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Theoretical Characterization of Chiral Carbon Nanotube Encapsulating Ellipsoidal C_{70}

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The molecular orientation of ellipsoidal C_{70} in carbon nanotubes is carefully studied by first principles calculations. Using (14, 7) single-wall carbon nanotube (SWCNT) as a prototype material, we explored that the weak chemical interaction between SWCNT and C_{70} was the crucial factor to determine the molecular orientation. However, the small energy difference makes the distinguishment of two possible molecular orientations difficult. By simulating scanning tunneling microscope images and optical properties, we found that local electronic states sensitively depended on the molecular orientation of ellipsoidal C_{70} , which provided a practical way of using scanning tunneling microscope to recognize the molecular orientation of ellipsoidal C_{70} .

Key words: Electronic structure, Chiral carbon nanotube, Density functional theory

I. INTRODUCTION

Discoveries of fullerenes [1] and carbon nanotubes [2] have triggered great research interest on these materials. Due to their amazing physical and chemical properties, single-walled carbon nanotubes (SWCNTs) and fullerenes have been broadly studied [3–11]. To control the electronic structures for building blocks in future nanoelectronics, doping fullerenes into SWCNTs has become one basic approach in this field. For example, transmission electron microscopy (TEM) studies have well explored that C_{60} , C_{70} , and C_{80} could be encapsulated in SWCNTs, and formed one-dimensional chains in nanotubes [12–16], which is called as nanopeapods.

Theoretically, many studies have been performed to investigate the stability of nano-peapods [17-24]. By comparing the total energy, the smallest radius of the nanotube which is capable of encapsulating C₆₀ is predicted around 6.4 Å [21, 22, 24]. Different from C₆₀, C₇₀ has "rugby ball" shape, which makes the encapsulating much more complex. Due to the ellipsoidal shape, not only the internal diameter of the nanotube but also the orientation of C₇₀ is important for the encapsulating process [18-21, 23]. Typically, there are two orientations of C₇₀ in SWCNTs, in a standing arrangement the long axis of C₇₀ is perpendicular to the chain direction, whereas in a lying arrangement the axis is parallel to the chain direction. Using photoluminescence (PL) method, Okubo *et al.* have found that encapsulated C_{70} has two different PL peaks, indicating C_{70} may switch from one arrangement to another one around the critical radius of 14.1 Å [18]. However, it is difficult to resolve the orientations of C_{70} in single SWCNT, because the PL peaks are sensitively dependent on the surrounding environments. Thus, it is interesting to study what determines the stability of C_{70} in SWCNTs, and how to distinguish the orientations of C_{70} in single SWCNT.

In this work, using first principles calculations based on density functional method, we study the aforementioned issues by taking (14, 7) chiral carbon nanotube as a prototype material. Through careful studying on the arrangement of C_{70} molecule in carbon nanotube, we found the chemical interaction was the main factor. Besides, we also found that the small energy difference and similar optical properties may make the experimental distinguishment difficult. By simulating scanning tunneling microscope (STM) images, we found that electronic states sensitively depended on the molecular orientation of ellipsoidal C_{70} , which provided a practical way to recognize the molecular orientation of ellipsoidal C_{70} .

II. CALCULATION METHOD

The calculations were performed using DFT in the local-density approximations (LDA) and the projectoraugmented-wave method with a plane-wave basis as implemented in the Vienna *ab initio* simulation package (VASP) code [25]. For the geometry optimization, a plane-wave basis set was defined by a cutoff of 400 eV. We adopt a supercell model in which a peapod is placed

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FIG. 1 Optimized geometric structures of (a) lying $C_{70}@(14, 7)$ and (b) standing $C_{70}@(14, 7)$. The left and right are side-views and top-views, respectively.

with its nanotube wall being separated by over 6.5 Å from another wall of an adjacent peapod [22, 23]. A lattice parameter c along the tube direction is 11.27 Å for all of the peapods studied here. Integration over one-dimensional Brillouin zone is carried out using two k points. The global break condition for the electronic self consistent loop is 10^{-5} eV. The break condition for the ionic relaxation loop is all forces, smaller than 10^{-2} eV/Å. In spite of not explicitly accounting for the long-range van der Waals interaction, DFT calculations have consistently produced correct results for kinds of nanopeapods [17, 20-24]. Our calculations are in good agreement with experimental and other theoretical results [18-21, 23]. We also tested the calcualtion with DFT-D2 method, and found their results are similar.

III. RESULTS AND DISCUSSION

A. Geometric structures of C70 peapods

As we know, the diameter of (14, 7) nanotube is about 14.50 Å. The long axis and short axis of C_{70} are approximately 7.92 and 7.12 Å, respectively. Figure 1 shows the optimized geometric structures of C_{70} encapsulated in (14, 7) nanotube. From the optimized structures, it seems there is no direct bonding between C_{70} and (14, 7) nanotube, because of the large atomic distances. To compare the stability of different arrangements of C_{70} encapsulated in (14, 7) nanotube, the reaction energy ΔE is calculated, which is defined as

 $E(C_{70}) + E(nanotube) \rightarrow E(C_{70}@nanotube) + \Delta E$ (1)

According to the reaction energies, it is thus concluded that the processes of C_{70} encapsulated in (14, 7) nanotube are exothermic, and the molecule adopts



FIG. 2 The calculated energy band structures of (a) (14, 7) carbon nanotube, (b) lying $C_{70}@(14, 7)$, and (c) standing $C_{70}@(14, 7)$. Arrows indicate the LU states.

a standing orientation, with energy lower than lying one by 0.21 eV. Combining with previous theoretical researches on armchair and zigzag carbon nanotubes [20, 21, 23], we come to the conclusion that the diameters instead of the chiral indices of nanotubes are the important factors to determine the orientation of C_{70} molecules, which agrees with the experimental observations.

B. Electronic structures of C₇₀ peapods

To investigate the effect of doping C_{70} on the electronic structures, we plotted the band dispersions of pure (14, 7) nanotube and $C_{70}@(14, 7)$ with two orientations in Fig.2. Due to the curvature effects, (14, 7) nanotube is semiconductor with an energy gap of 0.54 eV. And in an isolated C_{70} molecule, there are the triply bunched highest occupied (HO) states and the triply bunched lowest unoccupied (LU) states [26], which are separated by 1.7 eV. For the $C_{70}@(14, 7)$, the LU states are located in the gap of the nanotube in both lying and standing arrangements as shown in Fig.2 (b) and (c). Another interesting result is that the $C_{70}@(14, 7)$ peapods become indirect bandgap semiconductor.

Although our calculations have shown that standing arrangement of C_{70} is favored, the intrinsic mechanics response for the stability is still not clear. Typically, the reaction energy for standing arrangement is about 2.958 eV, much larger than the general physical interaction. To explore how C_{70} interacts with nanotube, we plotted the partial density of states (PDOS) in Fig.3(a). Compared with lying arrangement of C_{70} , the standing one has a lower energy in the occupied states. Considering the distance between C_{70} and nanotube, we conclude that there is chemical interaction between C_{70} and nanotube.



FIG. 3 (a) The calculated projected density of states (PDOS) for lying and standing C_{70} @(14, 7), respectively. (b) and (c) are charge difference density for lying and standing C_{70} @(14, 7), respectively. Red color shows the charge accumulated regions and blue color shows the charge depleted regions.

To confirm our hypothesis, we plotted the charge difference density, which is defined as

$$\rho_{\rm diff} = \rho_{\rm pd} - (\rho_{\rm C_{70}} + \rho_{\rm cnt}) \tag{2}$$

where $\rho_{\rm pd}$ is charge density of C₇₀@(14, 7) peapods, $\rho_{\rm C_{70}}$ and $\rho_{\rm cnt}$ are the isolated charge density of C₇₀ and nanotube. As shown in Fig.3 (b) and (c), the interaction between C₇₀ and nanotube is much stronger in standing arrangement, which well explains its stability. Therefore, our results reveal that the chemical interaction is the determined factor of molecular orientation.

On the other hand, although standing arrangement is the preferred orientation of C_{70} , the relative energy difference is too small, which can easily be switched by thermal dynamics. Moreover, the plots of calculated PDOS and band structures only show similar character for lying and standing arrangements, which makes the experimental resolving difficult.

Optical property is always taken as an effective way to distinguish materials. To investigate the possibility of distinguishing the orientation of C_{70} in nanotube, we calculated the optical adsorption for two possible orientations. As shown in Fig.4, there is no significant difference in the optical adsorption threshold for two orientations. Therefore, it is difficult to distinguish these structures just by optical measurement for limited samples.



FIG. 4 Calculated imaginary dielectric functions (IDF) versus energy for lying and standing C_{70} @(14, 7).



FIG. 5 (a) The plotted valence band maximum (VBM) and conduction band minimum (CBM) of lying and standing arrangements. VBM (lying), CBM (lying), VBM (standing), and CBM (standing) are placed from the left to the right. (b), (c), (d), and (e) are the simulated STM images for VBM (lying), CBM (lying), VBM (standing), and CBM (standing), respectively.

Interestingly, we found that the local density of states around the Fermi level is totally different for lying and standing arrangements from the calculated optical adsorption. As shown in the Fig.5(a), the plotted valence band maximum (VBM) of lying and standing arrangements has similar shape, while the plots of the conduction band minimum (CBM) have totally different characters. In this sense, the local density of states may be used to help us to resolve the orientations of doped C₇₀. As we know, scanning tunneling microscope (STM) images sensitively depended on the local density of states. It is interesting to explore whether the simulated STM images can provide direct information to distinguish the C₇₀ orientations.

Figure 5 (b)–(e) are the simulated STM images for lying and standing C_{70} . The occupied-states images for

both orientations are similar according to our simulations, which are consistent with the calculated PDOS plots. Interestingly, the simulated patterns of empty states are significantly different. For lying arrangement, C_{70} appears as two lobes. While for standing one, the simulated patterns distribute along the whole nanotube. Therefore, our results show that STM images are the effective way to resolve the molecular orientations of C_{70} in nanotube. Besides, it can also be used to explore similar questions, such as doping other molecules into nanotubes.

IV. CONCLUSION

In summary, using first principles calculations, we study the stability and orientations of C_{70} molecular in (14, 7) chiral carbon nanotube. It was found the chemical interaction is the main factor to determine the molecular orientations in nanotube. Besides, we also found that the small energy difference and similar optical properties may make the experimental distinguishment difficult. By simulating STM images, we found that electronic states sensitively depend on the molecular orientation of ellipsoidal C_{70} , which provides a practical way to recognize the molecular orientation of ellipsoidal C_{70} .

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