Mesoscopic origami with graphite: scrolls, nanotubes, peapods

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Abstract

This contribution describes the morphology and energetic stability of different types of nanostructured carbon, including fullerenes, nanotubes, scrolls, peapods, and more complex foams. When structurally perfect, these systems are very stable even under extreme conditions. Specific structural defects offer an unusual, energetically accessible path to an inter-conversion between different isomers. More complex systems follow a hierarchical self-assembly formation process. © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

In recent years, following the discovery of the C_{60} "buckybal" [1], a plethora of nanostructures attracted the attention of carbon scientists. Examples of these intriguing systems are other fullerenes, onions [2], nanotubes [3], and hybrid structures such as peapods [4]. Whereas most of these sp^2 bonded structures are known to grow from carbon vapor under extreme conditions, systems like multi-wall nanocapsules may form by activated bond rearrangement from ultra-disperse diamond [5]. All fullerene-based nanostructures show an amazing mechanical strength, chemical inertness, and often an unusually low content of atomic defects.

What appears to be common to all these structures are synthesis conditions that involve extremely high temperatures of close to (or beyond) 1000°C. While showing no signs of spontaneous decay at room temperature, all fullerene-derived structures are less stable than bulk graphite. Small variations in synthesis conditions, such as change of temperature or partial pressure of the cooling inert gas, appear to have an unusually large effect on the morphology of the product. Obviously, all these structures are formed under non-equilibrium conditions, which are characterized by a competition between the gain in free energy (which contains a significant amount of vibrational entropy) and the fast synthesis kinetics. Due to the fast dynamics of bond formation and fragmentation under the extreme synthesis conditions, only limited information can be extracted experimentally about the nature of the microscopic processes which occur while these structures are formed. Simulations and theoretical modeling of the self-assembly process may play a

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key role not only in the understanding of nanostructure formation, but also in optimizing synthesis conditions to form particular nanostructures.

This contribution addresses the physical properties of some of these nanostructures, in particular their stability. It will be shown how macroscopic concepts from elasticity theory translate down to the nanometer scale, where they provide quantitative predictions for the relative stability of nanotubes, scrolls, fullerenes, and peapods. With the help of ab initio total energy and molecular dynamics calculations, it is now possible to study the formation and inter-conversion mechanism of unusual systems, such as carbon foam [6] or peapods [7].

2. Energetics of sp^2-based carbon nanostructures

It is now well established that the strain energy involved in deforming an sp^2 bonded graphene sheet can be well described by continuum elasticity theory [8–10]. The key quantities in this formalism are the flexural rigidity of a graphene sheet, $D = 1.41$ eV and Poisson's ratio $\alpha = 0.165$. The energy needed to bend a graphene monolayer into a cylinder of radius R is

$$\Delta E_s = \pi DL/R = \varepsilon_{\text{cyl}}L/R, \qquad (1)$$

where $\varepsilon_{\text{cyl}} = 4.43$ eV and L is the axial length. The corresponding strain energy for a spherical structure is independent of the radius, and is given by

$$\Delta E_s = 4\pi D(\alpha + 1) = 20.6 \text{ eV}. \qquad (2)$$

The inter-layer interaction ΔE_i, which stabilizes multi-wall structures, is proportional to the contact area A. It is given by

$$\Delta E_i = \varepsilon_{VdW}A, \qquad (3)$$

where $\varepsilon_{VdW} = 2.48$ eV/nm^2. The latter value, obtained from graphite, is based on an inter-layer separation of 0.34 nm that is common to virtually all sp^2 bonded structures. Finally, there is an energy penalty ΔE_e associated with the generation of an exposed edge

$$\Delta E_e = \varepsilon_e L, \qquad (4)$$

where $\varepsilon_e \approx 21$ eV/nm is an average value for graphite [11] and L is the length of the exposed edge. The reference system in all these considerations is a large graphene monolayer with no exposed (or completely saturated) edges.

The similarities and differences between scrolls and tubes are visualized in Fig. 1. Formation of a scroll, in contrast to a structure consisting of nested perfect cylinders, requires the energy to form two edges along the entire axis and the strain energy associated with rolling up the sheet. A scroll will be stable as long as the energy gain upon forming inter-wall interactions outweighs this energy investment. It is conceivable that less stable scroll structures may exist as a precursor state to multi-wall nanotubes [10].

3. Using defects as construction elements

In fullerenes, the Stone–Wales transformation has been shown to assist efficiently in the ejection of C_2 molecules, thus shrink-wrapping the fullerenes. A similar mechanism may be at work when transforming defective nanotubes, which may contain scroll segments, into defect-free
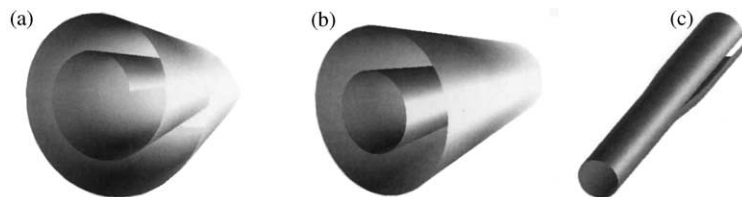

Fig. 1. Schematic view of (a) a scroll, (b) a nested multi-wall nanotube, and (c) a defect separating the two morphologies within one tube.

nanostructures. It is conceivable that insertion of particular defects may be used in the deterministic construction process of carbon nanostructures, such as of nanotubes with a particular chirality. A particular type of defect, illustrated in Fig. 1(c), may be able to transform a scroll [Fig. 1(a)] into a more stable multi-wall system of nested cylinders [Fig. 1(b)] by a "zipper-like" bond rearrangement transformation [12].

4. Carbon foam

A three-dimensional periodic arrangement of the type of defects depicted in Fig. 1(c) may result in a new structure, which has been discussed extensively in Ref. [6]. Initially a hybrid connecting sp^2 and sp^3 carbon atoms, the unusual "foam" structure shown in Fig. 2 combines the large active surface area of graphite layers with the structural rigidity of the diamond lattice. The "origami-style" folding process, depicted in Fig. 2(a), illustrates the close relationship between this structure and graphite. Quite intriguing is the fact that by changing the terrace size *a*, the foam covers the phase space between layered graphite and cubic diamond, the most stable carbon allotropes. While changing the size of the pores, the system maintains a metallic character [6].

5. Hierarchical self-assembly of hybrid structures: peapods containing fullerenes

Intriguing graphitic capsules containing fullerenes, shown in Fig. 3(a), have been observed after a thermal anneal of nanodisperse diamond
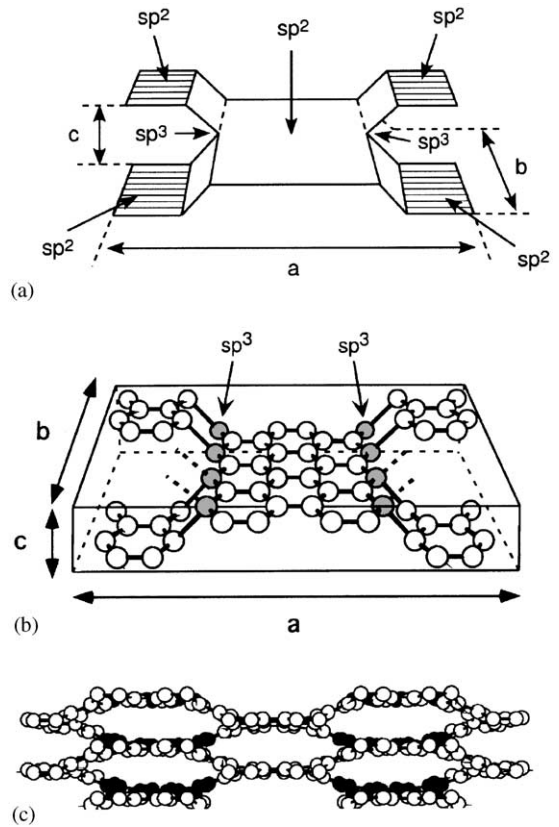

Fig. 2. Structural description of carbon foam. (a) Schematic illustrating the structural relationship between carbon foam and layered graphite. (b) Conventional orthorhombic unit cell of carbon foam, holding 64 atoms. Unit cell variations are possible by changing the number of carbon atoms along the *a*- and *b*-axis. Initially fourfold coordinated "sp^3" atoms are gray shaded, and the initial bond direction to their fourth neighbors is indicated by the dashed lines. (c) Perspective view of the 3D foam lattice structure, based on the above unit cell. Reproduced from Ref. [6] (© American Physical Society 2001).

Fig. 3. (a) Transmission electron microscope image depicting a multi-wall carbon nanocapsule. This simplest "peapod" with a single C_{60} molecule was formed by thermal annealing of nanodiamond powder. (b) The structural counterpart, a $C_{60}@C_{480}$ bucky shuttle. (c) A possible scenario of the peapod formation, involving a large vacancy in the tube wall. (a) and (b) are reproduced from Ref. [5] (© American Physical Society 1999).

powder [5]. Fig. 3(b) displays a possible structural realization, sometimes called a "bucky shuttle", since the encapsulated fullerene is relatively free to move back and forth along the axis.

Very recently, analogous hybrid structures, "peapods" consisting of fullerenes or metallofullerenes encapsulated in nanotubes, have been synthesized in large quantities [4]. Little is known about the formation mechanism, but the general consensus is that fullerenes enter the nanotubes after the latter are synthesized, through the open ends or possibly through defects in the tube wall, as depicted in Fig. 3(c) [7].

Peapods, like all of the above described structures, are nearly as stable as graphite. With the stability and versatility of the carbon bond, even more intriguing structures may be observed in the near future, with applications ranging from electronics components to specialized biocompatible materials and superconductors [13].

Acknowledgements

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