Current Applied Physics 18 (2018) 1034–1040

Contents lists available at ScienceDirect

Current Applied Physics

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

Electronic and magnetic properties of the [4Fe-4S] iron-sulfur clusters encapsulated in a single-walled semiconducting carbon nanotube

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ARTICLE INFO

Keywords:
Single-walled carbon nanotube
Charge transfer
Iron-sulfur clusters
Endohedral functionalization
p-degenerate semiconductor
Exchange coupling

ABSTRACT

The electronic and magnetic properties of the charge neutral iron-sulfur clusters, [4Fe-4S], encapsulated in a semiconducting single-walled carbon nanotube, CNT(17,0), are examined within the density functional theory approach. We verified that for the isolated cluster, due to exchange coupling between the electron spins on iron ions, the antiferromagnetic ground state with the total spin $S = 0$ is formed. The encapsulation provides the significant charge transfer from the carbon nanotube to the embedded molecule. In consequence, a shift of the molecular levels with broadening of the HOMO-LUMO gap is observed, and the significant *p*-doping of the surrounding nanotube with narrowing its energy band gap occurs. This transferred charge is found to be localized on the iron centers and contributes to the reduction of the value of the magnetic moments on the iron centers. We find that, the antiferromagnetic arrangement of the magnetic moments on the molecule is preserved after encapsulation and no net magnetic moment is induced on the carbon nanotube. We also ascertained that the considered hybrid system is of the *p*-degenerated semiconducting type.

1. Introduction

The carbon nanotubes are the cylindrical allotropes of carbon with the sp^2 hybridization, that exhibit the quasi-one dimensional electronic properties determined with their chirality and diameter. This nanomaterials has been intensively studied during last four decades due to the diversity of the interesting electronic [1–5], thermal [6,7], optical [8–11] and mechanical [12,13] properties resulting in a remarkable application potential in many fields of science and technology, from the nano-electronics [14–16] to the nano-medicine [17–19].

It is a well known fact, that the electronic properties of the carbon nanotubes may be adjusted not only by determining their diameter and chirality, but also through functionalization with various chemical groups, molecules and polymers [20–22]. The functionalization methods include defect formation [23,24], the covalent bounding with proper chemical groups, and non-covalent functionalization by molecules and chemical chains, that interact with the carbon nanotube *via* van der Waals forces, as well as the π–stacking [25–27]. These functionalizing elements may be appended externally, but also the methods for the endohedral functionalization are developed and the properties of the carbon nanotubes filled with molecules are studied theoretically and experimentally [28–30]. Recently, the functionalization of carbon nanotubes with the magnetic molecules attracts much attention, in the context of the magnetic sensors or the magnetic memory devices [31,32].

In biological systems iron complexes form a wide group of metalloproteins, that employs the oxido-reductive properties of the iron ions and are used for the charge transfer within the biological cells – the examples of those chemical species are the iron-sulfur clusters. The first descriptions of iron-sulfur complexes appeared in the 1960s, and addressed their photo-chemical and oxido-reductive functions. In the early 1970s also their synthetic analogues were initiated and their chemical properties investigated from then on [33–36]. The studies on the electronic and magnetic properties of the iron-sulfur clusters began in 1990s and are continued [37–40].

Here, we investigate the electronic and magnetic properties of the interface between the common in biology and known for its charge transfer properties molecule, and the nanoelectronic material – a semiconducting single-walled carbon nanotube. With the help of the standard density functional theory approach we attempted to verify the properties of the charge neutral isolated iron-sulfur tetramer, and thereafter we discussed the electronic and magnetic characteristics of the considered hybrid system.

2. System geometry and method

The considered iron-sulfur cluster consists of the four iron and four sulfur ions forming a cube-like molecule. In living organisms, the [4Fe-4S] clusters are incorporated into proteins, where the iron ions are terminated with the side amino chains – predominantly cysteine.

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https://doi.org/10.1016/j.cap.2018.05.020
Received 9 January 2018; Received in revised form 7 May 2018; Accepted 22 May 2018
Available online 25 May 2018

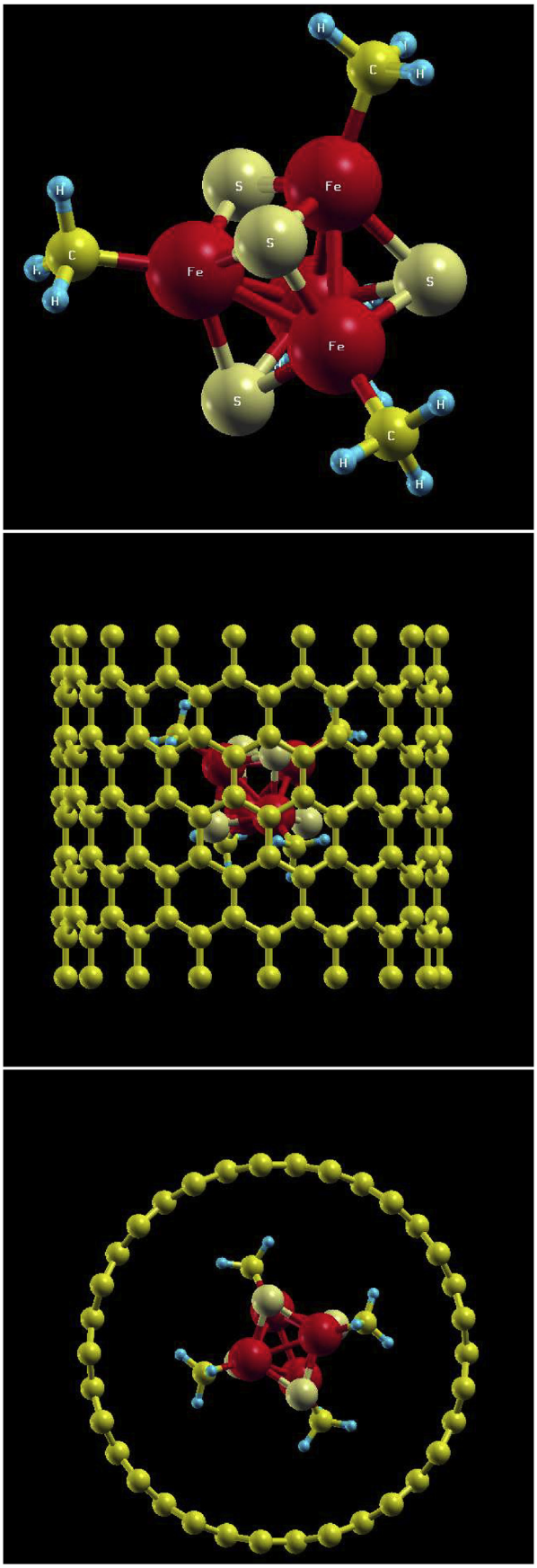

Fig. 1. The considered [4Fe-4S] cluster terminated with $–CH_3$ groups (upper panel), the considered cluster encapsulated in the CNT(17,0) (middle and bottom panels).

Table 1
The optimized distances between the corresponding atoms for the isolated and the embedded iron-sulfur cluster, given in Å.

	Isolated	Embedded
Fe_1– Fe_2	3.0310	2.4422
Fe_1– Fe_1	3.1460	2.4415
Fe_1– S	2.4358	2.1633
Fe_1– C	2.0516	2.0149

Within this work however, we consider the [4Fe-4S] clusters, where the iron ions are saturated with the $–CH_3$, but also CH_2 and –CH side groups, for simplicity. The single iron center of the cluster is placed in a deformed tetrahedral geometry, that is characterized by the C_{3v} point group. In order to analyze the magnetic properties of these clusters, the two types of the iron centers are distinguished within the molecule and denoted by Fe_1 and Fe_2. Each Fe_1 ion neighbors two Fe_2 ions and one Fe_2 ion, and *vice versa*. The studied molecules and supercells are presented in Fig. 1, while the optimized distances between the atoms for the free and the embedded molecule are given in Table 1.

We focus on the studies on the semiconducting carbon nanotube since their achievable applications in microelectronics, particularly as field-effect transistors [41,42], gas sensors [43] and in photovoltaics as light harvesting media [44]. We chose the value of the diameter of the considered carbon nanotube to be optimal e.g. large enough to provide the non-covalent bounding between the nanotube and the embedded molecule, and on the other hand sufficiently small to allow the DFT analysis. We also argue that to fulfill the non-covalent bonding condition the semiconducting carbon nanotubes of the larger diameter may be considered, while the side groups of the proper length are applied to the encapsulated molecule or while the assembly of the spatially helical distribution of the encapsulated molecules is arranged [45–47].

The considered carbon nanotube CNT(17,0) with embedded molecule is periodic in the z direction, while for the x and y directions the periodic slabs were separated by 10 Å of vacuum. The optimized diameter of the CNT(17,0) is 13.84 Å, while its optimized z-lattice constant is equal to 4.26 Å, and the optimized C–C distances within the carbon nanotube are 1.428 Å. The periodicity in the z direction of the supercell containing CNT(17,0) with embedded molecule ([4Fe-4S]-4(CH_3)@CNT) is 12.78 Å. To perform electronic structure calculations we used a uniform 3×3×6 Monkhorst-Pack k-mesh [48] to sample the first Brillouin zone of [4Fe-4S]-4(CH_3)@CNT, while the calculations of the electronic properties of an isolated molecule were performed for the Γ point with Martyna-Tuckerman correction, for the total energy and the self-consistent potential [49] as well. The geometry optimization was performed for the molecule and the carbon nanotube separately, before the encapsulation, and again for the carbon nanotube with the embedded molecule. The optimized distance of the embedded molecule and the inner wall of the CNT(17,0) is c.a. 3.1 Å, hence one can regard the considered CNT(17,0) as a non-covalently, internally doped with the [4Fe-4S] clusters.

The presented results were obtained using a DFT approach as implemented in the plane-wave pseudopotential Quantum Espresso code [50]. We used norm–conserving pseudopotentials in the Perdew-Burke-Ernzerhof (PBE) parametrization for the exchange–correlation functional [51]. A plane-wave energy cutoff was set to 80 Ry, for all atomic species. The applied pseudopotentials contain the $2s^2$, $2p^2$, $3d$ and $4f$ projections of valence states for carbon atoms, while $3s^2$, $3p^4$, $3d$ and $4f$ projections for sulfur atom. The projections for valence states of the iron atoms are $3d^6$, $4s^2$, $4p$ and $4f$. The Hubbard U corrections for the iron $3d$ orbitals, assuming $U_{\text{eff}} = U - J = 5$ eV [52,53], as well as the semi–empirical van der Waals corrections [54,55] were also taken into account within the calculations. The obtained results were thereafter verified with the different set of pseudopotentials in the PBE parametrization.