



Periodic density functional theory study of structural and electronic properties of single-walled zinc oxide and carbon nanotubes

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ABSTRACT

Periodic density functional theory calculations with the B3LYP hybrid functional and all-electron Gaussian basis set were performed to simulate the structural and electronic properties as well as the strain and formation energies of single-walled ZnO nanotubes (SWZnONTs) and Carbon nanotubes (SWCNTs) with different chiralities as functions of their diameters. For all SWZnONTs, the band gap, strain energy, and formation energy converge to ~ 4.5 eV, 0.0 eV/atom, and 0.40 eV/atom, respectively. This result suggests that the nanotubes are formed more easily from the surface than from the bulk. For SWCNTs, the strain energy is always positive, while the formation energy is negative for armchair and zigzag nanotubes, therefore suggesting that these types of nanotubes can be preferentially formed from the bulk. The electronic properties of SWCNTs depend on the chirality; all armchair nanotubes are metallic, while zigzag and chiral nanotubes can be metallic or semiconducting, depending on the n and m vectors.

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1. Introduction

Single-walled carbon nanotubes (SWCNTs) [1–5] have attracted great scientific and technological interest in nanoscience and nanotechnology fields, because of their unique chemical and physical properties.

In the last two decades, many potential nanotube applications have been investigated, including storage and energy conversion devices, sensors, semiconductors in nanoscale molecular sieves, hydrogen storage materials, additives for polymeric bracket materials in catalytic processes, etc [6]. However, many of these applications have yet to be analyzed and tested properly, although some have already reached the industrial production phase [6]. For this reason, for the large-scale preparation of CNTs, a variety of synthetic strategies have been recently developed and extended to inorganic materials, such as zinc oxide [7–9], titanium dioxide [10,11], aluminum nitride [12], boron nitride [13–15], and other systems [16–19]. In some cases, nanotubes of inorganic materials may be more advantageous than SWCNTs, owing to their interesting qualities and well-established properties, which can provide new scientific and technological perspectives.

The strong chemical similarities between SWCNTs and

graphene enable to apply the research experience and relevant methodologies developed for graphene to inorganic nanotubes [20].

In particular, CNT electronic properties sensitively depend on the diameter and chiral angle, i.e., slight differences in these parameters can cause significant changes in the material, such as that from metallic to semiconductor. Previous studies based on scanning tunneling microscopy [21,22] and performed at a large energy scale (~ 2 eV) confirmed the prediction that CNTs can be semiconducting or metallic depending on the tube diameter and the chiral angle between the tube axis and hexagon rows in the atomic lattice [23,24]. Specifically, armchair SWCNTs are always metallic, while zigzag and chiral nanotubes can be metallic or semiconducting [25], despite the metallic character of the carbon monolayer surface (graphene) [26].

As for graphene, nanotubes without band gap have restricted its application in electronics and, consequently, they are not suitable for semiconducting devices. Therefore, several ways to replace materials with such limitations have been studied in the last years.

Except for the nanotube diameter, no other geometric restrictions are present; however, it was believed that a nanotube could collapse and break when it reaches a diameter of ~ 25 Å. This collapse is linked to the short curvature of the tube [27]. Nevertheless, several experimental techniques are available to control

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the nanotube diameter and obtain SWCNTs with diameters up to 30 Å as well as multiwall CNTs with diameters of at least 1000 Å [28–31].

Owing to the close structural similarity between SWCNTs and single-walled ZnO nanotubes (SWZnONTs), the latter can provide new scientific perspectives to technological applications. The ZnO (0001) monolayer surface, which is formed by hexagons of Zn and O atoms with alternate vertices and has the same symmetry and structure observed in graphene sheets, is preferentially used to obtain SWZnONTs by adopting the conventional experimental methods [32,33]. This surface is polar, although the polarity disappears when it is rolled up. The formed nanotubes appear to be promising materials for application in the nanotechnology fields.

Until now, many methods to synthesize ZnO nanotubes have been reported, including thermal reduction [34], vapor phase growth [35], hydrothermal growth [36,37], gas-solid processes [38], sol-gel processes [39], plasma-aided molecular beam epitaxy [40], and metal organic chemical vapor deposition [41]. All ZnO nanotubes are grown with large diameter and thickness.

For instance, Zhang et al. [41] reported the formation of SWZnONTs by the metal organic chemical vapor deposition technique at moderate temperature, 350–450 °C. The obtained nanotubes were grown epitaxially on (0001) sapphire substrates, with both the ZnO *c*-axis and growth direction parallel to the substrate normal. All nanotubes had a hexagonal cross section and the same in-plane orientation. The well-defined hexagonal shape is an indication of epitaxial growth and, consequently, reveals the single-crystal nature of the tubes. According to Shen et al. [42], SWZnONTs with small diameters are more stable than nanowires or nanobelts, but become less stable if the diameter exceeds that of the (24,0) nanotube. Furthermore, Zhou and coworkers [43] studied the size-and-surface dependent stability of (8,0) SWZnONTs, observing a good surface texture. Rout et al. [44] explored the application of SWZnONTs as solar cells, photomicrocavities (owing to the hexagonal nature), and hydrogen and ethanol gas sensors.

In addition, Tu and Hu, [45] using density functional theory (DFT) calculations, found that the piezoelectric behavior of the SWZnONTs strongly depended on their chirality, and also obtained negative values of the binding energy (BE) in all the analyzed models. The strong dependence between structure, electronic profiles, and thermodynamic stability of the ZnO nanotube wall thickness was studied by Xu et al. [46] at the Generalized Gradient Approximation (GGA) level of theory; the close relationship between the band gap energy, E_{gap} , and the BE values was found to be inversely proportional to the number of zigzag edge configurations.

As many of these theoretical studies have shown considerably different results, this research topic is clearly still open and indefinite. Furthermore, several published works focused on models based on SWZnONTs with small diameters. Nevertheless, one-dimensional nanostructures have atomic order limited to the nanoscale thus, the use of theoretical quantum chemical calculations and more realistic theoretical models that can support the experimental findings are crucial to achieve an accurate understanding of the related phenomena. Theoretical chemistry methods are widely recognized as complementary tools for the interpretation of experimental data, and can help predict new results and practical strategies.

This paper discusses the structural and electronic properties of SWZnONTs with three different nanotube arrangements (armchair, zigzag, and chiral) and various diameters and chiral angles, based on the periodic DFT formalism.

The research in SWNTs arises from the variety of nanotube diameters and chiral angles, which can significantly affect the structural and electronic properties, showing an ensemble of

features that can complicate the foresight of possible technological applications.

The electronic properties were evaluated by analyzing the band gap energies, band structures, density of states (DOS), and density and electrostatic charge maps. The strain (E_{strain}) and formation (E_{form}) energies, which are not usually available as experimental data, were calculated to estimate its preferential formation. Thus, these theoretical findings may provide a rational development for designing of new nanoelectronic devices.

The results were compared with similar calculated properties of SWCNTs at the same computational level and formalism, as well as with data available in the literature.

2. Computing method and models

The theoretical simulations of SWZnONTs and SWCNTs were performed by using periodic DFT with standard hybrid B3LYP functional [47] and the CRYSTAL14 software [48].

CRYSTAL14 uses a Gaussian-type basis set to represent crystalline orbitals as a linear combination of Bloch functions defined in terms of local functions (atomic orbitals). An overview of the algorithms used in the introduction of the DFT into the CRYSTAL computer code is presented by Tawler and coworkers [49].

The usually B3LYP functional is described by the following equation:

$$E_{XC}^{B3LYP} = E_{XC}^{LDA} + 0.20 (E_{XC}^{HF} - E_{XC}^{LDA}) + 0.72 (E_{XC}^{GGA} - E_{XC}^{LDA}) + E_{XC}^{LDA} + 0.81 (E_{XC}^{GGA} - E_{XC}^{LDA}) \quad (1)$$

In contrast to the generally used B3LYP, the CRYSTAL code uses the local functional fitted to the accurate correlation energy of the uniform electron gas (Vosko–Wilk–Nusair-5) [50], which is used to extract the local part of LYP correlation potential.

Hybrid density functionals have been extensively applied to provide accurate descriptions of crystalline structures. In particular, this functional has been successfully employed to investigate electronic and structural properties in previous works [51–53]. However, other three different functionals were adopted for test: PWGGA [54], PBE0 [55], and HSE06 [56]. Upon analysis of the calculated structural and electronic properties of bulk, surface and nanotube, the functional B3LYP showed the best results.

The zinc, oxygen, and carbon atom centers were described by all-electron Gaussian basis sets: 86-411d31G [57] for zinc, 8-411d1 [58] for oxygen, and 6-21 G* [59] for carbon atoms. A very large grid with 99 radial points and 1454 angular points was adopted. The accuracy of the truncation criteria for bio-electronic integrals (Coulomb and HF exchange series) was controlled by a set of five thresholds (10^{-10} , 10^{-10} , 10^{-10} , 10^{-20} , 10^{-40}). These parameters represent the overlap and penetration for Coulomb integrals, the overlap for HF exchange integrals, and the pseudo-overlap (HF exchange series), respectively.

The DOS, and band structure were analyzed using the Properties14 routine implemented in the CRYSTAL code, employing the same *k*-point sampling as the diagonalization of the Fock matrix for the optimization process. The charge and electrostatic potential difference maps were built using the isolated atoms as references, taking isolines at ± 0.001 e/Å. This analysis is useful to infer on the difference of covalent and ionic character between SWZnONTs and SWCNTs.

The ZnO wurtzite structure has a direct wide band gap of 3.37 eV [60] and belongs to the space group $P6_3mc$ with two Bravais lattice ($a = 3.258$ Å, $c = 5.220$ Å) [61] and one internal coordinate $u = 0.382$ [61]. Its structure can be depicted as a zinc atom surrounded by four oxygen atoms with sp^3 -hybridization in a tetrahedron configuration along the *c*-axis, producing an accumulating normal dipole moment. We have previously studied this

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