



Polyiodide structures in thin single-walled carbon nanotubes: A large-scale density-functional study

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ABSTRACT

Using automatic structure generation algorithms and large-scale density functional computations we study polyiodide structures encapsulated within a 1 nm diameter single-walled carbon nanotube. The most energetically preferable confined iodine structures are the I_3^- , I_5^- and I_8^{2-} molecular anions and periodic single, double and triple chain systems. The formation energy drops with increasing number of iodine atoms, reaching a minimum for a single iodine chain. Double and triple chains are metastable but have higher formation energies due to spatial confinement within the thin carbon nanotube. The calculated electron transfer from the nanotube to the molecular structures is close to the integer charge values of the molecular anions. The corresponding Fermi energy shift depends on the iodine concentration. For the single, double and triple chains the calculated Fermi shift is ~ 0.13 , ~ 0.23 and ~ 0.19 eV below the top of the nanotube valence band, respectively. The computational approaches presented here require minimal *a priori* knowledge of the system under study, yet are able to predict stable iodine structures observed in experiment.

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1. Introduction

Very shortly after the atomistic characterization of carbon nanotubes (CNTs) [1], the possibility of filling the hollow space of these nanocylinders was predicted theoretically [2] and then realized in experiment [3]. Such filling not only allows modification of the electronic and optical properties of the nanotube [4–9], but is also interesting from the fundamental point of view. Within the tube inner channels the encapsulated atoms can form unique one-dimensional structures [10–17], which may not exist as free-standing systems. The structural characterization of such 1D crystals typically begins with transmission electron microscopy (TEM) imaging, however TEM projected images rarely provide sufficient information for complete structural identification, and the process of imaging can itself lead to structural modification. For these reasons it is important to support such studies with experiment-independent theoretical structure prediction methods, which determine the equilibrium crystal structure on the basis of total

energy calculations. These can be used for image simulation of hypothetical atomic geometries, and to study the properties of the encapsulated material.

In the present work we study the atomic arrangement of iodine atoms, encapsulated within a cylindrical CNT inner cavity. Iodine is known for its strong acceptor properties, and is frequently used for doping of conjugated polymers [18–21] and CNT films in order to increase their conductivity. Polyiodides present a rich variety of possible atomic geometries, from I_2^- , I_3^- and I_5^- molecular anions, to huge atomic arrays with complex structure [22]. TEM studies of I@CNT systems revealed the formation of helical chains and bulk-like crystals of iodine, depending on the SWCNT diameter [23,24]. Raman studies of iodine doped SWCNTs show peaks with frequencies close to those of I_3^- , I_5^- and I_8^{2-} molecular anions for different tube diameters [25]. Potential correlation between the nanotube wrapping vector and the helicity of polyiodide chains has been explored [23], but no such correlation was found [24]. The electronic structure of isolated helical iodine chains has been studied by means of tight-binding calculations [26], and the effect of the Fermi energy shift in the I@CNT systems was estimated within the plane-wave density-functional theory (DFT) approach [27]. The energetics of charged iodine chain structures and their

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impact on the nanotube conductivity have been studied in Ref. [28]. The structure of helical iodine chains inside boron nitride nanotubes was studied by means of empirical potentials [29]. However, in the case of the I@CNT system, the use of model potentials may result in insufficient accuracy, since the resulting polyiodide geometry will be affected by the interplay between charge transfer, covalent bonding and Van der Waals interactions. For example, recent experimental and computational studies revealed the influence of charge transfer on the geometry of the iodine chain structures within thin carbon nanotubes as a consequence of charge-density wave distortion [30].

In this present work we undertake a systematic investigation of polyiodide structures formed within SWCNTs by means of large-scale density functional computations. To keep the calculations tractable we focus on a sufficiently thin (~1.0 nm in diameter) SWCNT filled with a different number of iodine atoms. We also investigate the interaction between the nanotube and iodine structures and study the charge-transfer effects and Fermi energy shift in these systems.

2. Methods

Prediction of the stable atomic geometry is a problem of global function minimization in a high-dimensional space, that is usually accessed by a variety of approaches, including random search [31], metadynamics [32,33], simulated annealing [34,35], basin hopping [36], minima hopping [37] and genetic algorithms [38–44]. For 1D@CNT such calculations have been performed mostly by the use of classical molecular dynamics [45–52] and very recently by *ab initio* random structure searching [53].

In general, structural prediction of 1D crystals encapsulated within CNTs has the following peculiarities:

1. The length of the nanotube lattice vector is, in general, different from that of the encapsulated crystal. It is therefore needed to calculate an isolated 1D@CNT fragment or, if periodic boundary conditions are imposed, translate the unit cells of both structures to achieve commensurability of the two systems.
2. The information from TEM images is often limited, and exact knowledge about the number of atoms in the unit cell of the 1D crystal is rarely known – one has to “scan” a range of atomic concentrations in order to find the most preferred one.
3. The calculations can involve large number of atoms in the range of 100–1000 or beyond, and high-performance computation techniques are needed.
4. In some cases, charge transfer between the nanotube and the 1D crystal is present and this effect may have influence on the atomic geometry of the encapsulated structure. To cover this circumstance, a direct treatment of the electronic structure of the 1D@CNT has to be included, which limits the use of molecular mechanics methods and requires more expensive quantum chemical computations.

To relax the first restriction, connected with the incommensurability of the polyiodides and the CNT, we used a long (7 primitive cells, 29.82 Å length) supercell of a thin (~1.0 nm) (13,0) semi-conducting nanotube with a total of 364 carbon atoms. In order to determine the preferred iodine density we performed calculations for 1 to 72 iodine atoms, encapsulated within the CNT supercell. To consider the problem quantum chemically while keeping the computation time reasonable, we used a localized-basis set density-functional theory implementation (described below).

In order to obtain the atomic geometry of the polyiodide structures we used a conjugate gradient algorithm for finding a local energy minimum. Two different approaches were used to

construct initial geometries of the iodine. In the first approach multiple random structures were generated for each iodine concentration, with the constraint that the atoms must not be too close to each other. To avoid creating similar structures at random, we used the so-called fingerprint function [54] to compare the initial configurations and kept only those which are at some certain cosine distance from each other. In the second approach we started from the almost linear iodine chain (with small random displacements to break the symmetry of the system) inside the CNT, optimized its geometry, then compressed the atomic positions along the nanotube axis, and introduced a new iodine atom at the boundary of the unit cell in the empty space created by the compression. By doing so we increased the iodine concentration sequentially, linking the previous stable geometry to the next one. To speed up the calculations, we did not optimize the positions of the carbon atoms for all atomic densities under study, but allowed them relax for the most promising structures.

For DFT computations we used the AIMPRO package [55–57]. The action of core electrons was modeled using Hartwigsen-Goedecker-Hutter pseudopotentials [58] and the electron wave functions have been expanded on a basis set of Gaussian orbitals. A k-point grid with a separation between the mesh points of $\Delta k = 2\pi \times 0.034 \text{ \AA}^{-1}$ and a Fermi smearing of electronic occupations with effective temperature of 0.04 eV were used during the geometry optimization for all atomic densities. For selected structures, we used a more refined k-point grid with $\Delta k = 2\pi \times 0.017 \text{ \AA}^{-1}$ and effective temperature of 0.02 eV. During test calculations, as described in the results section, we used both the local density approximation (LDA) and the Perdew-Burke-Ernzerhof (PBE) generalized gradient approximation [59] with dispersion corrections included within the DFT-D2 [60] scheme as implemented in the Quantum-ESPRESSO package [61]. Since no covalent bonding between the iodine and carbon atoms of the SWCNT is expected, the main role of the nanotube was considered to act as a potential well for spatial confinement and electron donor for the iodine atoms. We therefore kept a minimum basis set for carbon atoms of four contracted functions to speed-up the computations during the geometry optimization procedure. The iodine basis consisted of a total of 40 *s*-, *p*-, and *d*-type functions. To calculate the Fermi level position we increased the number of carbon basis functions from 4 to 38 uncontracted *s*-, *p*-, and *d*-type functions and used a k-point grid with $\Delta k = 2\pi \times 0.002 \text{ \AA}^{-1}$ together with smearing temperature of 0.02 eV. The electronic densities of states have been computed with a total of 241 k-points ($\Delta k = 2\pi \times 1.4 \times 10^{-4} \text{ \AA}^{-1}$) and an energy broadening of 0.01 eV. The simulated TEM images have been obtained with the SIMULATEM software [62] at 120 keV with spherical aberration 0.3 mm, defocus set to the Scherzer value of –317 Angstrom and defocus spread 38 Å. STEM image simulations are produced using the QSTEM software package [63]. Simulation conditions are chosen to be consistent with experimental literature [64]. We used a high angle annular dark field (HAADF) detector (inner and outer radii of 55 and 195 mrad, respectively) with 30 mrad of convergence angle and applied voltage of 120 kV. Corresponding TEM and STEM images simulated at 80 keV are presented in Supplementary Information.

3. Results and discussion

3.1. Interaction between I and CNT

We first investigate the interaction between polyiodides and CNTs, by calculating the total energy of a linear iodine chain placed inside a 18 Å diameter (23,0) nanotube. To achieve the same translational periodicities of both structures, a supercell spanning

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