Polythiophene encapsulated inside (13, 0) CNT: A nano-hybrid system

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We present a first-principles calculation on the electronic and optical properties of a hybrid nanotube system consisting of a (13, 0) single-walled carbon nanotube encapsulated by polythiophene. This hybrid-system represents a complete new type of matter and is known as the peapod system. We analyze how the polythiophene changes the electronic and optical properties of the nanotube. In particular, we examine new features in the dielectric function due to the transitions between the states of the polymer and the nanotube. The electronic structure of the combined system appears to be a simple superposition of the individual constituents. The density functional theory calculations demonstrate van der Waals interaction as the bonding mechanism between the tube and the encapsulated molecule.

Keywords: electronic structure, peapod, density functional theory, polythiophene

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1. Introduction

One way to obtain tuneable nanophotonic devices is to make sturdy nanohybrids with variable emission in the visible spectral range, while keeping the features of pristine single-walled carbon nanotubes (SWCNTs). This aim is achieved by filling SWCNTs with a series of organic molecules.[1] We study a new nano-hybrid system, serving as the peapod, which is composed of a photoactive organic molecule (pea) inside the cage of a single wall carbon nanotube (pod). These nano-object systems represent a completely new type of matter. These hybrid-systems are expected to have new exciting physical and chemical properties stemming from their nanometric size, low dimensionality, and the interaction of the electronic states between the pea and pod. The vacuum space inside SWCNTs offers interesting possibilities for the inclusion, transportation, and functionalization of foreign molecules. Several molecules such as fullerenes, endohedral metallofullerenes or alkali halides have been successfully inserted into the interior of SWCNTs.[2] The presence of the encapsulated molecule in a nanotube can affect the nanotube properties in several ways, from the modification of the electronic structure to the mechanical distortions. In general, these effects have signatures that can be depicted by optical techniques such as Raman spectroscopy, high-resolution transmission electron microscopy, and photoluminescence. In contrast to unfilled nanotubes, peapods exhibit additional electronic features that are strongly dependent on the location along the nanotube. The organic molecules encapsulated in carbon nanotubes have been proposed for applications as semiconductors. They can be formed by exploiting the van der Waals interaction as a simple method to incorporate molecules into the carbon nanotubes. However, the existence of energy barriers near the open ends of carbon nanotubes can be a snag for molecules entering carbon nanotubes. The encapsulation of molecules inside carbon nanotubes not only offers the opportunity of tuning the properties of the new hybrids but also keeps the peculiar physical properties of nanotubes. Peapods can be used for opto-electronic devices since they combine the unique electronic and mechanical properties of nanotubes with the desired optical properties of encapsulated molecules.[3,4] Calculations show that the molecules inside influence the band structure of the tube only slightly.[5] The encapsulation of organic molecules inside SWCNTs has opened a new route to engineering the electronic properties of carbon nanotubes.[6] Up to now, only a few cases of encapsulating organic molecules inside SWNTs have been investigated.[7–10] Theoretical studies of the nano-hybrid structures may play a key role not only in understanding the physical properties and their nanostructure formation but also to antedate studying the possible formation of a specific hybrid structure. The nano-hybrid system investigated here exhibits exciting properties, which could fulfill many demand requirements for the design of nanomaterials and be expected to be used in future nanophotonic device applications. In this work, we have inserted polythiophene inside (13, 0) SWCNT. Our aim is to investigate the interaction between the encapsulated polythiophene and its host nanotube. Our research result offers an outlook to model electro–optical properties of weakly bonding nano-structures from the knowledge of their main components. This is clearly innovative and significant, owing to its broad implications.

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2. Computational details

The electronic structure and optical properties of the zigzag (13, 0) carbon nanotube filled with polythiophene are computed using density functional theory (DFT)[11] simulations. For the expansion into the wave function, the full-potential linearized augmented plane-wave (FPLAPW) method is used as implemented in the Wien2k code[12–14] which is an all-electron method suitable for systems with periodic boundary conditions. A supercell approach is adopted, where the repeat unit of the (13, 0) SWCNT is doubled to accommodate polythiophene (pT) inside. The periodic boundary condition is used with a tetragonal supercell of 20.18 Å × 20.18 Å × 8.525 Å, which consists of one polythiophene chain in two periodic unit-cells of (13, 0) zigzag SWCNT. A vacuum size of 10 Å in the perpendicular directions is large enough to prevent the neighboring tubes from interacting. In the first step, the geometries are considered to be relaxed when all atomic forces are smaller than 1 mRy/Å. The calculation of binding energy, E_b, reveals that (13, 0) CNT with a diameter of 10.18 Å is favorable to encapsulating polythiophene molecules. The following parameters are chosen for the self-consistency cycles in all computations. The muffin-tin radii of C, S, and H, are set to be 1.28, 1.73, and 0.77 bohr respectively. All the optical spectra are calculated by using 100 k-points in the full Brillouin zone (BZ). The unit cell is periodic in the z direction, as shown in Fig. 1.

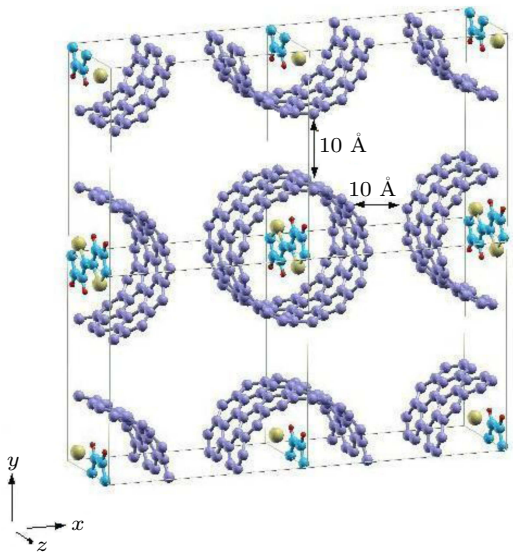


Fig. 1. (color online) (2*2*1) supercell of polythiophene encapsulated inside a (13, 0) CNT.

3. Results and discussion

3.1. Electronic structure

As shown in Fig. 1, polythiophene has embedded inside the (13, 0) SWCNT parallel to the tube axis (z direction). Figure 2 shows the electronic band structures of polythiophene and (13, 0) SWCNT. The Fermi energy level is set to be zero, which is between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). The Kohn–Sham electronic band structures of the hybrid system are displayed in Fig. 3. The electronic states stemming from polythiophene are highlighted in solid lines while dashed lines represent the bands originating from the (13, 0) SWCNT. The peapod bands arising from the tube are basically identical to those of the pristine tubes, and the interaction between pea and pod is mainly of the van der Waals type. Generally, one can conclude that the electronic structure of polythiophene peapods highlights the weak van der Waals like bonding between the two pristine systems. In fact, the electronic states stemming from different subunits of the peapod do not change the dispersion nor the band gap. The electronic structure of the combined system appears to be a simple superposition of the individual constituents, thus suggesting that there is hardly any interaction among the tube and the polythiophene. We attribute this to the comparably weak bonding between the polymer and the nanotube, which is of the van der Waals type. The density of states (DOS) of polythiophene, the (13, 0) SWCNT, and peapod systems are investigated by density functional theory calculations and are shown in Fig. 4. The DOS curve demonstrates a series of traits, van Hove singularities (vHs) near the Fermi energy, which are due to the one-dimensional nature of the electronic bands in SWNTs. The electronic band structure and DOS show that the (13, 0) carbon nanotube and peapod are semiconducting and have a direct band gap about 0.7 eV at the Γ point. The arrows in Fig. 3 indicate the possible new optical transitions between the two subsystems.

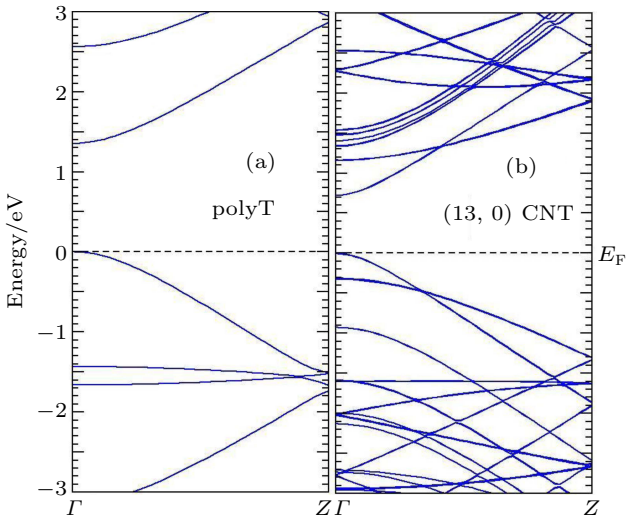


Fig. 2. (color online) Electronic band structures of (a) polythiophene and (b) (13, 0) carbon nanotube.

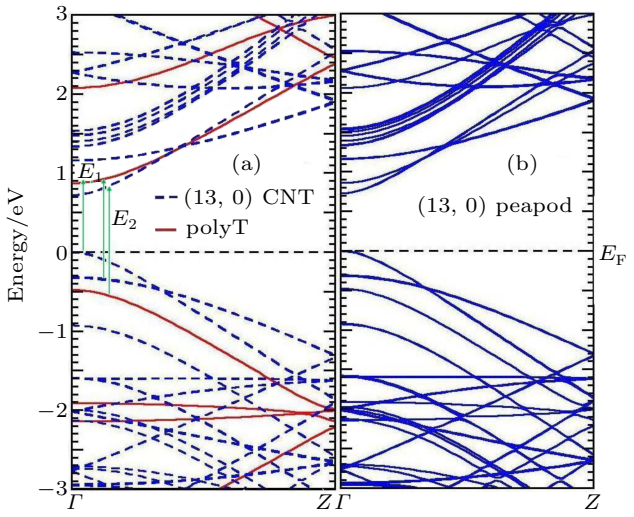


Fig. 3. (color online) Electronic band structures of a peapod consisting of a (13, 0) CNT with encapsulated polythiophene, the dashed lines in panel (a) indicate the bands originating from the tube, while the solid lines mark the levels arising from the polymer.

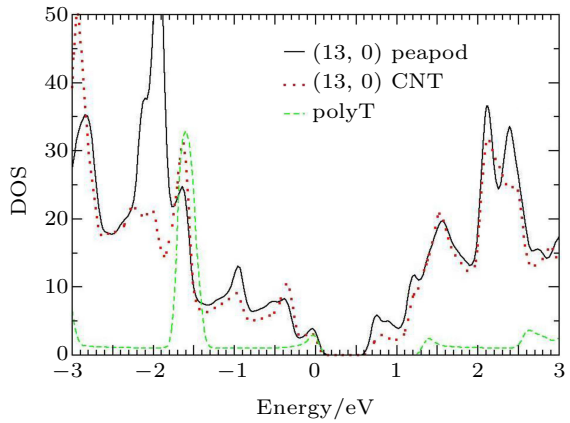


Fig. 4. (color online) Density of states of polythiophene, (13, 0) carbon nanotube, and peapod.

3.2. Optical spectra

In the limit of linear optics, in the case of non-spin polarization and within the frame of random-phase approximation, we can use the following well-known relation:[15,16]

$$\mathrm{Im}\,\varepsilon_{\alpha\beta}^{\{\mathrm{inter}\}}(\omega) = \frac{\hbar^2 e^2}{\pi m^2 \omega^2} \sum_{c,v} \int \mathrm{d}\boldsymbol{k} \langle c_k | p^\alpha | v_k \rangle \langle v_k | p^\beta | c_k \rangle \times \delta(\varepsilon_{ck} - \varepsilon_{vk} - \omega). \quad (1)$$

From the imaginary part of the dielectric tensor component, the corresponding real part is obtained by the Kramers–Kronig transformation as follows:

$$\mathrm{Re}\,\varepsilon_{\alpha\beta}(\omega) = \delta_{\alpha\beta} + \frac{2}{\pi} P \int_0^\infty \frac{\omega' \mathrm{Im}\,\varepsilon_{\alpha\beta}(\omega')}{\omega'^2 - \omega^2} \mathrm{d}\omega'. \quad (2)$$

The real and imaginary parts of the dielectric function of polythiophene, (13, 0) carbon nanotube and peapod for both polarizations, the electric field polarized in the direction parallel and perpendicular to the nanotube axis, are shown in Figs. 5 and 6 respectively. The difference curve in Fig. 6(a) denotes the difference in curve between the peapod and the sum of the isolated tube and the polythiophene. This curve shows the new optical transitions between pea and pod and we see more new features in the dielectric function when the electric field is aligned along the tube axis than when it is aligned in the direction perpendicular to the tube axis. We summarize the obtained optical constants and the electronic band gaps in Table 1. According to Figs. 5 and 6 and Table 1, it is clear that the optical spectra of the carbon nanotube significantly affect the parallel polarization by encapsulating the polythiophene, while for the perpendicular polarization, we do not see any significant change in the optical spectra of the peapod and the isolated tube. For the electric-field vector polarized in the direction parallel to the nanotube axis, the absorptive part of the optical dielectric function in the low-energy region for polythiophene incapsulated in the (13, 0) CNT is displayed in Fig. 7. In this figure, the peak positions of the difference curve are more visible. The first and second peak indicated by E_1 and E_2 at 0.8 eV and 1.3 eV, show the new optical transitions between the polytiophene and the (13, 0) CNT from HOMO to LUMO + 1 and HOMO − 1 to LUMO + 1, HOMO − 2 to LUMO respectively. We also indicate these new optical transitions in the band structure in Fig. 3 with arrows.

Table 1. Calculated optical constants and band gaps (in eV) of polythiophene, the (13, 0) carbon nanotube, and peapod for both polarizations parallel (z) and perpendicular (x) to the tube axis.

Nanotube	Parallel optical gap $E_{11}z$/eV	Perpendicular optical gap $E_{11}x$/eV	Dielectric constant ε_z	Dielectric constant ε_x	Electronic band gap E_g/eV
polyT	1.4	6.6	2	1.11	1.35
(13 ,0) CNT	0.76	1.35	10.4	4.8	0.72
(13, 0) peapod	0.76	1.35	12	4.87	0.71

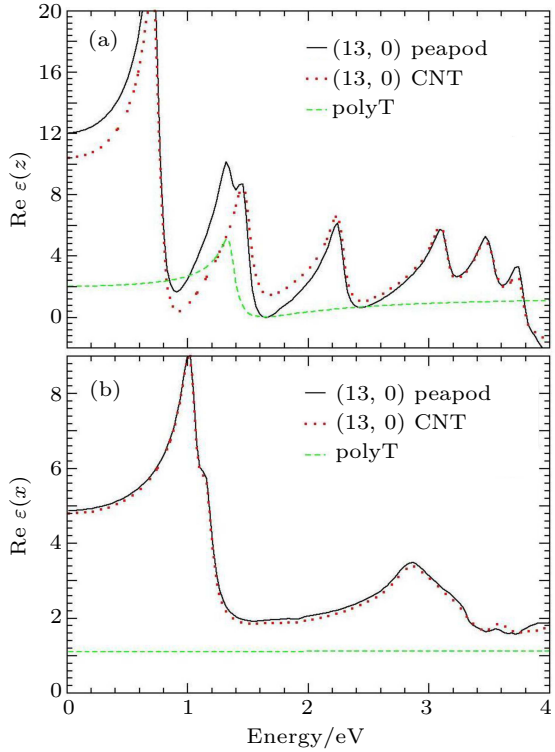


Fig. 5. (color online) Real parts of the dielectric function of polythiophene, the (13, 0) carbon nanotube, and peapod for polarizations (a) parallel and (b) perpendicular to the tube axis.

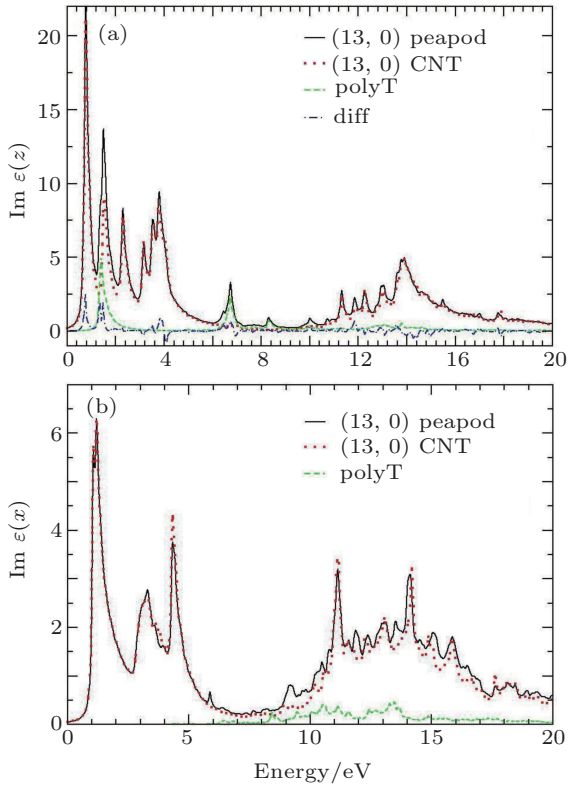


Fig. 6. (color online) Imaginary parts of the dielectric function of polythiophene, the (13, 0) carbon nanotube and peapod for polarizations (a) parallel and (b) perpendicular to the tube axis.

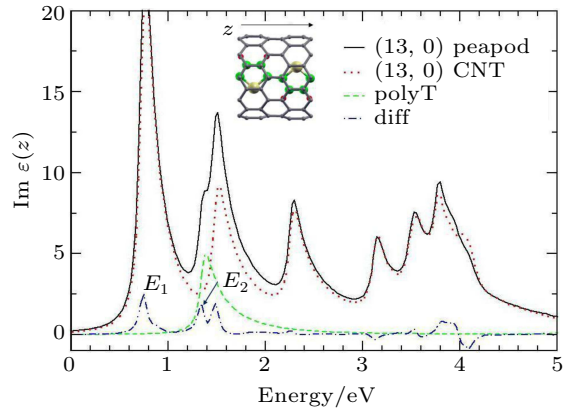


Fig. 7. Imaginary parts of the dielectric function of polythiophene, the (13, 0) carbon nanotube, and peapod for parallel polarization in the visible region.

4. Conclusions

In this paper, we presented a first-principles study of the electronic structure and optical properties of a hybrid nanotube system consisting of a (13, 0) SWCNT encapsulated polythiophene. The calculations show van der Waals interaction between the polythiophene and the nanotube. It is revealed that the electronic levels of the combined system can be understood in terms of its constituent' properties. We find new features in the dielectric function due to the transitions between the states of the polymer and the nanotube. Besides the optical transitions arising from the pristine systems, there are additional low-intensity features in the optical spectra, indicating interaction between pea and pod in the excited state. It is revealed that the optical spectra of the carbon nanotube significantly affect the parallel polarization by encapsulation polythiophene.

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