First-principles study of a hybrid carbon material: Imperfect fullerenes covalently bonded to defective single-walled carbon nanotubes

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The electronic properties of a novel hybrid carbon material, the NanoBud, is investigated by using a first-principles method. Our results suggest that NanoBuds of zigzag carbon nanotubes are semiconductors, no matter whether the zigzag nanotubes are metallic or semiconducting. Local states appear in the band gap of the NanoBuds near the Fermi level. NanoBuds of armchair carbon nanotubes remain metallic. These properties may have great potential applications in future nanodevice design.

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I. INTRODUCTION

Carbon nanotubes[1] have novel electronic properties due to their quasi-one-dimensional structures. The tubes can be either metals or semiconductors depending on their diameters and chiral vectors.[2–4] Both fullerenes and single-walled carbon nanotubes (SWCNTs) exhibit many advantageous properties and are considered to have great potential applications in nanotechnology and nanoscale engineering.[5–12] Carbon nanotube junctions have also attracted considerable attention since junctions have become a critical issue in nanostructures and are considered to be promising candidates as building blocks for nanoelectronic and microelectromechanic devices.[13–15] Various stable geometries, such as cross, Y, and T shapes, have been fabricated in experiments[16] and investigated by theoretical studies.[17–19] Recently, a novel hybrid carbon material that combines fullerenes and SWCNTs into a single structure in which the fullerenes are covalently bonded to the outer surface of the SWCNTs has been discovered, and called a NanoBud.[20] The field-emission characteristics of these NanoBuds suggest that they may possess advantageous properties compared with SWCNTs or fullerenes alone, or in their nonbonded configurations.[20] However, a detailed study of the electronic structure of carbon NanoBuds is still lacking. In this paper, we investigate the electronic properties of NanoBuds by using a first-principles method. Our results suggest that the band structures of NanoBuds are quite different from those of the corresponding SWCNTs, which may have unique applications in future nanodevice design, e.g., for light-emission devices.

II. MODEL SYSTEMS AND COMPUTATIONAL METHODS

In the present study, the NanoBud geometry involves imperfect fullerenes, covalently bonded to defective SWCNTs. Such bonded structures, reminiscent of buds on a branch, with a neck connecting the fullerene and the SWCNT, are depicted in Fig. 1, and can be recognized in experiments.[20] The highest fullerene density achieved in experiments was more than one fullerene per nanometer, with the fullerenes arranged in a continuous stream along the SWCNT.[20] We chose the defective zigzag (12,0) SWCNT as the representative SWCNT, covalently bonded to an imperfect C_{60} fullerene, and investigated NanoBuds with different bud heights (Fig. 1). The necks connecting the fullerenes and the SWCNTs are simulated by zero, one, and two periods of the (6,0) SWCNT, with the bud heights being about 7, 11, and 15 Å (denoted by Bud 1, Bud 2 and Bud 3), respectively. [The (6,0) SWCNT is chosen as the neck because when the (12,0) SWCNT and C_{60} both have a defect that lacks a hexagon of carbon atoms, the (6,0) SWCNT will match the defects well.] Along the axis of the (12,0) SWCNT, the unit cell contains four periods of the zigzag (12,0) SWCNT and the distance between the nearest fullerenes is about 17 Å. We also investigated the influence of different fullerene densities on the electronic properties of carbon NanoBuds. Bud 2 was selected as the representative system and the distance between the nearest fullerenes was increased to 26 Å, corresponding to six periods of the zigzag (12,0) SWCNT. For comparison, the electronic properties of NanoBuds of zigzag (14,0) and armchair (8,8) SWCNTs have also been studied. In all simulations, the sizes of our unit cells are about 23×38 Å^2 in the plane perpendicular to the axis of the (12,0), (14,0), or (8,8) SWCNT, with the thickness of the vacuum layer included in each model being larger than 10 Å. Our unit cells contain about 240–360 carbon atoms.

The structural optimization and the corresponding total energy calculations are performed by using the Vienna *ab initio* simulation package (VASP),[21–23] which is based on den-

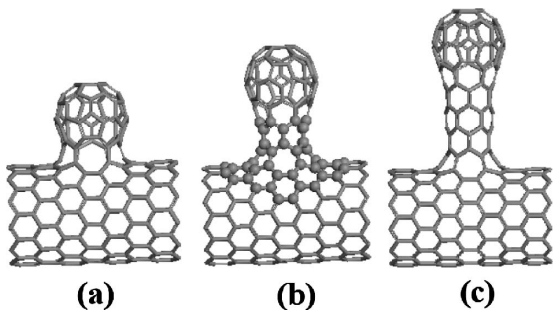

FIG. 1. Optimized geometries of NanoBuds of zigzag (12,0) SWCNTs with different bud heights: (a) Bud 1, (b) Bud 2, and (c) Bud 3. Contact atoms of Bud 2 that make major contributions to the local states in the band gap above the Fermi level are denoted by gray balls.

TABLE I. The calculated deformation energy E_d of different systems. In the table, (12,0)Bud2–26 Å and (8,8)Bud2–26 Å refer to Buds 2 of (12,0) and (8,8) SWCNTs with the distance between the nearest fullerenes being about 26 Å, respectively. For other systems the distance between the nearest fullerenes is about 17 Å.

System	E_d (eV)
(12,0)Bud1	7.93
(12,0)Bud2	−3.79
(12,0)Bud3	−11.91
(12,0)Bud2–26 Å	−3.84
(14,0)Bud2	−3.74
(8,8)Bud1	8.18
(8,8)Bud2	−3.64
(8,8)Bud3	−11.86
(8,8)Bud2–26 Å	−3.70

sity functional theory (DFT).[24,25] The electron-ion interaction is described by an ultrasoft pseudopotential[26] and the wave functions are expanded in a plane wave basis set with an energy cutoff of 400 eV. The Perdew-Wang 1991 exchange-correlation functional[27] within the generalized gradient approximation (GGA) is used. The positions of all atoms are relaxed until all the force components are smaller than 0.02 eV/Å. We use 11 k points in the direction parallel to the tube axis for the Brillouin zone integration.

III. RESULTS AND DISCUSSION

The optimized geometries of NanoBuds of zigzag (12,0) SWCNTs with different bud heights (Bud 1, Bud 2, and Bud 3) are shown in Fig. 1. The heights of the buds are calculated to be about 7.2, 11.3, and 15.5 Å, respectively, compared with the diameter 7 Å of C_{60}. The C-C bond length alternates between 1.37 and 1.45 Å.

We calculated the deformation energy of the NanoBud, which is defined as

$$E_d = E_{\text{total}} - N_{\text{trunk}}\bar{E}_{\text{CNT}} - N_{\text{neck}}\bar{E}_{\text{ncnt}} - N_{\text{head}}\bar{E}_{C_{60}},$$

where E_{total} is the total binding energy of the NanoBud system, N_{trunk} is the number of atoms of the defective SWCNT without a fullerene bud, $\bar{E}_{\text{CNT}}$ is the average binding energy of the corresponding free-standing (12,0), (14,0), or (8,8) SWCNT (total binding energy of the free-standing SWCNT divided by the number of atoms), N_{neck} is the number of atoms of the (6,0) SWCNT neck, $\bar{E}_{\text{ncnt}}$ is the average binding energy of the corresponding free-standing (6,0) SWCNT, N_{head} is the number of atoms of the imperfect C_{60} fullerene, and $\bar{E}_{C_{60}}$ is the average binding energy of the perfect C_{60} fullerene. From the results listed in Table I, we can see that the deformation energy of Bud 1 is positive while those of Bud 2 and Bud 3 are negative. This indicates that Bud 1 is not as stable as Bud 2 and Bud 3. The deformation energy of Bud 3 is lower than that of Bud 2, which means that, when the neck length increases, the NanoBuds become more stable. For NanoBuds with different fullerene densities [Bud 2 of (12,0) or (8,8) SWCNTs with the distance between the nearest fullerenes being about 17 and 26 Å], it was found that, as the fullerene density decreases, the deformation energy changes only slightly. On the other hand, Buds 2 with (12,0), (8,8), and (14,0) SWCNTs have similar deformation energies and so have Bud 1 and Bud 3. These results suggest that the fullerene density, the chirality, and the diameter of the SWCNTs have only a small effect on the stability of the NanoBuds.

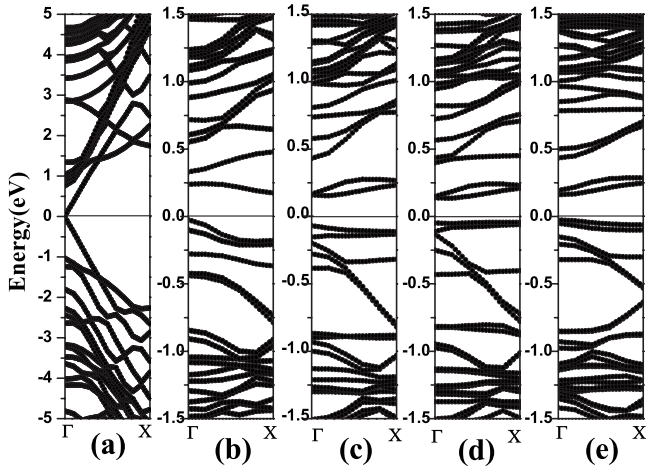

FIG. 2. Band structures of pure (12,0) SWCNT (a) and NanoBuds of (12,0) SWCNT with different bud heights, (b) Bud 1, (c) Bud 2, and (d) Bud 3. The distance between the nearest fullerenes is about 17 Å. (e) Band structure of Bud 2 of (12,0) SWCNTs with the distance between the nearest fullerenes being about 26 Å. The Fermi level is set to zero.

Figures 2(a)–2(d) display the calculated band structures of free-standing (12,0) SWCNTs and NanoBuds of (12,0) SWCNTs with different bud heights (Bud 1, Bud 2, and Bud 3). The distance between the nearest fullerenes is about 17 Å for these NanoBuds. The attachment of fullerene to the metallic (12,0) SWCNT leads to a band gap opening and changes the conductive properties of the nanotube. The NanoBuds become semiconductors. It is interesting to note that local states appear in the band gap near the Fermi level. The band structure of Bud 2, especially the local states in the band gap, is a little different from that of Bud 1, but similar to that of Bud 3. This may also be due to the structural difference of the contact between the bud and the defective (12,0) SWCNT: both Bud 2 and Bud 3 have a (6,0) SWCNT neck while Bud 1 does not. The change of the band structure may not be evident when the neck length is increased.

We also investigated the influence of fullerene density on the band structure of the NanoBud. Figure 2(e) displays the calculated band structure of Bud 2 with the distance between the nearest fullerenes being about 26 Å. As the distance between the fullerenes increases, a period of the NanoBud system contains more atoms and, in the k space, the size of the first Brillouin zone becomes much smaller. There are more local states between 0 and 1 eV in Fig. 2(e) than in Fig. 2(c), which suggests that, as the fullerene density decreases, more isolated local states may appear near the Fermi level.

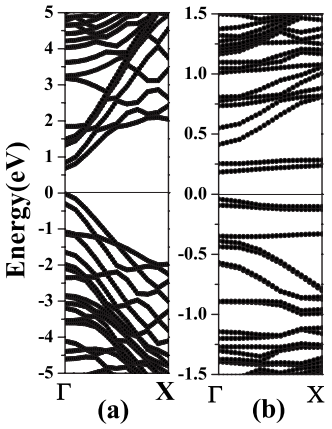

FIG. 3. Band structures of (a) pure (14,0) SWCNT and (b) Bud 2 of (14,0) SWCNT with the distance between the nearest fullerenes being about 17 Å. The Fermi level is set to zero.

The band structure of Bud 2 of the semiconducting zigzag (14,0) SWCNT is also calculated for comparison (Fig. 3). The distance between the nearest fullerenes is about 17 Å. As seen from Fig. 3(b), the NanoBud remains semiconducting and local states appear in the band gap near the Fermi level. These results suggest that NanoBuds of zigzag SWCNTs are semiconductors, no matter whether the zigzag SWCNTs are metallic or semiconducting.

The site-projected wave function of each band was also calculated by projecting the wave functions onto spherical harmonics that are nonzero within spheres of a radius 0.863 Å for C atoms around each ion. For NanoBuds of (12,0) and (14,0) zigzag SWCNTs, we analyzed the site-projected wave function character of the local states in the band gap above the Fermi level (between 0 and 0.5 eV) and found that the states are mainly contributed by the atoms of the contact between the bud and the defective zigzag SWCNT. [For example, contact atoms of Bud 2 are denoted by gray balls in Fig. 1(b).] The atoms of the imperfect fullerene near the contact also have some contribution, but the atoms away from the contact have very little contribution.

Figure 4 displays the band structures of NanoBuds of metallic armchair (8,8) SWCNTs, which are quite different from those of NanoBuds of zigzag SWCNTs. In this case, the NanoBuds remain metallic and no obvious band gap at the Fermi level is found. We also investigated the influence of bud height and fullerene density on the band structures of NanoBuds of (8,8) SWCNTs, and found that the NanoBuds remain metallic [Figs. 4(b)–4(e)].

The work function of the system was also calculated, defined as $\phi - E_F$, where ϕ is the vacuum level and E_F is the Fermi level of the system.[28,29] The vacuum level ϕ is determined from the average potential at the center of the vacuum region where it approaches a constant. For all the NanoBuds of (12,0), (14,0), and (8,8) SWCNTs, the work function is about 0.2 eV higher than that of the corresponding free-standing SWCNT, which is disadvantageous for field emission. The experimental fact that the NanoBuds possess

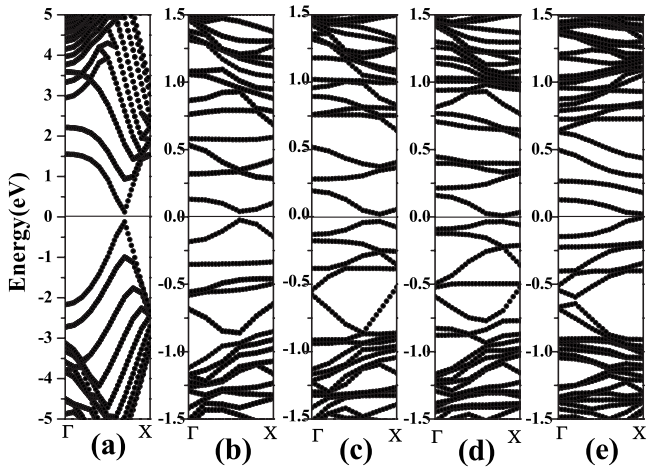

FIG. 4. Band structures of pure (8,8) SWCNT (a) and NanoBuds of (8,8) SWCNT with different bud heights, (b) Bud 1, (c) Bud 2, and (d) Bud 3. The distance between the nearest fullerenes is about 17 Å. (e) Band structure of Bud 2 of (8,8) SWCNTs with the distance between the nearest fullerenes being about 26 Å. The Fermi level is set to zero.

advantageous field-emission properties compared with SWCNTs may be due to the unique geometry of the NanoBuds, with a large number of highly curved fullerene surfaces acting as emission sites.[20,30]

IV. CONCLUSIONS

In summary, we have studied the electronic properties of a novel hybrid carbon material discovered recently in experiments, the carbon NanoBud, which combines imperfect fullerenes and defective SWCNTs into a single structure by forming covalent bonds on the outer surface of the SWCNTs. Our results suggest that the attachment of fullerenes to zigzag SWCNTs leads to band gap opening and the NanoBuds become semiconductors, no matter whether the zigzag SWCNTs are metallic or semiconducting. It is interesting to note that local states appear in the band gap of the NanoBuds near the Fermi level. However, the NanoBuds of armchair SWCNTs remain metallic and no obvious band gap at the Fermi level is found. The influence of bud height and fullerene density on the properties of NanoBuds, and the field-emission properties of NanoBuds, have also been briefly discussed. These properties may have great potential applications in future nanodevice design, e.g., in light-emission devices.

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