

Smallest Nanotube: Breaking the Symmetry of sp^3 Bonds in Tubular Geometries

Dragan Stojkovic, Peihong Zhang, and Vincent H. Crespi*

Department of Physics, The Pennsylvania State University, 104 Davey Lab, University Park, Pennsylvania 16802-6300
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We describe how sp^2 carbon, threefold coordinated by other carbons, can be replaced by sp^3 carbon, also threefold carbon coordinated, to produce extremely small-diameter (~ 0.4 nm) carbon nanowires with only minimal bond-angle distortion. Under a naming convention analogous to that for ordinary carbon nanotubes, the smallest sp^3 tubes have wrapping indices (3,0) and (2,2). These systems have large band gaps and a stiffness larger even than that of traditional sp^2 -bonded carbon nanotubes. They therefore form the stiffest one-dimensional systems known.

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The atomically thin two-dimensional covalent structure of a graphene sheet can be distorted in the third dimension with a modest energy cost (quadratic in the mean curvature, with Gaussian curvature taken up, in e.g., five or sevenfold rings), thereby producing topologically distinct low-energy structures such as nanotubes [1] and nanocones [2]. However, in very small-diameter nanotubes (below 1 nm in diameter) the curvature penalty of distortion becomes more severe as the bond angles deviate far below the ideal 120° sp^2 angles. Here we describe how sp^2 carbon, threefold coordinated by other carbons, can be replaced by sp^3 carbon, *also threefold carbon coordinated*, to produce extremely small-diameter (~ 0.4 nm) highly stable carbon nanowires with minimal bond-angle distortion. Such systems represent the extreme limit of a small-diameter, rigid one-dimensional atomic structure [3].

The key idea here is to break the tetrahedral symmetry of an sp^3 -hybridized carbon precursor by attaching one relatively tightly bonded group (e.g., hydrogen or fluorine) and three more weakly bonded groups as shown in Fig. 1. Eliminating the weakly bonded groups then produces a carbon building block with three reactive bonds per carbon, whose mutual angles match well to a highly curved small-radius cylinder. The precursor molecule could also contain multiple carbons (e.g., $C_2H_2X_2$), so long as each carbon has exactly one relatively inert ligand.

The resulting carbon structures satisfy Euler's rules for closed polyhedra in exactly the same manner as does carbon in more familiar sp^2 structures, so long as one ignores the topologically irrelevant capping ligand on the fourth bond. Since the stoichiometry of tightly bound ligands is fixed at one per carbon, it is impossible to form a capped three-dimensional interlinked hexagonal ring structure without rearranging these ligands. (In the small-radius tubes that we consider, energetically unfavorable rings of fewer than five sides are also required to form a Euler cap.) Therefore, if growth conditions are such that the capping ligands are tightly bound and immobile, then the system will always have an active growth edge, whose energy is minimized by restriction to a small-radius one-dimensional growth axis.

The result is an extended one-dimensional structure formed from pure hexagonal rings [4]. The symmetry analysis developed for the usual nanotubes [5] remains applicable, except now we have two types of atoms, so the tubes are described by two orbits of the group action. One can even follow an analogous wrapping-index naming convention as for sp^2 carbon nanotubes: the most stable sp^3 tubes, and the ones which we examine in detail, are then the (3,0) and the (2,2) tubes shown in Figs. 2 and 3. The (3,0) tube is essentially a polymer of a close variant of adamantane [6], the most stable hydrocarbon known when measured as the binding energy per carbon atom.

We have performed density functional total energy calculations in the pseudopotential approximation for the (2,2) and (3,0) sp^3 -carbon nanotubes. As a basis for the representation of the Kohn-Sham equations we used plane waves with the cutoff energy of 816 eV. To fully exploit the tube symmetry, we arranged the (2,2)

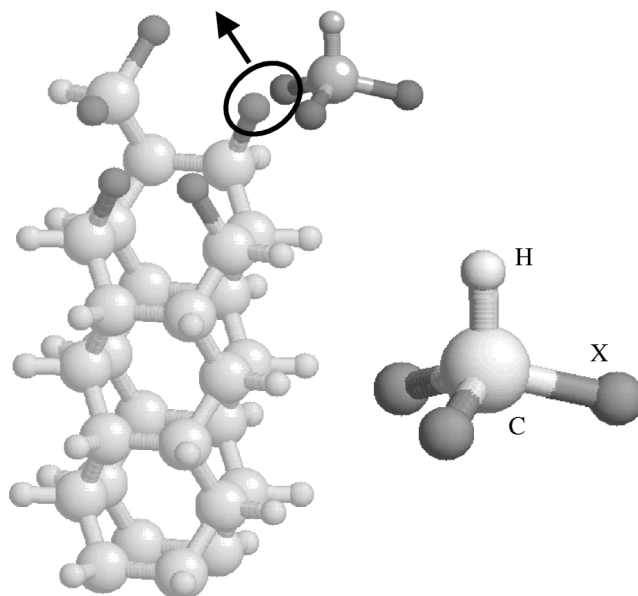


FIG. 1. The proposed precursor and an illustrative growth configuration showing the role of the capping ligand.

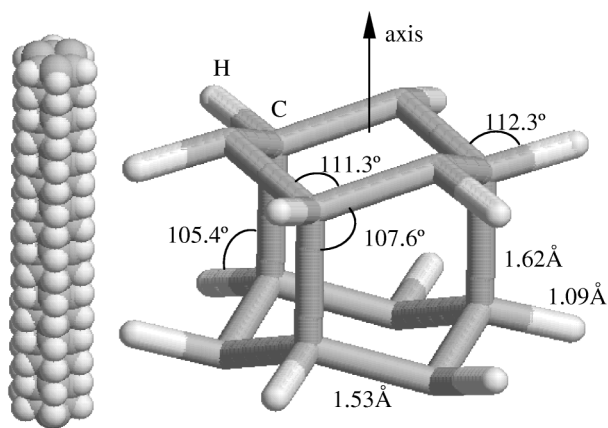


FIG. 2. The relaxed structure of the (3,0) tube, both a doubled unit cell and a space-filling model of the tubular structure.

nanotubes in a square lattice and the (3,0) nanotubes in a hexagonal lattice. The distance between the axes of the adjacent tubes is held at 10.5 Å so that the interaction between tubes is negligible and we can use a purely axial k -point grid (of eight points). Atoms are described with Troullier-Martins pseudopotentials [7] with cutoff radii of 0.619 Å for carbon and 0.360 Å for hydrogen.

The calculated bond lengths (see Figs. 2 and 3) are similar to C-H and C-C bond lengths in alkanes (i.e., 1.11 Å and 1.54 Å). The bond angles are close to the ideal tetrahedron value, 109.5°, so the material comprises a nearly optimal sp^3 bonding structure with no dangling bonds. Therefore the band structures (Fig. 4) have large band gaps typical of saturated hydrocarbons. These band gaps greatly exceed those obtainable in sp^2 carbon nanotubes, since in that case the semiconducting bandgap arises solely from a nanometer-scale circumferential boundary condition [8], whereas in sp^3 tubes the gap arises from the local sp^3 bond saturation. The bands of the (3,0) tube are particularly flat, due to relatively long axially directed carbon-carbon bond (1.62 Å). The lower

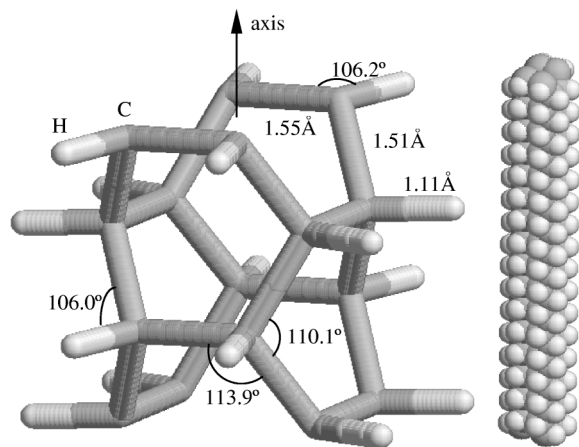


FIG. 3. The relaxed structure of the (2,2) tube, both a single unit cell and a space-filling model of the tubular structure.

bands of the (2,2) nanotube seem to evoke the folded band structure of a hydrogenated graphenelike sheet. The large band gaps and binding energies of these structures (see below) suggest that their synthesis should be favored so long as capping can be maintained on the final sp^3 bond, which should be possible for a judicious choice of feedstock molecule (i.e., one with three weak C-X bonds and one strong C-Y bond, such as C-H) and growth conditions (i.e., which differentially favor the breaking of C-X above C-Y).

The *ab initio* total energies for the (2,2) and (3,0) tubes are very close: the (2,2) tube is favored by roughly 0.05 eV per carbon atom. The (2,2) tube is also 0.22 eV per carbon atom *more stable* than benzene, a well-known cyclic hydrocarbon of identical 1:1 carbon:hydrogen stoichiometry. To compare with standard sp^2 -bonded tubular structures, one must create a reference system comprising a purely carbon sp^2 tube of similar diameter plus the requisite number of isolated H_2 molecules. Since sp^2 tubes so small in diameter do not exist, we favor the sp^2 system slightly and compare the sp^3 systems to standard (4,0) and (6,0) tubes plus the appropriate H_2 's. Our proposed (2,2) is 1 eV per carbon atom and 0.55 eV per carbon atom more stable, respectively, than the (4,0) and (6,0) sp^2 variants. (It is also 0.11 eV per carbon atom more stable than the "infinite-radius" limit of a graphene sheet plus molecular hydrogens.) Earlier theoretical considerations [9] and simulations [10] suggested that the (4,0) tube is the thinnest possible metastable sp^2 carbon nanotube. Such thin tubes have just recently been synthesized, but only inside of multiwall nanotubes [11] or zeolite channels [12], which surround the tube and stabilize its delicate structure.

The (2,2) and (3,0) sp^3 tubes extend one-dimensional carbon systems to the smallest possible radii. They are also the beginning of an entire family of sp^3 tubes. As the tube diameter increases, it becomes untenable to populate only the outer surface with capping hydrogens, since bond-angle distortions become severe. However, by inverting some capping ligands onto the *inner* surface, one can stabilize these larger structures. Figure 5 depicts the stablest geometries (calculated within a tight-binding total energy formalism [13]) for the (8,8) and (5,0) sp^3 tubes. Unrolled, the (8,8) system forms a pleated honeycomb C-H plane with up-down alternated hydrogens, similar to the pleated structure considered for some Si-H systems [14]. The tubes undergo an interesting transition from purely external capping groups to a mixture of internal and external caps as the radius increases. For example, within tight binding the (4,0) structure is most stable with entirely external hydrogen. In contrast, the preferred (5,0) structure has one row of hydrogen on the inner surface. These inner hydrogens minimize bond-angle distortions by increasing the mean curvature of the remaining surface. Within the tight-binding total energy scheme, the total energies per carbon atom for all of the sp^3

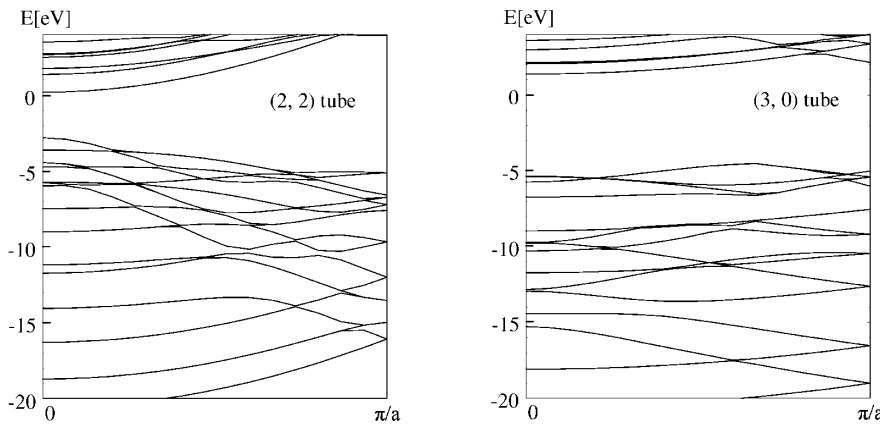


FIG. 4. The electronic band structures of the (3, 0) and (2, 2) nanotubes, showing the large band gap. Residual band folding is visible. The (3, 0) tube has weakly dispersive bands due to the rather long axial carbon-carbon bondlength of 1.62 Å. Horizontal axes use the same scale in both plots.

tubes studied are only slightly higher than that of the (2, 2) tube (by 0.1 to 0.15 eV) and remain more stable than, e.g., benzene [15].

It is particularly fascinating to consider the results of partially removing hydrogen (e.g., thermally) from an sp^3 tube to form a mixed sp^2/sp^3 hybrid with novel electronic boundary conditions and the possibility for tuning semiconducting/metallic properties similar to that described for graphene strips [16]. Such partial removal may be particularly facile for the tubes in the transition region of diameter between pure external and mixed internal/external capping ligands.

The smallest-diameter (2, 2) and (3, 0) sp^3 tubes are also extremely stiff. A calculation of Young's modulus requires as input a meaningful cross-sectional area perpendicular to the axis of the tube. One must take particular care in defining this area for very thin tubes. We define the cross-sectional area of the (2, 2) and (3, 0) tubes as that corresponding to an equivalent number of carbon atoms in a core sample through a bulk diamond structure. The reference to a bulk structure of similar bonding geometry minimizes the arbitrariness in defining the "outer surface" of the tube. Bulk diamond (when calculated here with the same pseudopotential method) has a volume of 5.536 Å³

per carbon atom. Assigning a similar volume per atom to the tubular structures [17], the appropriate volumes of the (2, 2) and (3, 0) unit cells are 17.94 Å³ and 15.94 Å³, respectively. Dividing by the (well-defined) unit cell lengths, the resulting cross-sectional areas are equivalent to those of disks with radii of 2.39 and 2.25 Å, respectively. Such values are quite reasonable, considering the transverse dimensions of the structures given in Figs. 2 and 3. The corresponding Young's moduli are 1.78 TPa for the (3, 0) tube and 1.53 TPa for the (2, 2) tube. These values are substantially larger than those of more familiar sp^2 nanotubes: The (4, 0) tube, calculated here with a similar method, has a Young's modulus of 1.18 TPa. Earlier calculations [18] for single sp^2 tubes gave 1 TPa, while experimental results [19] cluster around 1.3 TPa.

Since cross-sectional areas are really only well defined in macroscopic systems, a more direct and fair comparison between sp^2 and sp^3 carbon tubes is provided by the following thought experiment: Given a box of N carbon atoms and a distance L to span with filament(s) of maximal stiffness, should one choose sp^2 or sp^3 structures? The suitable quantity of comparison is then the stiffness per unit linear carbon atom density along the axis. This quantity (in units 10⁻⁸ J m⁻¹) is 3.44 for the (2, 2) tube, 2.36 for the (3, 0) tube, and only 1.59 for a (4, 0) sp^2 tube (larger-diameter sp^2 nanotubes have only slightly larger values). From both points of view, these new sp^3 structures are more rigid than traditional sp^2 tubes, which were previously believed to be the most rigid structures known.

Carbon nanotubes ultimately depend for their stability on the topological rules which allow threefold coordinated atoms to form extended open polyhedra (or equivalently, closed polyhedra of genus one [20]) of arbitrary length in systems with exclusively hexagonal faces. We demonstrate here that sp^3 bonded carbon can assume the same topology as sp^2 , so long as the fourth bond is capped with a tightly bound ligand. The resulting structures possess unique properties inaccessible in their sp^2 brethren: a very large insulating band gap, high stability at an extremely small diameter, and Young's moduli exceeding 1.5 TPa.

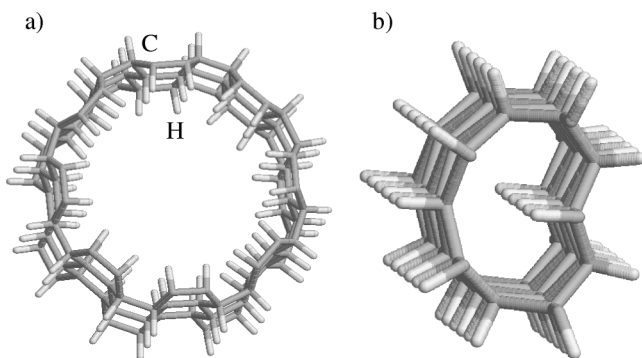


FIG. 5. The tight-binding relaxed structure of the (a) (8, 8) and (b) (5, 0) sp^3 tube (three unit cells are shown).

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*Electronic address: vhc2@psu.edu

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