight Haeckelite nanotubes of Ref. [25] were all metallic.

The infinite, two-dimensional Haeckelite sheet having the structure of Fig. 2, from which the nanotubes were rolled up, is a zero-gap semiconductor like graphene. Because it is a planar structure, the π states are not coupled to the σ states. The zero of energy is the energy of the C 2p orbital. Two π bands cross each other at the Fermi energy located at $E_F = -0.43$ eV. Due to the absence of symmetry in the first Brillouin zone, almost all of the nanotubes built from the Haeckelite sheet in Fig. 2 will be semiconductor, because it is very unlikely that the Fermi wave vector of the 2D sheet be an allowed wave vector of the nanotube when cyclic periodic conditions are imposed along the circumference, except for very large diameters.

5. EXPERIMENTAL OBSERVATIONS AND DISCUSSION

It is well known that the carbon nanotubes grown using the low temperature catalytic methods (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 [28]. A quantitative investigation by X-ray diffraction (XRD), TEM, and electron micro-diffraction 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 $d_{0NT(200)} = 0.34235$ nm, and this spacing decreases after the highest temperature annealing to $d_{NT(200)} = 0.33982$ nm [29]. High-resolution TEM (HRTEM) images of catalytically grown nanotubes taken in as-grown state show from mild [30] to strong [31] 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 [31]. 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 [32] - 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: the CVD nanotubes are constituted of graphene sheets or of Haeckelite sheets? A further argument can be mentioned in the favor of Haeckelite type structures: 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 [14], that this can be very easily achieved with an azulenoic stripe, i.e., 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 structure characteristic for a given Haeckelite sheet. The result will be a regularly coiled, or curled carbon nanotube. If stability is not achieved the result will be a randomly curved nanotube as it is most frequently found in the CVD material.

Following the early experimental observation of the regularly coiled and curled carbon nanotubes [5], recently more complex shapes have been observed experimentally: a carbon nanotube double helix was found by STM in a sample grown by CVD from acetylene [14], double and triple coils have been produced selectively using a lanthanide oxide-catalyst [15], and necklace type structures have been found in a high pressure experiment in nitrogen containing atmosphere [16]. It is worth pointing out that in the high pressure experiment several types of structures have been generated within the same run and the HRTEM images of necklace structures as compared with the images of the fish-bone type tubes, very clearly show that the layers constituting these structures are different: while the layers of the necklace shown in Fig. 7 of Ref [16] are crumbled, the layers seen in Fig. 8 of Ref [16] are well graphitized. We believe that this experimental result is a strong evidence that within the same experiment it is possible to grow both graphene and Haeckelite structures and that by careful tuning of the growth conditions one may achieve the selective growth of the Haeckelite structures. The large variety of Haeckelite structures, if exploited on purposeful basis may provide a much larger variety of physical, mechanical and chemical properties than found in the case of graphitic nanotubes.

6. CONCLUSIONS

The possible ways of building regularly coiled and curled tubular carbon nanostructures from Haeckelite type sheets characterized by non-hexagonal to hexagonal ring ratio higher than unity was examined. We showed that in a similar way like straight carbon nanotubes are wrapped from a graphene sheet it is possible to wrap systematically tubular carbon nanostructures which are regularly coiled and in which the non-hexagonal rings do not constitute defects, but are regular building blocks of the structure. The cohesion energy of the Haeckelite tubes is such that with respect to their stability they are placed between the graphitic carbon nanotubes and C_{60} . All structures for which electronic structure calculation were carried out were found to be semiconductor. Experimental observations of Haeckelite type structures indicate that these structures can be produced using the various growth procedures developed for carbon nanotube production. Work is needed for the optimization of the growth conditions in such way that will allow the selective growth of Haeckelite structures.

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