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Square- and hexa-cross sectional carbon and boron-nitride nanoneedles – A theoretical study

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ABSTRACT

Square- and hexa-cross sectional carbon nanoneedles and their boron-nitride counterparts are investigated as a new class of nanomaterials. In contrast with the ordinary carbon nanotubes, the band gaps of the introduced carbon nanoneedles are not *strongly* dependent on the size of the cross sections, whereas for the boron-nitride needles such a dependency is not observed. Note that any attempts to optimize the octa-cross sectional nanoneedles, change the structure to an ordinary nanotubes; therefore it seems that octa-cross sectional nanoneedles could not be synthesized. Topological analysis also indicates that although C—C bonds have covalent nature, the B—N bonds show ionic character.

1. Introduction

Nanotubes are on the light spot of nanoscience and nanotechnology owing to their outstanding physical properties and their tremendous applications in molecular electronics [1–3], nanomechanics [4], optics [5], sensors [6,7], catalysis [8] and even pharmaceutical purposes [9]. Carbon nanotubes (CNTs) can be either metallic or semidonducting, depending on their diameters and chirality [10]; but the cytotoxicity of these compounds brings considerable risk to their use in living organisms. Therefore since the discovery of CNTs by Iijima [11], many researches have been devoted to investigate the stable structures of non-carbon based nanotubes. Boron-nitride nanotubes (BNNTs), which are analogeous to CNTs, possess many desirable properties. For example they are more chemically inert and structural stable than CNTs and found to be wide band gap semiconductors, typically independent of on the diameters and chirality of the tube [12]. On the other hand, it is shown that BNNTs can deliver DNA oligomers to the interior of cells with no apparent toxicity [13].

In spite of the condensed-materials in which the goal usually pursued is "the higher, the better", in the case of nanomaterials the goal might be rephrased as "the smaller, the better". It should be recalled that dimensionality and symmetry restrictions affect electronic behavior of the system. Therefore interesting physics invariability emerges as material dimensions approach the atomic scale and quantum size effects influence how electrons interact with each other. Hence it is expected that nanotubes, nanowires and nanoneedles should show a variety of electronic properties. Of particular interest are the structures that do not exist at macroscale but can be formed at least as meta-stable states at nanoscale. For example using ab initio calculations it is shown that stacked hexagonal boron nitride rings are stable [14].

Among the mentioned nanostructures, the nanoneedles defined as structures with a thickness or diameter constrained to tens of nanometers or less and an unconstrained length, play an important role in electronic industry. It should be mentioned that at these scales, quantum mechanical effects are important. Due to their tapered shapes, nanoneedles can potentially be applied as probe tips with high spatial resolution but any damage to probed microstructures should be minimal. They can also be used as field-emission tips with outstanding field enhancement factors [15]. Unlike nanowires of uniform diameter, nanoneedles with sharp tips are difficult to prepare. Only a few kinds of semiconductor nanoneedles have been reported, such as silicon [16], ZnO [17], Se [18] and ZnSe [19].

The main purpose of this article is to introduce a new class of nanomaterials included square- and hexa-cross sectional carbon and boron-nitride nanoneedles(which are smaller than the ordinary nanotubes) and investigation of their structural as well as electronic properties.

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2. Computational details

Calculations were performed using the density functional theory (DFT) with generalized gradient approximation (GGA) as parameterized by Perdew–Burke–Ernzerhof (PBE) and a split valence double-ξ polarized (DZP) basis set implemented in SIESTA code [20–22]. The interaction between core and valence electrons was represented by the Troullier-Martins norm-conserving pseudopotentials [23]. A grid cutoff 500 Ry and 400 Ry were used for carbon and boron-nitride tubes, respectively. In all cases a $1 \times 1 \times 8$ Monkhorst–Pack k-point sampling of the Brillouin zone was set, and the atomic positions were relaxed until the residual forces on each atom were lower than 0.04 eV/Å. The suppercells of square-, hexa- and octa-cross section nanotubes are consisted of 24, 36 and 48 atoms, respectively; and the periodic boundary condition was applied to the suppercells. In order to perform atoms in molecules (AIM) analysis, the wave functions of the relaxed geometries are created at B3LYP/6-31G* level of theory using Gaussian 98 program [24]. AIM2000 software [25] is applied for topological analysis of the considered structures.

3. Results and discussion

Three kinds of cross section needles (included square, hexa and octa nanoneedles) are considered. In both carbon and boron-nitride cases, the structures of octa-cross section nanoneedles change to an ordinary CNT and BNNT, respectively. Therefore it seems that, although it is possible to synthesize square- and hexa-cross section nanotubes, any attempt for synthesize of octa-cross section nanoneedles should be unsuccessful.

The optimized structures for the considered cross-sectional nanotubes are depicted in Fig. 1. The bent angles in the obtained structures imply to this fact that significant stress/strain is present in these systems. These strains causes that the p orbitals located on each atom could be available for an electron acceptor system; such as hydrogen molecule. Therefore these nanoneedles have high weight (H2)/weight(nano). Hence it seems that the surface of the considered cross sectional nanostructures could be good candidates for hydrogen adsorption or hydrogen storage of different molecules because of a significant strain presented in their surfaces.

The calculated geometrical parameters for the considered structures are given in Table 1. It is clear that two kinds of bonds (edge and ring) could be distinguished for each nanoneedle. The edge bonds are longer than the ring bonds in both carbon nanoneedles, whereas for the considered boron-nitride nanostructures the edge bonds are shorter than the ring ones. Surprisingly in both carbon and boron-nitride structures the bond lengths do not show size dependency. For example in both square- and hexa-cross section carbon nanoneedles the length of edge bond is 1.61 Å and for ring bond is 1.58 Å. Hence it could be concluded that there is a strong resonance between the atoms of a given ring. It is recalled that although such a resonance is expected between the atoms of a ring in hexa-cross section (which are aromatic), but it is strange for the atoms of square-cross section nanoneedles (which are antiaromatic!!!).

Table 1
Calculated bond distances (d) and topological parameters (ρ and $\nabla^2\rho$) for the considered cross sectional nanotubes.

	Square		Hexagonal	
	Carbon	BN	Carbon	BN
Edge				
d	1.611	1.518	1.613	1.510
ρ	0.1881	0.1581	0.1902	0.1598
$\nabla^2\rho$	−0.2619	0.3016	−0.2735	0.3316
Ring				
d	1.584	1.681	1.574	1.639
ρ	0.2360	0.1246	0.2359	0.1336
$\nabla^2\rho$	−0.5097	0.0909	−0.4967	0.1357

Topological analysis is performed on the considered nanostructures. The positions of the Bond Critical Points (BCPs) in these systems are shown in Fig. 1. It is clear that in boron-nitride nanoneedles the observed BCPs are close to B atoms, which indicates to the electron depletion around the boron atom because of high electronegativity of nitrogen atoms; whereas for carbon nanoneedles these BCPs are appeared at the middle of C—C bonds. This implies to the ionic and covalent bond characters for boron nitride and carbon nanoneedles, respectively. Also topological parameters, included electron density (ρ) and laplacian of electron density ($\nabla^2\rho$) at the BCPs are calculated and gathered in Table 1. Note that two kinds of BCPs are observed in these nanostructures (edge and ring BCPs). Although the values of ρ at the edge and ring BCPs for boron-nitride nanoneedles are close to each other's (0.1581 and 0.1246 for square-; 0.1598 and 0.1336 for hexa-), in carbon nanoneedles these values show a significant difference with each other's (0.1880 and 0.2360 for square-; 0.1902 and 0.2359 for hexa-). Therefore it seems that in carbon cases the electrons are more accumulated at the rings than the edges. On the other hands, the calculated $\nabla^2\rho$ for carbon and boron-nitride nanoneedles are

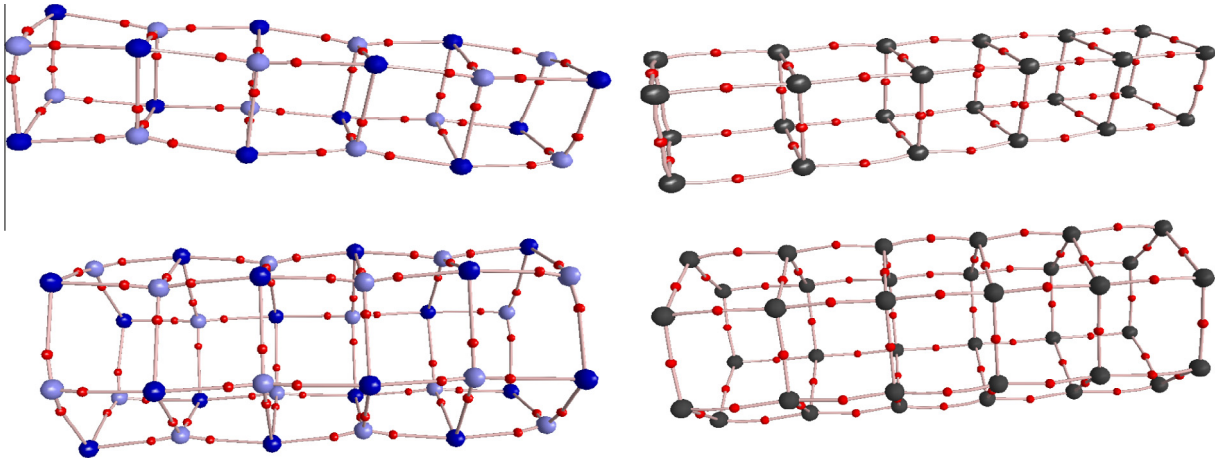

Fig. 1. The optimized structures and the corresponding bond critical points for the considered nanostructures.