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Carbon nanotube with square cross-section: An *ab initio* investigation

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Recently, Lagos *et al.* [Nat. Nanotechnol. **4**, 149 (2009)] reported the discovery of the smallest possible silver square cross-section nanotube. A natural question is whether similar carbon nanotubes can exist. In this work we report *ab initio* results for the structural, stability, and electronic properties for such hypothetical structures. Our results show that stable (or at least metastable) structures are possible with metallic properties. They also show that these structures can be obtained by a direct interconversion from SWNT(2,2). Large finite cubanelike oligomers, topologically related to these new tubes, were also investigated. © 2010 American Institute of Physics. [doi:10.1063/1.3483237]

I. INTRODUCTION

The study of the mechanical properties of nanoscale systems presents new theoretical and experimental challenges.^{1,2} The arrangements of atoms at nano- and macroscales can be quite different and affect electronic and mechanical properties. Of particular interest are the structures that do not exist at macroscale but can be formed (at least as metastable states) at nanoscale, specially when significant stress/strain is present. Examples of these cases are atomic suspended chains³⁻⁵ and helical nanowires.⁶

More recently,⁷ it was discovered the smallest metal (silver) nanotube from high resolution transmission electron microscopy experiments. These tubes are spontaneously formed during the elongation of silver nanocontacts. *Ab initio* theoretical modeling⁷ suggested that the formation of these hollow structures requires a combination of minimum size and high gradient stress. This might explain why these structures had not been discovered before in spite of many years of investigations. Even from theoretical point of view, where low stress regimes and small structures have been the usual approach, no study predicted their existence. The unexpected discovery of this new family of nanotubes suggests that such other “exotic” nanostructures may exist. One question that naturally arises is whether carbon-based similar nanotubes [i.e., carbon nanotubes with square cross-section [CNTSC]] could exist (Fig. 1).

From the topological point of view, CNTSC tubes would require carbon atoms arranged in multiple squarelike configurations. Molecular motifs satisfying these conditions, the so-called cubanes, do exist and they are stable at room temperature (Fig. 2).⁸ Cubane (C₈H₈) is a hydrocarbon molecule consisting of eight carbon atoms in an almost perfect cubic arrangement (thus its name). Hydrogen atoms are bonded to each carbon atom (Fig. 2), completing its four-bond valency.

The 90° angles among carbon atoms create a very high strained structure. Because of this unusual carbon hybridization, cubane was considered a “platonic” hydrocarbon and believed to be almost impossible to be synthesized.⁸ However, in 1964, Eaton and Cole⁹ achieved its breakthrough synthesis. Since then the cubane chemistry evolved quickly.^{8,10} Solid cubane¹¹ proved to be remarkably stable and polymers containing up to substituted 40 cubanes units have been already synthesized.⁸ However, up to now no tubular structure has been reported.^{12,13}

In this work we have theoretically investigated structural, stability, and electronic properties of CNTSC tubes. We have considered infinite (considering periodic boundary conditions) and finite (oligomers up to ten square units, Fig. 2) structures.

II. METHODOLOGY

We have carried out *ab initio* total energy calculations in the framework of density functional theory, as implemented in the DMol³ code.¹⁴ Exchange and correlation terms were treated within the generalized gradient functional by Perdew *et al.*¹⁵ Core electrons were treated in a nonrelativistic all electron implementation of the potential. A double numerical quality basis set with polarization function was considered, with a real space cutoff of 3.7 Å. The tolerances of energy, gradient, and displacement convergence were 0.000 27 eV, 0.054 eV/Å, and 0.005 Å, respectively.

Initially we optimized the CNTSC unit cell with fixed *a* and *b* parameters set to 20 Å in order to ensure isolated (noninteracting) structures. The axial *c* lattice parameter was varied, and the total energy per unit cell was calculated. All internal atomic coordinates were free to vary. Total energy versus unit cell volume was fitted using the Murnaghan procedure¹⁶ to obtain the equilibrium *c* lattice parameter. For comparison purposes we have also considered graphite, diamond, and carbon nanotube SWNT(2,2). SWNT(2,2) was chosen because, although ultrasmall carbon nanotubes have been theoretically investigated,¹⁷⁻²⁰ it remains the smallest

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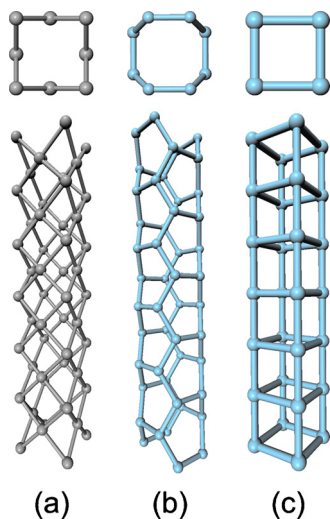


FIG. 1. Structural nanotube models. Frontal and lateral views: (a) Silver tube (Ref. 7), (b) SWNT(2,2), and (c) CNTSC. See text for discussions.

CNT experimentally observed with an estimated diameter of 3 Å.^{21,22} Graphite and diamond were also included in our study because they are the two most stable carbon form and to provide a benchmark for the relative stability between the different tubes and these structures.

III. RESULTS AND DISCUSSIONS

The results are presented in Table I. As expected, graphite is the structure with the lowest energy (most stable), followed by diamond, SWNT(2,2), and CNTSC, respectively. Although the CNTSC energy per atom is relatively high (in part due to the strained C–C bonds, as in cubanes), its relative energy difference to SWNT(2,2) (0.0384 Ha) is similar to the difference between SWNT(2,2) and cubic diamond (0.0395 Ha).

In Fig. 3 we present the binding energy per unit cell. As a direct comparison, it is not possible because the number of

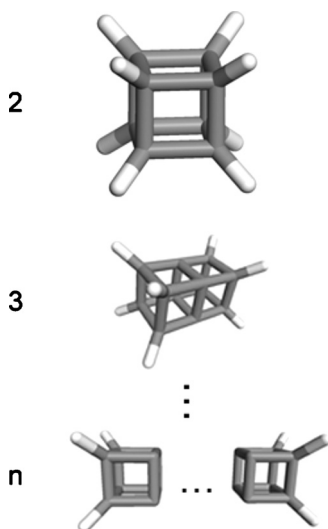


FIG. 2. Cubane and its “polymerized” units. The label refers to the number of square cross-sections in the structure. We considered structures from cubane up to $n=10$. Stick models, C and H atoms are in grey and white colors, respectively.

TABLE I. DMol³ results for crystalline carbon allotropic structures: (a) graphite, (b) cubic diamond, (c) SWNT(2,2), and (d) CNTSC.

	(a)	(b)	(c)	(d)
Energy/atom (Ha)	-38.085	-38.081	-38.041	-38.003
Lattice parameters:				
a (Å)	2.46	3.57	20.0	20.0
c (Å)	6.80	3.57	2.53	1.62
C-C bond-length (Å):	1.423	1.537	1.447	1.580
			1.464	1.616

atoms in the minimum unit cell is different for SWNT(2,2) and CNTSC (eight and four, respectively), we used a double CNTSC unit cell. As can be seen from Fig. 3, the results suggest that stable (or at least metastable, as a well defined minimum is present) CNTSC structures are possible.

Our results also suggest that a direct interconversion from SWNT(2,2) to CNTSC is unlikely to occur via axial (longitudinal) stretching. The extrapolation of the stretched SWNT(2,2) curve (Fig. 3, circle data points) could be misleading, suggesting that it would be possible an interception with the stretched CNTSC curve (Fig. 3, square data points). However, this did not occur, the SWNT(2,2) cannot preserve its tubular topology when its c -value is beyond 3.2 Å.

We then investigated whether if an assisted interconversion would be possible, in our case we considered a continuously decrease of the tube radii value [in order to mimic an applied external (radially) pressure] while keeping the tube free to expand/contract longitudinally [see Fig. 4 and video1 (Ref. 23)].

We have performed these calculations starting from an optimized SWNT(2,2) unit cell and then continuously decreasing its radii value and re-equilibrating the system and measuring the new c -values (Fig. 3, triangle data points). Our results show that under these conditions, there is a pathway that permits a direct interconversion from SWNT(2,2) to CNTSC.

In Fig. 4 we present a sequence of snapshots from the simulations representing the interconversion process. The strain energy injected into the system by the radial compression [Fig. 4(a)] produces a c -lattice expansion, leading to a structural transition [Fig. 4(d)]. The compression process produces new C–C bonds followed by carbon rehybridizations. The processes is better visualized in the supplementary materials (video1).²³

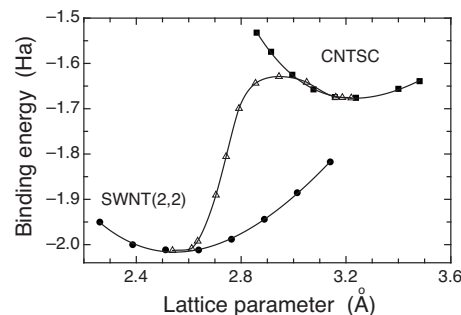


FIG. 3. Binding energy per unit cell as a function of axial c lattice parameter for SWNT(2,2) (circles) and CNTSC (squares). It is also shown its interconversion curve (triangles). See text for discussions.

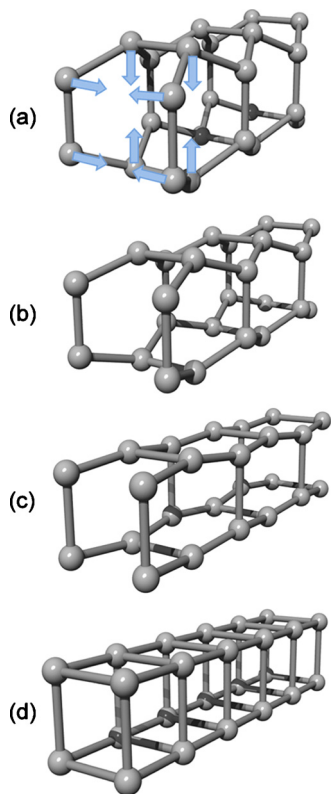


FIG. 4. Snapshots from the axial compression process, showing the interconversion of SWNT(2,2) to CNTSC. (a) Initial SWNT(2,2), [(b) and (c)] intermediates, and (d) final CNTSC structures (enhanced online). [URL: <http://dx.doi.org/10.1063/1.3483237.1>]

We then proceeded with the CNTSC electronic structure analysis. In Fig. 5 we displayed the band structure and the density of states (DOS) for SWNT(2,2) and CNTSC tubes. Both structures present a finite DOS at the Fermi energy, characteristic of metallic regimes. Although CNTSC exhibits unusual carbon hybridization, it follows the general trends that small diameter carbon nanotubes are metallic.^{24,25}

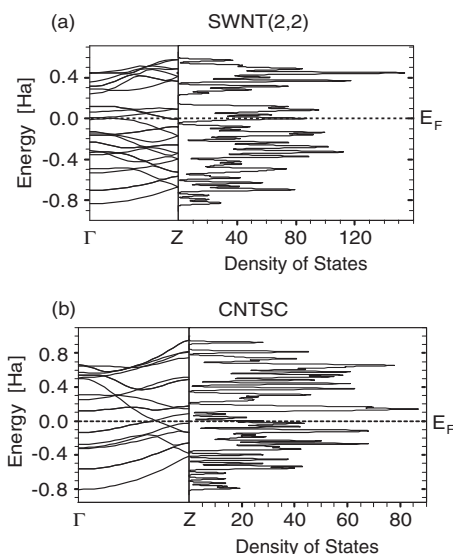


FIG. 5. Band structure and total density of states (in electrons/Ha) results for the (a) SWNT(2,2) and (b) carbon square-cross-section CNTSC. Energy is relative to Fermi level (dashed horizontal lines). Primitive unit cells have eight and four carbon atoms for SWNT(2,2) and CNTSC, respectively.

TABLE II. Total energy per carbon atom (in Ha) for the structures shown in Fig. 2. The corresponding value for the infinite structure is also presented.

n	$e_t(n)$
2	-38.647
3	-38.429
4	-38.323
5	-38.259
6	-38.216
7	-38.186
8	-38.163
9	-38.145
10	-38.131
\vdots	\vdots
CNTSC	-38.003

It is possible that synthetic methods used to produce CNTs (such as laser ablation, chemical vapor deposition, and arc discharge²) could also produce CNTSC, specially inside CNTs of different chiralities, as in the case of SWNT(2,2).^{21,22} Another possibility could be a polymeric synthetic approach, such as the topochemical ones to produce carbon nanotube of specific types that have been recently discussed in the literature.^{26,27} Considering that cubane molecules and their polymers exist and are stable, we decided to investigate the local stability and endothermicity of cubanelike tubular oligomers that are topologically related to CNTSC. We carried out DMol³ calculations for the molecular structures displayed in Fig. 2. The terminal C atoms were passivated with H atoms.

In Table II we present the results for the total energy per carbon atom as a function of the number of square cross-sections. Our results show that although the oligomer formation would require an endothermal (energetically assisted) process, the structures are stable and the energy per carbon atom converges asymptotically to the corresponding value of the infinite tube (see also supplementary materials²³).

In summary, based on a recent discovery of the smallest possible silver nanotube with a square cross-section,⁷ we have investigated whether a similar carbon-based structure could exist. We have used *ab initio* methodology to investigate the structural, stability, and electronic properties of carbon nanotubes with square cross-section (CNTSC). Our results show that stable (or at least metastable) CNTSC (finite and infinite) structures can exist. They also show that it is possible to convert SWNT(2,2) to CNTSC under radial contraction. CNTSCs should share most of the general features exhibited by “standard” nanotubes. Although the CNTSCs have not yet been observed, we believe our results had proven their feasibility. We hope the present work will stimulate further works for this new family of carbon nanotubes.

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