Journal of Molecular Graphics and Modelling 42 (2013) 115–119

Contents lists available at SciVerse ScienceDirect

Journal of Molecular Graphics and Modelling

journal homepage: www.elsevier.com/locate/JMGM

Electronic properties of functionalized (5,5) beryllium oxide nanotubes

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ARTICLE INFO

Article history:
Accepted 29 March 2013
Available online 6 April 2013

Keywords:
Beryllium oxide nanotubes
Hydroxyl
Point defects
Work function
DFT theory

ABSTRACT

Using the density functional theory (DFT) we study the structural and electronic properties of functionalized (5,5) chirality single wall beryllium oxide nanotubes (SW-BeONTs), i.e. armchair nanotubes. The nanotube surface and ends are functionalized by the hydroxyl (OH) functional group. Our calculations consider the Hamprecht–Cohen–Tozer–Handy functional in the generalized gradient approximation (HCTH-GGA) to deal with the exchange–correlation energies, and the base function with double polarization (DNP). The geometry optimization of both defects free and with point defects nanotubes is done applying the criterion of minimum energy. Six configurations are considered: The OH oriented toward the Be (on the surface and at the end), toward the O (on the surface and at the end) and placed at the nanotube ends. Simulation results show that the nanotube functionalization takes place at the nanotube ends with the Be—O bond displaying hydrogen-like bridge bonds. Moreover the nanotube semiconductor behavior remains unchanged. The polarity is high (it shows a transition from covalent to ionic) favoring solvatation. On the other hand, the work function low value suggests this to be a good candidate for the device fabrication. When the nanotube contains surface point defects the work function is reduced which provides excellent possibilities for the use of this material in the electronic industry.

1. Introduction

Since the carbon nanotubes discovery by Iijima [1] these 1D structures have attracted the attention of the scientific community, they have been investigated both theoretically and experimentally. Similar studies have been performed on boron nitride nanotubes [2,3], zinc oxide nanotubes [4–8] and nanosheets [9,10]. However less attention has been paid to the earth alkaline compounds such as the 2D beryllium oxide (BeO) which was predicted to exist by Continenza et al. [11] in 1990. BeO nanosheets display graphene-like hexagonal configuration with sp^2 hybridization. Simulation studies on the BeO nanosheets by Baumeier et al. [12] and Wu et al. [13] have demonstrated that the pristine nanosheets behave as semiconductors however when they are fluorinated and hydrogenated [14] transform into semimetal. At the same time Baumeier et al. [12] have predicted the single wall BeO nanotubes (BeONTs) formation with semiconductor behavior and wide band gap in the interval of [7.3,8.8] eV for different chiralities (zig–zag and armchair structures). It is important to remark that these BeONTs display properties which are helicity independent. Studies on BeONTs [15] doped with carbon and nitrogen considering different chiralities show energy gap reductions from 5.59 eV for pristine (6,6) BeONT, to 1.1 for BeONT:B, to 1.5 for BeONT:C and to 1.0 eV for BeONT:N. At the same time the beryllium vacancies induce an increase in the magnetic moment. As it stands doped BeONTs may be applied technologically in the spintronic industry. Therefore in this work we address the study of structural (bond lengths and nanotube diameters) and electronic properties (polarity, chemical potential and work function) of single wall (5,5) BeONTs. The nanotubes are considered in the armchair configuration and functionalized at the ends and surface by the hydroxyl group (OH). The choice of (5,5) chirality is because this structure exhibits a strain energy of 0.058 eV/atom which is low compared with other chiralities such as the (n,0). This energy value indicates that the nanostructure may easily phase transform from 2D to 1D [12]. We also analyze the point defect effects on the BeONT–OH properties by paying attention on the vacancies of Be and O. Our studies are done using molecular simulation (local properties) within the density functional theory in order to explore possible applications in molecular sensing or field emission devices.

2. Simulation models and methods

First principles total energy calculations are performed to study (5,5) SW-BeONTs–OH structural and electronic properties. To deal

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http://dx.doi.org/10.1016/j.jmgm.2013.03.007

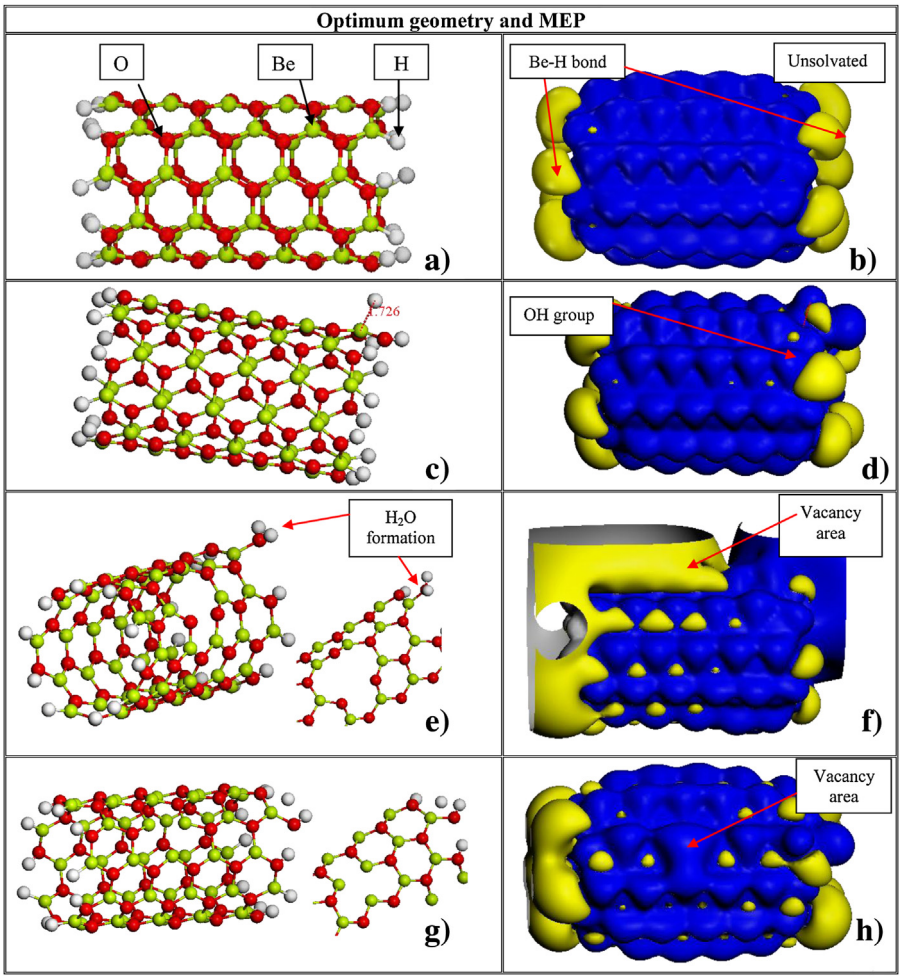

Fig. 1. This figure shows optimized structure for (a) pristine BeONT, (b) MEP for BeONT, (c) BeONT–OH, (d) MEP for BeONT–OH, (e) BeONT–OH with beryllium mono-vacancies, (f) MEP for BeONT–OH with beryllium mono-vacancies, (g) BeONT–OH with oxygen mono-vacancies, and (h) MEP for BeONT–OH with oxygen mono-vacancies. Yellow, red and white spheres represent Be, O and H, respectively. Blue color is for the positive charge and yellow color is for the negative charge.

with the exchange–correlation energies we apply the functional of Hamprecht–Cohen–Tozer–Handy (HCTH) [16] within the generalized gradient approximation (GGA). The base function DNP with double polarization [17] (we use a *p*-orbital for H, and a *d*-orbital for Be and O) is used as implemented in the quantum chemistry DMol^3 code [18]. Six OH orientations have been investigated: In (C1) the fragment is oriented toward a Be, in (C2) the fragment is oriented toward an O, in (C3) the molecule is within the central hexagon of the surface, in (C4) the OH is at the nanotube end making a bond with Be, in (C5) the OH is at the nanotube end making a bond with a O and in (C6) the fragment is on the nanotube closed end, at the center of the cover. Charge neutrality and multiplicity 1 have been taken into account for both pristine BeONT and BeONT–OH structures. Simulations have been done considering the armchair model for the (5,5) SW-BeO nanotubes with length of 1.42 nm and diameter of 0.76 nm for the end mono-hydrogenated nanotubes (nanotube with open ends, Fig. 1a). The nanotube structure is composed of 120 atoms (50 Be, 50 O and 20 H) and the hydroxyl functional group contains 2 atoms.

Calculations have been also done to determine the chemical potential using the formula (HOMO+LUMO)/2 provided (analogue) the Fermi level corresponds to that of the electron gas and it is at the middle of the energy gap. The work function is determined as the difference between the vacuum level (LUMO) and the Fermi level (chemical potential), this represents the minimum energy required to remove an electron from the Fermi level to the vacuum level. The molecular electrostatics potentials (MEPs) surfaces have been determined as commonly reported in the literature [19]. We have employed a cut radius of 0.33 nm for the (OH) functional group and 0.40 nm for the single wall BeONT–OH structure with and without point defects, with a total energy convergence tolerance of 1.0×10^{-6} Ha. The structural stability has been dealt with the criterion of non complex vibration frequency [20].

3. Results and discussion

It is important to remark that 1D BN nanotubes, with open ends and saturated by N and B atoms instead of H atoms, are suitable systems to perform molecular simulations as already demonstrated by Hao et al. [21] in 2006. Hao et al. investigated the BN nanotubes magnetic properties with results showing variations produced by the saturation process. Moreover there exist reports showing that the most stable BN nanotubes configurations correspond to the (*n*,*n*) [22] geometries. This fact is supported by the possible synthesis of such nanotubes with open ends [23]. BN nanotubes of short length may be functionalized by polymers making them suitable for applications in biomedicine and to form composites with high mechanical resistance [3,4]. These results motivate the study of structural and electronic properties of functionalized SW-BeONTs as earlier reported by Chigo et al. [24–27].