First-principles studies of zigzag pristine boron nitride nanotubes doped with one iron atom

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Abstract Interaction of one iron atom with pristine zigzag boron nitride nanotubes with different diameters, ranging from (8,0) to (12,0), have been investigated using density functional theory calculations. Departing from four initial configurations, considering each of them interacting with the tubes’ walls either from inside or outside, we have analyzed the adsorbate migration to the most favorable positions together with the related binding energies and the equilibrium distances as well as the electronic structure of the final systems. It was observed that the smaller the radius of the tube the lower is the binding energy for all studied structures, and also that the inner configuration is more stable than the outer one for small radius. For the preferred position for the iron atom, it was seen that it varies according to the starting configuration and that the iron-first-nitrogen-neighbor bond length works as a constraint in determining the most favorable position for the adsorbate. Finally, for the electronic structure, it was observed that the presence of the dopant introduces localized levels at the band gap of the nanotubes and that those levels are mostly related to the orbitals 3d and 4s of the iron atom. For the inside case, as a consequence of higher hybridization and a confinement effect, the gap closure is more pronounced for small diameter tubes. For all studied structures, it was observed a net-spin-polarization equal to 4 μB.

1 Introduction

Boron nitride (BN) nanotubes have been the subject of extensive study for years [1, 2]. BN nanotubes are known as semiconductor materials with large band gaps of about 5.8 eV almost independent of tube chirality and morphology [3, 4]. Also, BN tubes possess interesting properties, such as strong hardness, high thermal conductivity, and excellent mechanical properties being more chemically and thermally stable than their carbon (C) analogues [5–8]. It is expected that BN nanotubes would be good alternatives to C nanotubes for possible applications in nanoelectronics, since allied with this stability advantage, they present uniform semiconducting properties that can be possibly tuned according to specific needs. Chemical functionalization of nanotubes with transition metals (TM) has proved to be an effective way for tuning their electronic properties. There are some experimental results about BN nanotubes doped with TM, such as iron–nickel (Fe–Ni) and pure Fe nanowire-filled BN multi-walled tubes, BN nanotube supported gold (Au) nanoparticles, and yard-glass BN nanotubes filled with periodic magnetic Fe nanoparticles [9–12]. Besides, Fe is a commonly used catalyst in the synthesis of BN nanotubes [13]. Recent theoretical studies were realized regarding the interaction of TM and iron atoms with pristine (8,0) BN nanotubes [14, 15]. However, as far as we know, no analysis was performed considering curvature effects related to the tubes diameter variation as well as the dopant localization (inside or outside the tubes).

In this work, the adsorption of Fe atoms on pristine BN nanotubes with different diameters are systematically investigated using spin-polarized density functional theory (DFT)
Calculation. Experimental results have shown that these systems prefer a zigzag orientation during the growth [16]. In this sense, we have analyzed (6,0), (7,0), (8,0), (9,0), and (12,0) pristine boron-nitride nanotubes. Four different starting positions were considered for the adsorbate as it can be seen at Fig. 1 and each position is considered both inside and outside the tube. According to previous results, it was observed that the Fe atoms can adsorb on perfect tubes exothermically [15]. Also, it is shown that the smaller the tube radius the lower is the binding energy, and hence the more stable the system. About the energetic difference between adsorption inside or outside the tube, it was concluded that, for a given diameter, the iron atom is more strongly bound to the inner wall and that this difference, as expected, tends to decrease as the diameter increase. For the electronic structure, it was shown that the incorporation of the iron atom induced a decrease in the energy gap of the nanotubes in a sense that they started to behave like small gap semiconductors. In addition, we have verified that the adsorption of the Fe atom inside the nanotubes produced a larger gap reduction when compared to the case where it is adsorbed outside the structures. Finally, it was seen that these systems present spin-polarization equal to 4 \( \mu_B \).

2 Calculation procedure

A pictorial scheme for the four starting configurations is shown in Fig. 1. We have considered the iron atom approaching the tube surface both from outside (Fig. 1e), labeled “out”) and inside (Fig. 1f) that will be called “in”) and, for each case, the adsorbate is: above the center of a hexagon formed by BN atoms (Fig. 1a), labeled HC), over the center of an axial BN bond (Fig. 1b), AB), over a B atom (Fig. 1c), TB), and over a N one (Fig. 1d), TN). A periodical boundary condition is employed along the tube axis with unitary cells long enough to prevent Fe-Fe interactions at the supercell, and a vacuum region (more than 30 Å between tube centers) is assumed in their lateral direction. In this sense, we have 48, 56, 64, 72, and 96 atoms (plus one Fe atom) for the unitary cells of the tubes (6,0), (7,0), (8,0), (9,0), and (12,0) nanotubes, respectively, with diameters ranging from 4.9 to 9.6 Å. It is interesting to notice that the Fe–Fe interaction amongst adjacent unitary cells (in the axis direction) is extremely important when determining the magnetic properties of such systems and that the tubes’ diameter as well as the Fe-tube bond length work as control parameters of this interaction. For example, for the (8,0) tube only a unitary cell that is twice the size previously mentioned could avoid Fe–Fe pairing which resulted in a spin-polarization equal to zero for the smaller cell.

In this work, we carried out first-principles calculations based on the density functional theory [17, 18]. We used the pseudo-potential method as implemented in the SIESTA code [19], which is a fully self-consistent DFT method based on a linear combination of atomic orbitals basis set with linear scaling. Double-\( \zeta \) plus polarization basis set, which has been shown to yield high-quality results for most of the systems studied, was used. Norm-conserving pseudo-potentials for B, N, and Fe were generated using the Troullier–Martins method [20] within the generalized gradient approximation, as established on the parametrization scheme of Perdew–Burke–Ernzerhof [21]. A cutoff of 150 Ry for the grid integration was utilized to represent the charge density. The conjugate gradient (CG) algorithm [22] is adopted to fully relax the structures until the residual force acting on the each atom is no more than 0.1 eV/Å. We have also realized a “control” calculation where the residual