

An approach to control the radius and the chirality of nanotubes

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Abstract

The success of future nanotechnologies will strongly depend on our ability to control the structure of materials on the atomic scale. For carbon nanotubes it turns out that one of their structural parameters—the chirality—may not be controlled during synthesis. We explain the basic reason for this defect and show that novel classes of nanotubes like boron nanotubes, which are related to sheets with anisotropic in-plane mechanical properties, could actually overcome these problems. Our results further suggest that extended searches for nanomaterials similar to pure boron might allow for one of the simplest and most direct ways to achieve structural control within nanotechnology.

(Some figures in this article are in colour only in the electronic version)

Carbon nanotubes (CNTs) [1] are certainly the most prominent member of a whole family of nanotubular materials with technologically interesting properties like WS₂ [2], BN [3] or the recently discovered pure boron nanotubes [4, 5]. In general the electronic and mechanical properties of single walled nanotubes depend quite strongly on their structure, which may be characterized by two parameters: the radius R and the chiral angle θ (chirality). One usually encodes R and θ by two integers (n, m) referring to the basis vectors of the underlying primitive lattice [6]. Unfortunately, it turns out that for the standard synthesis of CNTs one may achieve some control over their radii [7, 8] but little control over their chiralities, which implies that in general there is little control over the properties of the end products of the synthesis. As CNTs may be either metallic or semiconducting, depending on their radii and chiralities [6], this poor structural control will also imply a rather poor control over the electronic properties of CNTs. And for nanotubular systems other than carbon, we are not necessarily facing a better situation.

The strain energy of a nanotube is defined as $E_{\text{strain}} = E_{\text{sheet}} - E_{\text{NT}}(R, \theta)$, where E_{sheet} and E_{NT} are the cohesive energies [9] of the sheet and the tube, respectively. E_{strain} can be understood in the following ways: it quantifies (1) the difference in cohesive/total energy among different (R, θ) nanotubes, (2) the deformation (curvature) energy per atom,

which is necessary to roll up a single sheet into a nanotube of certain radius R and chiral angle θ , and (3) it is a measure of the mechanical tension of a nanotube. This tension stabilizes the tubular shape (it makes the tube round), and it is also responsible for radial breathing mode vibrations.

For CNTs the strain energy refers to a graphene sheet and, as shown in figure 1(a) and discussed in textbooks [6, 10], the strain energy effectively depends on the radius R but not on the chirality: $E_{\text{strain}} = E_{\text{strain}}(R) = C/R^2$ (in figure 1(a) $C = 2.178 \text{ eV } \text{Å}^2$). This radial dependence is easy to understand: the radius is just a measure for the curvature of a CNT, and the smaller its radius the more energy is needed to bend a graphene sheet. But why is the strain energy independent of chirality? This behaviour may be attributed to the nearly isotropic in-plane mechanical properties of the graphene sheet, as quantified by its elastic moduli for stretching and bending. For example, the diagonal elements of the elastic tensor C_{11} and C_{22} are the same, due to a hexagonal symmetry of the honeycomb lattice [6]. Therefore, when stretching a graphene sheet along different in-plane lattice directions, one will observe the same stiffness, and the systems will behave like a homogeneous 2D continuum. From a chemical point of view this mechanical isotropy is caused by a hexagonal network of stiff sp² σ bonds, as shown in figure 2(a). Thus when rolling up a graphene sheet along

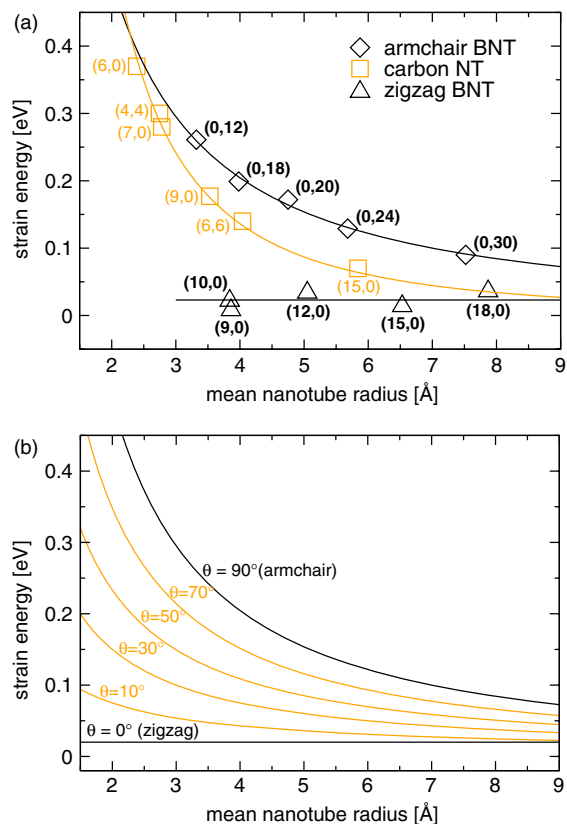


Figure 1. Calculated strain energies for different (n, m) carbon nanotubes (carbon NT) and (k, l) boron nanotubes (BNT) [13]. (a) The strain energies of carbon nanotubes with different chiral angles can be described by a single curve (orange/grey), which is just a function of the tubular radius. Armchair $(0, m)$ and zigzag $(n, 0)$ boron nanotubes instead have two distinct strain energy curves (black). (b) The black curves for armchair and zigzag boron nanotubes are taken from (a), while the orange (grey) curves illustrate other chiral angles θ (see text).

different in-plane directions (chiral angles) to form various nanotubes with similar radii, this process will require similar deformation energies. Therefore E_{strain} will be independent of the chirality of the CNT. This mechanical behaviour is analogous to a simple sheet of paper that is rolled up to form a tube. This process will require little energy for big radii, and it is becoming more and more costly with decreasing radii. But due to the isotropic in-plane mechanical properties of the paper sheet, the energy needed to roll up a paper tube is independent of the ‘roll up direction’ (chiral angle). A similar behaviour is also known for BN, BC_3 [11] and MoS_2 [12] nanotubes.

In a recent theoretical study of boron nanotubes (BNTs) [13] we found that the lattice structure of the related boron sheet is rectangular rather than hexagonal, and therefore the chiral angle θ of BNTs ranges from 0° to 90° , in contrast to 0° to 30° known for CNTs⁴. Thus BNTs and CNTs relate to reference lattices of different symmetry, and therefore one has to use different chiral indices for CNTs and

⁴ Restricting the chiral angle θ to the above ranges implies that for chiral nanotubes the indices $(n, m)/(k, l)$ actually specify an enantiomeric pair (optical isomers), i.e. nanotubes that are mirror images of each other. These enantiomers have opposite chiralities (right-handed versus left-handed) and different line group symmetries [14].

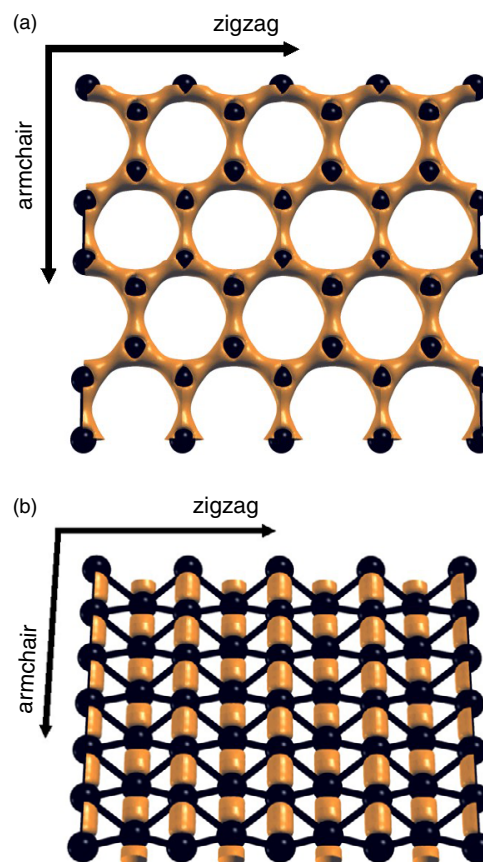


Figure 2. Sigma bonds in (a) graphite and (b) boron sheets. The black balls and sticks in (a) and (b) represent the atomic lattice. The orange (grey) charge density contours at (a) 1.8 and (b) $0.9 e \text{ \AA}^{-3}$ show the presence of sp^2 and sp type σ bonds, respectively.

BNTs [13, 14]. In the following we use (n, m) for CNTs and (k, l) for BNTs. Furthermore, the boron sheet has anisotropic in-plane mechanical properties, where the ratio between the diagonal elements of the elastic tensor was calculated to be $C_{22}/C_{11} \sim 2$, ($C_{11} = 420 \text{ GPa}$, $C_{22} = 870 \text{ GPa}$) [13]. Our *ab initio* calculations were based on the local density approximation (LDA) of density functional theory (DFT) using a plane wave basis set and ultrasoft pseudopotentials [15]; for details about the calculations we refer to [13]. Figure 2(b) shows that the boron sheet has parallel linear chains of stiff sp σ bonds lying along the sheet’s armchair direction, whereas along the zigzag direction, one finds softer bonds of multi-centre character [16] (not shown in figure 2(b)). Therefore, stretching the sheet along its armchair direction (involving C_{22}) will be much harder than stretching it along its zigzag direction (involving C_{11}). Similarly, bending the sheet along the armchair direction, which involves bending of rather stiff σ bonds, will take more energy (strain energy) than bending the BNTs along their zigzag direction, where no σ bonds will be affected. This is quite evident from figure 1(a), where we show that armchair BNTs have high strain energies, whereas zigzag BNTs have nearly vanishing strain energies. Thus the strain energy of BNTs depends on their radii and their chiral angles: $E_{\text{strain}} = E_{\text{strain}}(R, \theta)$. For the whole range of chiral angles ($0^\circ < \theta < 90^\circ$) we expect individual strain energy curves

located between both extremes, as illustrated in figure 1(b). Thus the boron sheet will basically behave like a piece of cloth that is reinforced along one direction with parallel chains of stiffeners (the σ bonds). Bending the cloth along the lines of stiffeners (armchair direction) takes significantly more energy than bending the cloth perpendicular to it (zigzag direction).

Our calculations further predict that BNTs are always metallic, independent of their radii and chiralities. The Fermi surface of the boron sheet has some well pronounced contours in the 2D Brillouin zone, and backfolding of the Fermi surface into the 1D Brillouin zone of a BNT is possible for any radius and any chirality [13]. For graphene, on the other hand, the Fermi surface just exists at the K points of the Brillouin zone, and backfolding of these special points into the 1D Brillouin zone of a (n, m) CNT is possible, but only if $(n - m)$ turns out to be a multiple of 3 [6]. Thus for CNTs their electronic properties (semiconducting versus metallic) vary quite strongly with radius and chiral angle, but their energies are independent of chirality. BNTs are just the opposite, in the sense that their electronic properties will not depend on the structure type but their total energies actually do. To our knowledge this is the first nanotubular system for which the theory predicts a direct control over its basic structural and electronic properties.

The spectrum of nanotube radii obtained during synthesis of CNTs will depend on the specific reaction conditions (temperature, pressure, catalyst, reaction gas, etc), and it can be shifted and/or broadened by changing these conditions. Nevertheless, the CNT chiralities remain random and rather uncontrollable. This was demonstrated by Iijima *et al*, Bethune *et al* and Journet *et al* [7], who were all synthesizing single-walled CNTs using the arc-discharge method, but they reported different mean diameters of 1.0, 1.2 and 1.4 nm, respectively. Furthermore they noted that the chiral angles varied quite strongly for a given tube diameter. This a direct consequence of the $E = E(R)$ dependence of CNTs, as during synthesis the reaction conditions will just determine a certain energy range for the resulting nanotubes, and by virtue of the $E = E(R)$ dependence of CNTs (figure 1(a)) this energy range fixes a certain range of radii but leaves the chirality totally unspecified. In contrast to this, the energies of nanotubes like BNTs, which are derived from a sheet with anisotropic in-plane mechanical properties, will strongly depend on their chiralities and radii $E = E(R, \theta)$, and the reaction conditions will influence both structural parameters. Such a behaviour might ultimately allow for better structure control among nanotubular materials, because now the different chiral angles should be energetically separable and thus experimentally accessible.

As for the radii of the nanotubes, the former may be controlled by growing the nanotubes out of porous materials with well defined pore sizes [5, 8]. And their (strain) energies may be controlled by tuning the reaction conditions. Thus after limiting the ranges of radii and strain energies, it should be possible to actually synthesize a rather narrow range of nanotubes with similar radii and chiralities (see figure 1(b)), or even one specific type of nanotube only.

In summary, we have proposed a different route to achieve structural control within nanotechnology. By analysing the unfavourable case of CNTs, we have shown that the current inability to control the chirality of nanotubes is caused by isotropic in-plane mechanical properties of the

related graphene sheets, leading to isoenergetic nanotubes with similar radius but a whole range of different chiral angles. This 'degeneracy' is lifted for nanotubes that are derived from a reference sheet with anisotropic in-plane mechanical properties. As demonstrated for the case of BNTs, this anisotropy will make the different chiral angles energetically separable, and this should be experimentally accessible. Generally speaking, it might actually pay to supplement current efforts to achieve a higher degree of structural control over nanotubular materials with a systematic search for nanotubular systems which are related to sheets with anisotropic in-plane mechanical properties. Short segments of such materials may then serve as templates to handle less controllable materials such as CNTs, where the template will impress radius and chirality through stable intramolecular heterojunctions, as shown in [17].

Acknowledgments

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