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Interactions of lead with carboxyl and hydroxyl-decorated(10, 0) single-walled carbon nanotubes: First-principle calculations

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ABSTRACT

Absorption of Pb on a zigzag (10, 0) carbon nanotube (CNT) surface, pure and functionalized with carboxyl ($-\mathrm{COOH}$) and hydroxyl ($-\mathrm{OH}$) groups was investigated using the density functional theory. Binding energy calculations were performed and indicated that adsorption of the Pb metal on the surface of the three nanotubes were stable, through a chemisorption. Therefore, CNTs are a feasible active material for filters that retain such metal. After Pb adsorption, the CNT and COOH-CNT conductivity changed, from semiconductor to half-metallic for CNT and from semiconductor to metallic for COOH-CNT, which can serve as a signal for Pb sensor. In all three cases adsorption produced a change in nanotube magnetism, which can also serve as a sensitive signal for chemical sensors. After adsorption of Pb, the changes in binding energy, charge transfer, conductance and magnetism may lead to the different response in the CNTs-based sensors. Thus, it is expected that these results could provide helpful information for the design and fabrication of the Pb sensing devices.

1. Introduction

Recently, several studies have shown that carbon nanotubes (CNTs), discovered by Iijima in 1991 [1], have many interesting features such as nanocapillarity, porosity, large surface area and electronic properties sensitive to the environment exposed [2] which makes this material a promising raw material for manufacturing filters and sensors [3–5].

Notwithstanding all these features, other studies have shown that pure CNTs have a reduced reactivity due to their strong $\mathrm{C-C}$ bonds with hybridizations sp^2. However, it is known the possibility to functionalize this material, e.g. by linking functional groups, atoms, doping or production of defects (vacancies) in the tube wall [6–10], opening up many possibilities of applications, because of structural, electronic and mechanical changes that may occur. Organic carboxyl and hydroxyl groups are among the elements most used in functionalization of CNTs. These groups have acted as mediators in the interaction between CNTs and organic and inorganic substances both experimentally [11–13] and theoretically [14–16]. Functionalization with these two groups may be conducted by chemical treatment in oxidation processes with strong acids and also by plasma oxidation [3,17–19].

We present a study on the interaction of pure nanotubes and functionalized nanotubes with lead. Lead is classified as a heavy metal and belongs to the group of the most polluting metals [20] together with Cd (cadmium), Cr (chromium), Cu (copper), Hg (mercury), Ni (nickel) and Zn (zinc). Some of these metals are considered critical, since they play important biological roles in the metabolism of a number of organisms. However, Pb has no known biological activity and has extreme toxicity [21]. In addition, its form of interaction with pure and functionalized CNTs is not well known.

In literature, there are reports on the aid of computational tools in understanding possible routes of interaction of various metals with nanomaterials, helping in the process of understanding and clarifying experimental results [22,23,14,24–26]. Given this context, this article theoretically investigates the interaction between Pb and the external surface of carbon nanotube (CNT), pure and functionalized with oxygenated groups carboxyl (COOH) and hydroxyl (OH).

This paper is organized as follows. In Section 2, we describe the methodology and parameters used in the calculations, as well as the configurations for each system. In Section 3.1 we present the results of structural properties; in Section 3.2 the results of electronic properties; and, lastly, in Section 4, we present our conclusions.

2. Modeling details

We used the density functional theory (DFT) implemented in the SIESTA code [27] and the local density approximation (LDA) for

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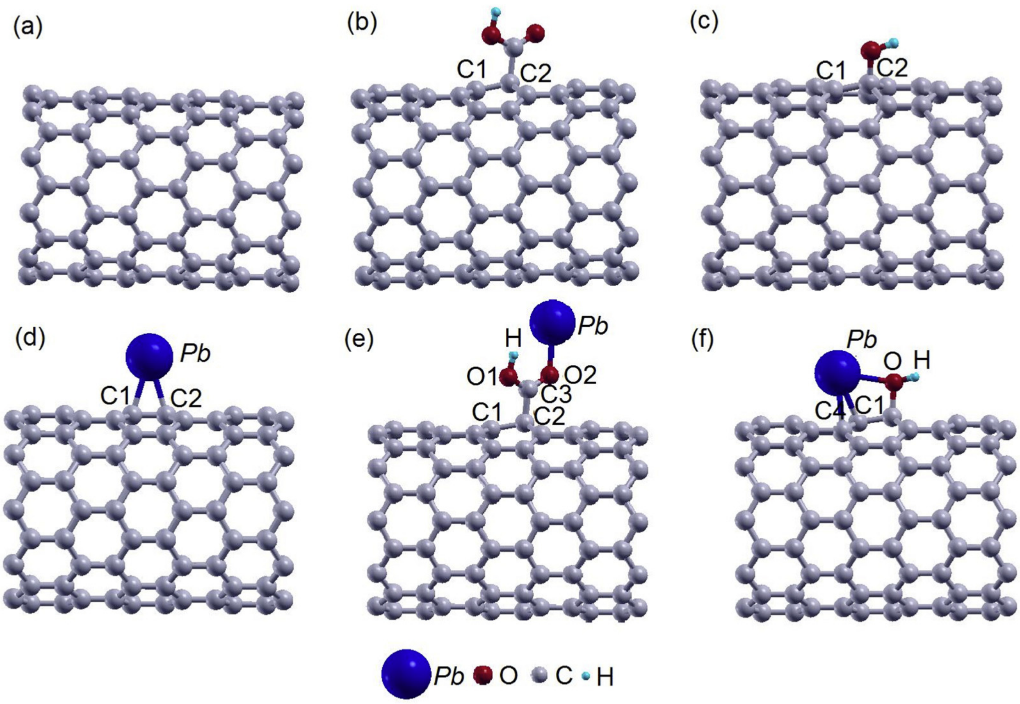

Fig. 1. Geometric configuration of the structures: (a) CNT, (b) COOH-CNT, (c) OH-CNT and geometric structures of the systems with their minimized energies: (d) CNT-Pb, (e) COOH-CNT-Pb, (f) OH-CNT-Pb.

the exchange correlational potential. Both the Ceperley–Alder (CA) [28] scheme and Perdew and Zunger parameters [29] (PZ) were used. To avoid explicit treatment of the core electrons, the norm-conserving Troullier–Martins pseudopotentials [30] were used. For the valence electrons, we used a split-valence double-zeta basis set with polarization functions (DZP) [31].

To simulate one-dimensional infinite nanotubes, periodic boundary conditions were applied along the tube axis (z-direction). In the lateral (x, y) directions, vacuum regions were ~10 and ~22 Å, respectively, to avoid image–image interactions between neighboring supercells.

To produce sufficiently accurate results, convergence studies were performed for the grid (mesh) cutoff energy and the number of **k**-points. The total energy convergence for the different systems was generated for a mesh cutoff at ~200 Ry; however, we used 300 Ry to ensure accuracy. For the number of **k**-points, the Brillouin zone was sampled in accordance with Monkhorst and Pack [32]; convergence was generated for a $1 \times 1 \times 8$ set, but a $1 \times 1 \times 11$ **k**-point sampling set was used.

The electronic properties were calculated on systems with fully relaxed atomic coordinates during geometry optimization until the Hellman-Feynman forces were below 0.04 eV Å^{-1}. The binding energies (E_b) for the Pb absorbed on the CNTs were calculated using the following expression [33]:

$$E_b = E_{\text{CNT+Pb}} - E_{\text{CNT}} - E_{\text{Pb}} - E_{\text{CC}}, \tag{1}$$

where E_{CNT} and E_{Pb} are the Kohn–Sham energies for the CNT and metal, respectively, $E_{\text{CNT+Pb}}$ is the Kohn–Sham energy of the complex CNT+metal and E_{CC} is the counterpoise correction that accounts for the effects of the basis set superposition error (BSSE), as follows.

$$E_{\text{CC}} = E_{\text{ghost-Pb}} - E_{\text{Pb}} + E_{\text{ghost-CNT}} - E_{\text{CNT}}, \tag{2}$$

where $E_{\text{ghost-Pb}}$ and $E_{\text{ghost-CNT}}$ are the metal and CNT Kohn–Sham energies, respectively, and the atoms were replaced by ghost atoms [27].

The atomic charge distribution can be determined from first principle calculations. In this work, we examine the topological charge density distribution using the Mulliken [34,35] population analysis implemented in the SIESTA code. The metal charge variations from transfer between the CNTs and Pb were calculated using the following expression:

$$\Delta Q_{\text{Pb}} = Q_{\text{Pb}}^{\text{abs}} - Q_{\text{Pb}}^{\text{iso}}, \tag{3}$$

where $Q_{\text{Pb}}^{\text{abs}}$ is total charge on the metal after adsorption, and $Q_{\text{Pb}}^{\text{iso}}$ is the total charge for the isolated Pb.

3. Results

3.1. Pb adsorption at the CNT, COOH-CNT and OH-CNT surface

The equilibrium geometries of pure, carboxylated and hydroxylated CNT, are shown in Fig. 1(a)–(c), respectively. It may be observed that following functionalization of CNT, there was a distortion radially outwards of the tube, in the carbons named C1 and C2 (Fig. 1(b) and (c)), which suggests this distortion is caused by local re-hybridization of the C1—C2 bond from sp^2 to sp^3, according to a first-principles study by Veloso et al. [16].

After structural relaxation of the CNTs used in this study, the potential adsorption sites of Pb were assessed, namely: top site (directly on the carbon atom), hollow site (over the center of the hexagon) and bridge site (on C—C bond). According to some theoretical studies [23,3], bridge site adsorption has higher stability in the binding energy. Accordingly, for all CNTs studied in this work, we place the Pb atom on the C1—C2 bond.

The equilibrium position after structural relaxation of all systems (CNTs and Pb) is shown in Fig. 1(d)–(f). The notation adopted is: CNT-Pb, for the pure CNT after adsorption of Pb; COOH-CNT-Pb, for the COOH-CNT after adsorption of Pb and OH-CNT-Pb for the OH-CNT after adsorption of Pb.

For CNT, the adsorption of the Pb atom occurred preferentially on bridge site with C1 and C2 (Fig. 1(d)), as expected. For