High-resolution transmission electron microscopy and energetics of flattened carbon nanoshells

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Abstract

When examined under a high-resolution transmission electron microscope, carbon soot produced alongside buckytubes in an arc-discharge is found to contain a small percentage of flattened carbon shells. These objects are shown to be small graphite flakes which eliminated their dangling bonds by terminating their edges with highly curved junctions. Ideal models for these structures are presented, and their energy estimated. The calculations show that the establishment of highly curved junctions is energetically favourable for a graphite flake in an inert atmosphere. Flattened shells also appear more stable than their "inflated" counterparts (fullerene "onions" and buckytubes) when the shell dimensions obey specific criteria.

1. Introduction

Since the discovery of buckminsterfullerene (C_{60}) in 1985[1], a variety of novel structures with trigonally-bonded carbon has been discovered: nano- or buckytubes[2], nested spheroidal shells or "onions"[3], giant fullerene shells[4], interconnected fullerene-like cages[5], cross-linked graphitic cages[6]; many more have been postulated[7, 8, 9]. Much attention has been focussed towards buckytubes due to their inherent high tensile strength[10] and the unusual electronic characteristics that have been predicted[11, 12]. Since the realisation of these properties requires seamless, defect-free tubes[11] or the presence of specific defects in specific locations[12], some authors have investigated the deformations occurring in carbon nanotubes[13, 14]. Perhaps the most dramatic deformation so far observed in a carbon nanotube is its occasional complete collapse to a flattened ribbon[14]; this process was shown to be favoured for a particular range of tube diameters and number of walls[14].

In this article we present high-resolution transmission electron microscopy (HR-TEM) observations of graphitic sheets terminated by highly curved junctions, leading to structures analogous to collapsed tubes. These objects were found in the soot deposited alongside buckytubes in an arc-discharge system. It is shown that the observed configuration arises from the joining of flat graphitic sheets rather than from the collapse of a shell, and therefore should be considered as a novel carbon nanostructure. Two ideal models are suggested which are the flattened equivalent morphologies of a fullerene and a nanotube. Energetics calculations show that these structures should be stable in an inert atmosphere. Although flattened shells were found to be relatively rare in the arc-discharge generated soot, suggestions are offered regarding their formation in larger quantities.

2. Experimental procedure

The structures described below were found in nanoporous carbon originating from a cathode rod kindly supplied by Dr. S. Iijima (NEC Labs., Japan). The main components of this nanoporous carbon have already been studied by the authors[4, 15]. The cathode was grown using the arc-discharge method of Ebbesen and Ajayan[16] for producing macroscopic quantities of buckytubes. The sample in question was deposited in a helium atmosphere of 200 Torr, which was found to give the best yield in buckytubes and nanoporous carbon. The specimen was prepared for viewing in the electron microscope by crushing small specks from the desired region of the cathode and mounting the resulting dry powder onto a clean copper grid. The high-resolution (HR)TEM observations were performed on a JEOL4000EX instrument operated at 400 keV and with a point resolution of 1.7Å.

3. HRTEM results and analysis

Fig. 1 shows two sets of hairpin-shaped dark fringes, which can be interpreted as graphitic sheets terminated by highly curved sections. Due to the almost identical sizes of the two sets and their close relative positions, it seems probable that they belong to the one object. A schematic representation of the proposed structure is inset as Fig. 1(b). It consists of four flat graphitic sheets stacked on top of each other and linked at their edges via tubular sections. In this drawing the structure is shown bent in order to account for the difference in contrast in the image, stronger contrast resulting from portions of the object that are more or less parallel to the incident electron beam[4]. Furthermore the equal intensity of the white fringes on the inner and outer side of the hairpins implies that they represent tubules and not caps[4]. This morphology is very much like the model suggested for Fig. 1(a) in (b). In addition, the structure depicted as Fig. 1(b) is analogous to one half of the collapsed tube configuration proposed by Chopra *et al.* (see Fig. 3(b))[14]. According to Chopra *et al.*'s model these structures were once inflated shells but collapsed as a result of collisions or an external force. An alternative and more plausible explanation for the morphology of Fig. 1 is that a small, four layers thick graphitic flake formed and later eliminated the unsaturated bonds along its edges by joining via truncated tubules. These junctions do not require the inclusion of pentagons or other non-six-membered rings so they should form relatively easily. Furthermore, such a formation process would presumably entail the generation of fewer defects in the structure than the collapse mechanism. The strong contrast exhibited by the straight fringes of Fig. 1 does indicate that the object is relatively defect-free, which favours the second hypothesis.

Other examples of highly curved terminations are shown in Fig. 2. Figs. 2(a)-(c) are all single flattened shells whereas in Fig. 2(d) the large graphite flake exhibits multiple terminations, each comprised of three to five layers. However, all cases present the same feature as described for Fig. 1(a): fairly defect-free graphite flake, and when visible, equal intensity of the white fringes on both sides of the "hairpins". Hence these images are more compatible with the terminated-flake scenario than with the collapsed-shell model.

4. Energetics

Simple energetics arguments will now be used in order to test the hypothesis that joining dangling edges via highly curved tubules may be advantageous to a multiple-layer ribbon. A number of authors[17, 18, 19] agree that the strain energy arising from the bending of graphitic layers can be described analytically using the continuum elasticity formalism, even down to sizes comparable with C_{60}'s. For an uncapped cylinder of radius R and length H, the total strain energy compared with a flat graphene sheet is approximated well by

$$E_s = Q_c \frac{H}{R} \tag{1}$$

where Q_c is a constant equal to 5.1 eV[18]. The Van der Waals energy can also be described easily provided edge effects are neglected and the interaction range is less than two interlayer spacings, which is a good approximation[20]. The total interlayer energy is then proportional to the contact area between adjacent layers. In the following, a value of $E_{vdW} = 10$ meV per atom will be used for the Van der Waals energy of two layers; this is half the value for an infinite number of layers[20, 21]. The dangling bond energy was first introduced in an analytical energetic model by the authors[22] in order to simulate the effect of an inert atmosphere, where a value of ξ=3 eV per dangling bond was found to be reasonable. Thess *et al.* subsequently deduced an almost identical value[23].

It is now possible to estimate the change in energy on creating curved junctions. Schematic representations of the two configurations are shown in Fig. 3 assuming two layers. Fig. 3(b) is identical to Chopra *et al.*'s postulated geometry for collapsed tubes[14]. To express the fact that the objects reported herein probably did not result from the collapse of once inflated shells, we will refer to Fig. 3(b) as a *flattened* nanotube. Using the notation of Fig. 3, the energy of the open double layer system (case (a)) can be written:

$$E_f = \xi(2\rho_H H + 2\rho_L L) - \frac{E_{vdW}}{a_0} LH \tag{2}$$

where a_0 is the average area occupied by a carbon atom within a graphene plane, equal to 2.62Å^2; ξ is the energy per dangling bond and ρ_H and ρ_L are the number of dangling bonds per unit length in a graphene plane with edges of length H and L respectively. E_f must now be compared with the energy of the partly closed object (Fig. 3(b)):

$$E_j = Q_c \frac{aH}{\pi r^2} + 2\xi\rho_L L - \frac{E_{vdW}}{a_0}(L - a)H. \tag{3}$$

The joined sheets will be energetically favoured over the open sheets when $E_f > E_j$. This requirement is independent of L or H and depends only on ξ and the geometrical characteristics a and r (a is a function of r and t, the interlayer separation):

$$\xi > \frac{a}{2\rho_H}\Big(\frac{E_{vdW}}{a_0} + \frac{Q_c}{\pi r^2}\Big). \tag{4}$$

We chose r= 3.4Å for the largest possible curvature, the interlayer separation t= 3.4Å and hence a= 17.8Å. The minimum dangling bond energy required is then computed to be 2.8 eV for ρ_H=0.47Å^{-1} (corresponding to a (112) edge) and 3.2 eV for ρ_H=0.41Å^{-1} (for a (101) edge). These values are close to the estimated ξ=3 eV for the dangling bond energy in an inert atmosphere[22]. Curved tubular junctions of smaller curvature, such as r=6.8Å (as in C_{240}), yield ξ=1.3 eV for ρ_H=0.41Å^{-1}. This result suggests that when the dangling bond energy is high the joining of the edges of flat graphitic sheets is favourable even for highly curved junctions. Of course the above analytical description of the problem is rather simplistic. For example, a more faithful representation of the junction zone between the two layers could be more continuous, a bit like a sheet folded back onto itself.

This simple calculation can easily be extended to more than two layers; two possible configurations are shown in Fig. 3(c)-(d). The structure depicted in (d) entails the formation of junctions that are less curved than in (c) thus lowering the curvature energy term, plus a gain in interlayer energy between the caps; it means that (d) must be more favourable than (c). This is in partial agreement with experimentally observed terminations, which are found to be multi-shell (three to five layers — see Fig. 2(d)). However the observation that the entire ribbon does not end into a truncated giant "onion" may be due to kinetic reasons; perhaps several "seeds" of terminations nucleate at the same time. Alternatively it could be an indication that the terminations formed at the same time as the flat portion of the ribbon.

The possibility that such junctions could arise on all sides of a flake and result in a closed object, like the one shown in Fig. 4(a), must also be investigated. The outer bulging section of the structure can be likened to part of a torus. Itoh *et al.* have generated a large variety of toroidal graphitic surfaces[8]. To date only tori having low curvature have been observed: 4-8nm wide nanotubes "biting their tails" and resulting in 3-4μm-wide "crop-circles"[24]. The variation of the tori's energy as a function of size or geometry is not well known, although they appear much less favoured energetically than fullerenes[25]. A rough estimation of the energy of a structure like Fig. 4(a) indicated that they are much less stable than spherical shells. As was found to be the case for collapsed tubes[14], there may be a critical radius above which the squashed configuration has a lower energy than the inflated configuration. However, this critical radius appears to be very large due to the high energy cost in creating a toroidal bulge when squashing a spherical fullerene. The energy cost of joining all edges of two hexagonal sheets to form the object depicted as Fig. 4(a) was estimated using the strain energy of tori calculated elsewhere[25]. At high dangling bond energy the raft-like object of Fig. 4(a) appeared to prevail over the open configuration; this is due to the fact that the increase in strain energy brought about by the torus is more than compensated by the decrease in dangling bond and Van der Waals energies.

5. Discussion

The previous calculation showed that the formation of tubules joining parallel flat sheets will lower the energy of the structure when the dangling bond energy is high. The stability of a flattened tube with respect to inflated cylinders was investigated by Chopra *et al.*[14], who found that the flattened configuration should prevail over the inflated one when the tube radius exceeds about 30Å for a single-wall tube (i.e. when the width of the ribbon is greater than some 80Å). The critical ribbon width was calculated to increase with the number of layers n, reaching about 240Å for n=8. Yet, as pointed out by Chopra *et al.*, "collapsed" tubes having smaller dimensions than required for their stability with respect to inflated tubes will be unlikely to spontaneously re-inflate. In any case, the inflation of a structure like Fig. 1 into a cylinder appears very improbable; otherwise, graphite flakes exhibiting large basal planes and few layers would have been observed to turn into buckytubes ! Consequently, the raft-like objects are probably quite stable once formed.

The question then arises, how likely is it that at least a two-layer flake will grow instead of a tube, a sphere, or a single sheet ? A number of theoretical studies have shown that spherical shells are the most stable form energetically[17, 19, 22]. It was also shown that a flat rectangular sheet may lower its energy by rolling into a cylinder to eliminate some of its dangling bonds[11]; but a hexagonal graphite plane is energetically favoured over tubes because it has fewer dangling bonds than a rectangle of same size. Finally, the stacking of a layer on top of a flat flake was found to be energetically favourable when the double sheet is at least 400Å wide. This is to be compared with spheres, whose maximum diameter as single shells was computed to be 50Å only[20]. The distribution of size versus number of stacked layers (n) for closed graphitic shells observed under HRTEM was found to match the predictions quite well, at least within the small range of sizes encountered experimentally[15]. Specifically, an average innermost shell diameter of 35Å for $n<5$ and a rapidly growing outermost shell diameter as n increases was observed both through HRTEM and in the theoretical results[15]. All this points to the prediction that spherical geometry should be dominant in an inert atmosphere.

Experimentally the predictions appear validated. Only very large graphite ribbons (like Fig. 2(d)) were seen in the sample; small objects, i.e. 100-200Å wide, were invariably closed or almost closed shells[4, 15]. This indicates that small, flat graphitic flakes are indeed very unstable compared with closed surfaces in experimental conditions favouring buckytube growth. This may explain why objects like the ones imaged in Figs. 1,2(a)-(c) were relatively rare. Therefore it is clear that different experimental conditions are required. First, to favour the initial nucleation of small, flat graphitic flakes, and then the need to remove dangling edges by developing tubular junctions, as described above. From a kinetic point of view this mechanism appears more likely than a total rearrangement of the structure into a spherical onion, the lowest energy state. However there is also a possibility that elimination of edges will be carried out by creating cross-links between different flakes, as is thought to be the case in glassy-carbon-like materials[6, 15]. It is not clear yet what conditions would avoid the development of cross-links. But assuming this was achieved, the structure could then close off by joining at all its edges (see Fig. 4(a)) and therefore prevent further growth.

By analogy with fullerenes and buckytubes, a graphitic flake joined along two parallel sides could keep growing in one direction (see Fig. 4(b)). The latter case might preferably occur in conditions of anisotropic velocity distribution of the carbon ions, as proposed for the growth of buckytubes[26]. This could yield very long ribbons, defect-free equivalent to fully collapsed nanotubes. Interestingly, large graphite ribbons terminated by multiple curved junctions as shown in Fig. 2(d) have already been observed in char by Ban[27]; they were also seen in buckytube-rich deposits fabricated by replacing the composition of the electrodes in the arc-discharge apparatus from the usual graphite to amorphous carbon[28]. This suggests that conditions favourable to the growth of small flattened carbon shells may not be too difficult to achieve.

This new class of trigonally-bonded carbon structures would probably display interesting electronic properties as a result of their closed surfaces — provided that at least one of the dimension is small enough. Mechanically, these objects appear rather prone to bending and twisting, as evident in Fig. 1 and more dramatically so in Chopra *et al.*'s collapsed tubes. However, the highly defective nature of collapsed buckytubes may be partly responsible for the kinks. Together with high tensile strength, the existence of edge terminations might prevent sliding between sheets, which occurs in graphite as a consequence of much weaker interlayer bonding compared with the in-plane bonding. But the stability of the junctions would be worth investigating; these highly curved regions may be relatively fragile chemically as is known to be the case for capped buckytubes, which can be opened by heating in an oxydizing atmosphere[29]. In any case, further study of these flattened nanotubes must await their synthesis in larger quantities.

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FIGURE CAPTIONS

Figure 1:

(a) Electron micrograph showing two sets of hairpin-shaped fringes (indicated by arrow) which appear to correspond to the same object. (b) Schematic representation of the proposed structure for (a).

Figure 2:

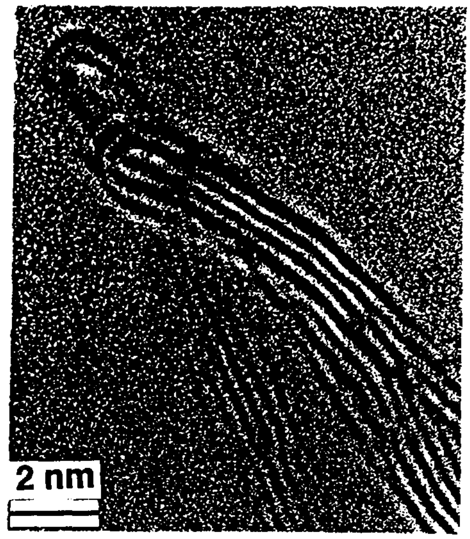
Further examples of highly curved terminations of graphite flakes: (a) object similar to Fig. 1(a) but not twisted and seen almost edge on; (b) flake with junctions visible on opposite ends of the flake (see arrows); (c) bent junction containing two layers inside an inflated shell; (d) large ribbon terminated by multiple "hairpins".

Figure 3:

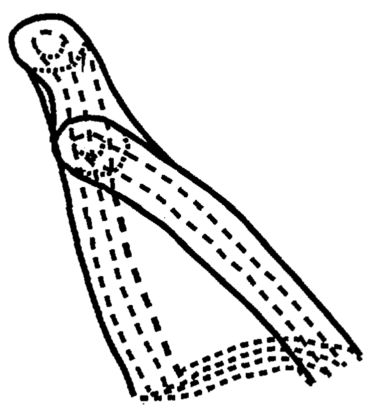
Diagrams showing (a) a two-layer structure with dangling edges, and (b) joining two of its parallel sides via open tubules; (c)-(d) extension of (b) to six layers, indicating two possibilities of terminating one side of the dangling edges.

Figure 4:

Schematic representation of (a) a fully-terminated hexagonal graphitic flake; (b) a flattened ribbon corresponding to a long flake terminated in one direction only.



(a)



(b)

FIG. 1

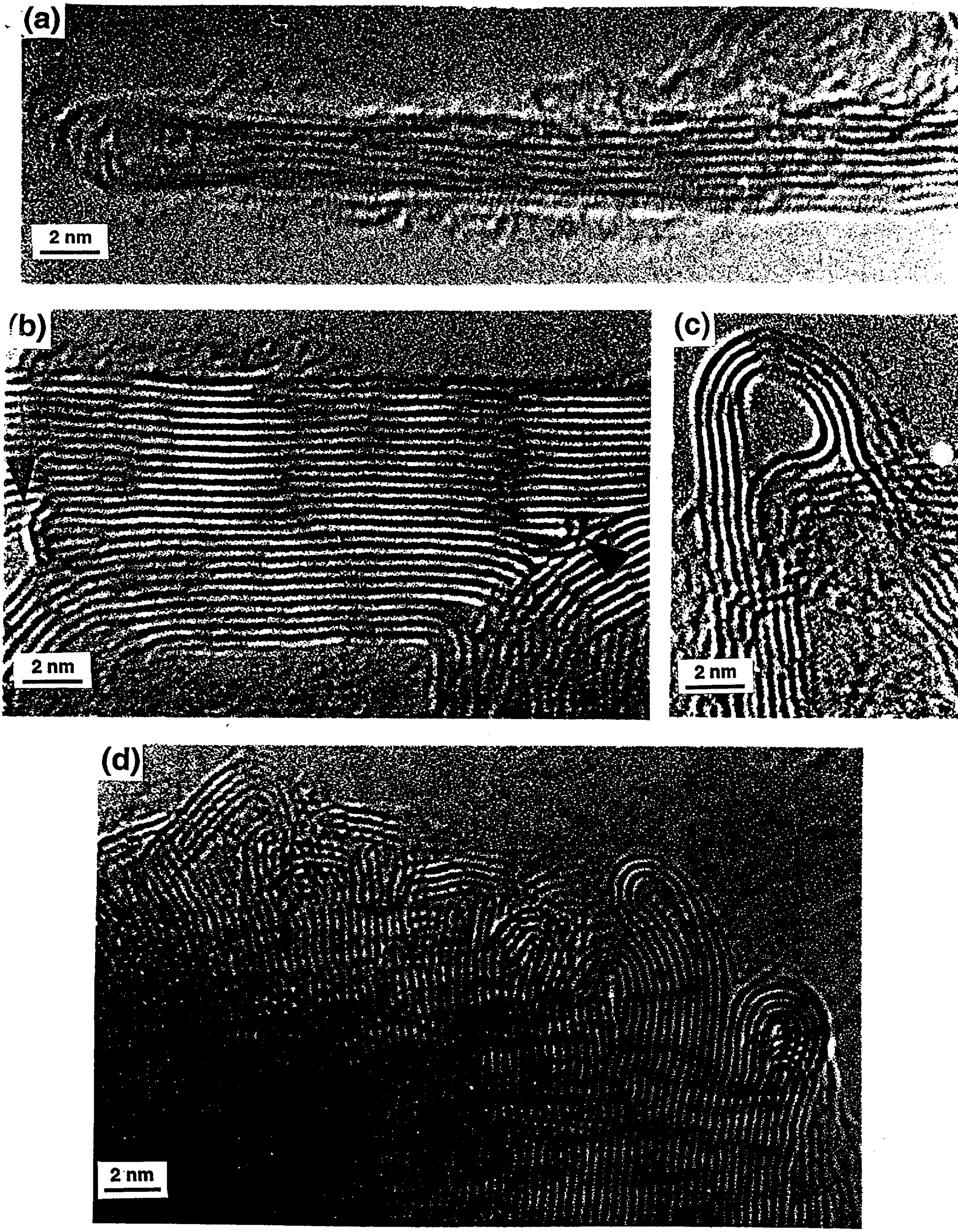


FIG. 2

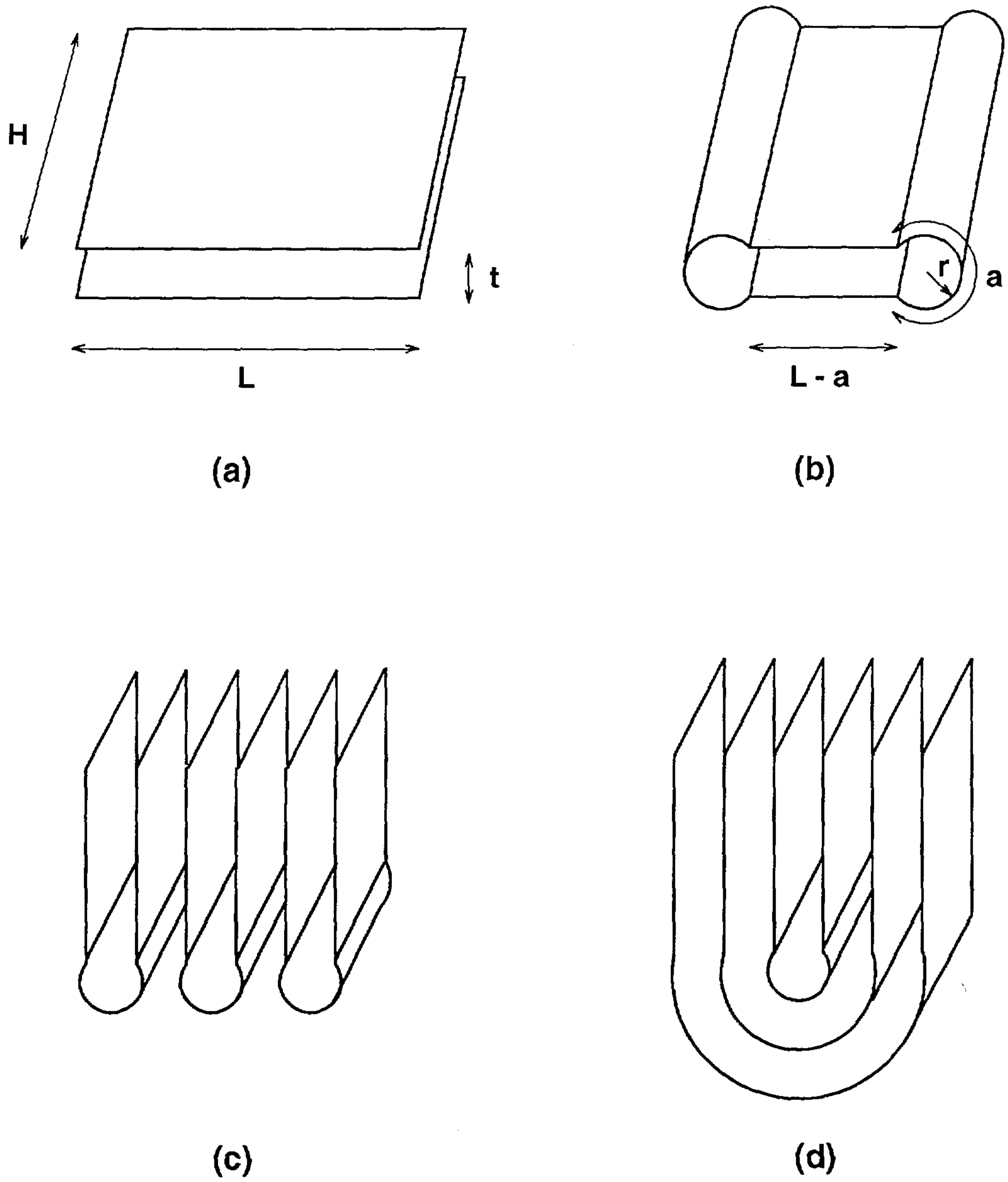


Figure 3:

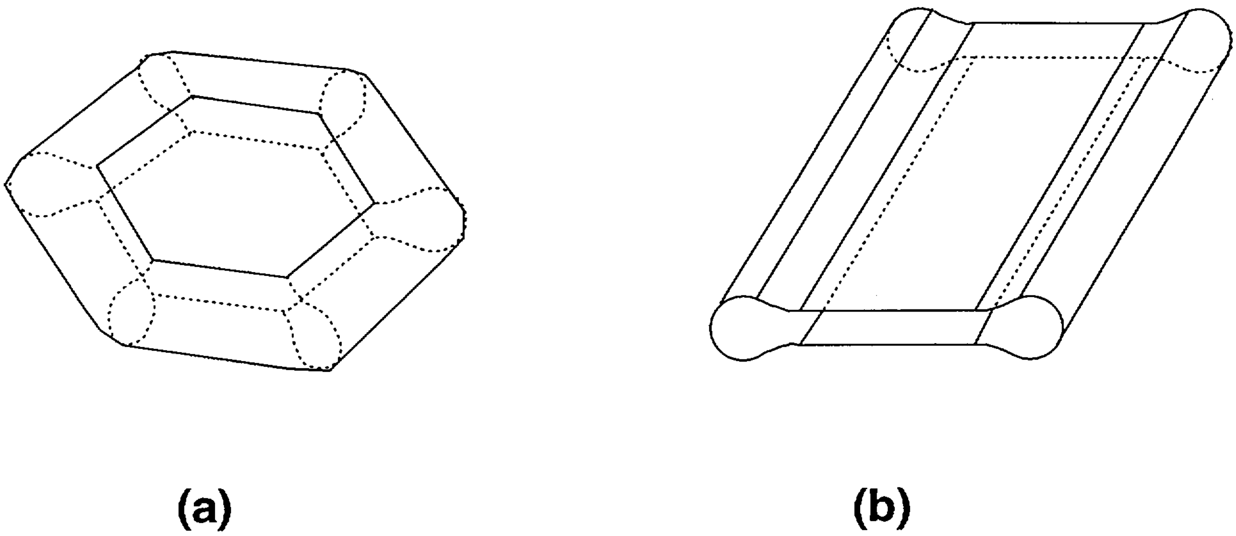


Figure 4: