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Electronic and optical properties of bundled single-walled carbon nanotubes investigated by the first-principles method

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ABSTRACT

We performed first-principles calculations to investigate the energetic, electronic and optical properties of bundled armchair and zigzag carbon nanotubes (CNTs). The nanotubes are assumed to be aligned in a hexagonal closed-packed array in the bundle. The total energy and electronic band structure show stronger dependence on the orientation of the tube for the (n, n) and $(n, 0)$ bundles if $n = 3q(q = \text{integer})$ than if $n \neq 3q$. The optical properties are also sensitive to the orientation of the tubes. For the (n, n) tubes, the calculated imaginary part of the dielectric functions of the tube bundles are similar to that of the isolated tube, except for the appearance of broadened peaks and an extra peak at low energies due to the avoided crossing of the π and π^* bands. This extra peak is absent in the (n, n) tubes with $n = 3q$ in special orientations where the symmetry of the tube is compatible with that of the hexagonal lattice. For the $(n, 0)$ tubes, the imaginary part of the dielectric functions of tubes with larger radius are very similar to that of the isolated tube, while for the (5,0) and (6,0) tubes with smaller radii, coupling causes gaps near the Fermi level, which contribute to an extra peak at low energies.

1. Introduction

Carbon nanotubes (CNTs) [1,2] are promising candidates for the next generation of nanometer-sized electronic device components [3–5]. Due to their special structures, the electronic and optical properties of single-walled CNTs have gained interest from many research groups. Some experimental and theoretical studies on the optical properties of isolated CNTs have been conducted, showing rich characteristic peaks in the absorption spectra and interband transitions that can be traced to one-dimensional (1D) Van Hove singularities (VHSs). Moreover, the positions of such prominent absorption features can be related to the radius and chiral angle of the CNTs. If the electromagnetic field of the external light source is polarized along the tube axis, only vertical transitions are allowed from the π to the π^* subbands with the same band indices. Polarized optical absorption spectra of single-walled 4 Å CNTs fabricated inside inert AlPO4-5 zeolites has been reported [6]. The spectra for light polarized along the tube axis agreed well with the local density functional calculation [7,8]. For the case of perpendicular polarization the measured absorption is small and flat. The spectra can be described correctly only when the crystal local-field effects are included [9].

Guo et al. [10] found that diameter and chirality play important roles in determining the electronic properties and optical characteristics of CNTs. They found that the absorptive part ε_2 of the optical dielectric function for small nanotubes in the low-energy region exhibits a few distinct peaks if the electric-field vector is polarized parallel to the nanotube axis. For larger nanotubes, the characteristics of ε_2 along both electric-field polarization directions are similar to those of graphite with electric-field polarization parallel to the graphene layers.

Electronic and optical properties may change significantly when CNTs are bundled together. Kozinsky and Marzri [11] studied the static dielectric properties of isolated single-walled and multiwall CNTs and nanotube bundles by density-functional perturbation theory. For SWCNTs the longitudinal polarizability is proportional to the inverse square of the band gap and the transverse polarizability is proportional to the square of the effective radius. For the case of bundled nanotubes, the longitudinal polarizabilities are the same as those of isolated nanotubes and the transverse polarizabilities depend strongly on

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the tube–tube distance of the bundles. Using Rayleigh scattering spectroscopy, Wang et al. [12] investigated the optical transition of given individual CNTs in their isolated and bundled form. They concluded that the bundling effects produce a red shift of optical transitions due to the mutual dielectric screening of CNTS in a bundle. Delaney [13] used the empirical pseudopotential method to study effect of the tube-tube interaction on the electronic structure in aligned and misaligned bundled (10, 10) CNTs. They observed a pseudogap in the density of states of width 0.1 eV at the Fermi level due to symmetry breaking in the bundles. This observation was confirmed by scanning tunneling experiment [14] and other theoretical study [15]. The magnitude of the pseudogap depends inversely on the square root of the tube radius [14]. A pseudogap significantly alters conductivity and other transport properties of bundles relative to isolated tubes. Our previous work on bundles revealed that the electronic structure of armchair-type bundles, especially near the Fermi level, changes significantly when tubes are bundled to ropes [16]. This is ascribed to intertube interaction, which gives rise to an additional band dispersion perpendicular to the tube axis and to the possibility of opening up a pseudogap at the Fermi level. Lin et al. [17] studied, in tight-binding method, the absorption spectra of bundles of CNTs. The bundles are made up of different CNTs. They concluded that the optical excitations of a nanotube bundle is the superposition of those of different CNTs. Using a localized pseudoatomic orbitals basis set, Reich et al. [18] investigated the band structure of (6, 6), (10, 0), and (8, 4) bundles. They found that the (10, 0) bundle becomes metallic due to dispersion perpendicular to the tube axis. Agrawal et al. studied the effect of the orientation of the tube on the electronic and optical properties of (3, 3) bundles [19]. They observed a strong peak below 1 eV for different orientations. Pressure and polymerization effects on selected nanotube bundles have been studied by Okada et al. [20]. They observed that the widest of the pseudogap depends strongly on the intertube orientation.

In this work, we systematically investigate the energetic, electronic, and optical properties of armchair and zigzag carbon nanotube bundles with different orientations using density functional calculations. We calculate the total energy and band structure for a series of armchair [(3, 3), (4, 4), (5, 5), (6, 6)] and zigzag [(5, 0), (6, 0), (9, 0), (10, 0)] bundles with various tube orientations with respect to the lattice axes. The total energy and band structure show stronger dependence on the orientation of the tube for the (n, n) and $(n, 0)$ bundles if $n = 3q$ (q = integer) than if $n \neq 3q$. The imaginary part of the dielectric functions (ε_2) of these bundles are investigated. For the (n, n) tubes, the calculated ε_2 functions show an extra peak at low energies due to the avoided crossing of the π and π^* bands. This extra peak is absent in the (n, n) tubes with $n = 3q$ in special orientations where the symmetry of the tube is compatible with that of the hexagonal lattice. For the $(n, 0)$ tubes, the ε_2 functions of tubes with larger radius are very similar to that of the isolated tube, while for the (5, 0) and (6, 0) tubes with smaller radii, coupling causes gaps near the Fermi level, which contribute to an extra peak at low energies. In order to explain the physical origin of the above phenomena, the energy dispersion along the k_z direction for different perpendicular components $k_\perp = (k_x, k_y)$ of k vectors in the irreducible Brillouin zone (IBZ) is presented. The relation between the band structure and the optical spectrum is also presented and discussed.

2. Method of calculation

Calculations were done within the framework of local density approximation (LDA) [21] using the Ceperley-Alder form of exchange–correlation functional [22] and highly accurate projected augmented wave (PAW) method [23,24] with a plane wave cutoff of 450 eV, as implemented in the *Vienna Ab-initio Simulation Package* (VASP) [25–27]. We studied bundles of armchair and zigzag carbon nanotubes in which the tubes were aligned with various fixed rotational angles. The nanotube bundles were modeled by a hexagonal periodic lattice of nanotubes with intertube distances determined by total energy optimization. Such a model is a good representation of bundles with large cross-sections, in which the surface effect is small. Bundles with different tube orientations were generated by rotating each nanotube in different angles with respect to the axis of the unit cell. Schematic illustrations of the 0° and 20° rotations for the (3, 3) bundles and of the 0° and 15° rotations for the (6, 0) bundles are shown in Fig. 1. The length of the unit cell along the tube axis was determined by minimizing the total energy of the system in the bundle with 0° orientation at the optimized tube-to-tube distance. All atoms were fully relaxed until the maximum magnitude of the force was less than 0.02 eV/Å. The k-point sampling was $1 \times 1 \times 60$ for isolated nanotubes and $12 \times 12 \times 60$ for periodic nanotube arrays.

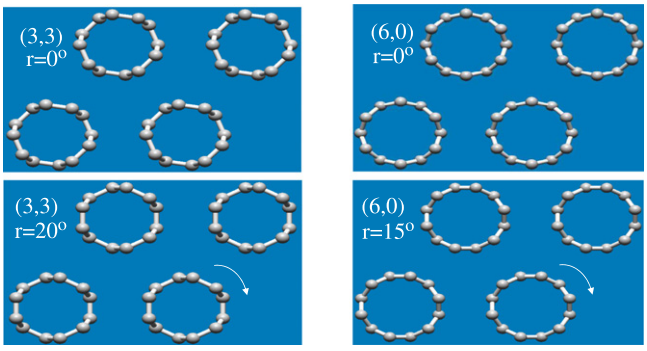

Fig. 1. (Color online) Schematic drawings that show the arrangement of the nanotubes in (a) (3, 3) bundle with rotation 0°, (b) (3, 3) bundle with rotation 20°, (c) (6, 0) bundle with rotation 0°, and (d) (6, 0) bundle with rotation 15°.

Within the framework of random-phase approximation and neglecting local-field corrections, the imaginary part of the dielectric function with the electric field polarized in the α-direction is given as a function of the photon energy, $\hbar\omega$ [28]:

$$\varepsilon_2(\omega) = \frac{4\pi^2}{\Omega\omega^2} \sum_{i\in VB, j\in CB} \sum_k w_k P_{ij}^{\alpha}(k)\delta(\varepsilon_{kj} - \varepsilon_{ki} - \omega), \tag{1}$$

where Ω is the volume of the unit cell, and VB and CB denote the conduction and valence band, respectively. The matrix elements $p_{ij}^{\alpha}(\vec{k}) = \left|\langle i, \vec{k}|\hat{p}_\alpha|j, \vec{k}\rangle\right|^2$ were obtained from the self-consistent band structures within the PAW formalism [29], $w_k$is the weighting factor for the kth point, and $\hat{p}_\alpha$ is the α component of the momentum operator. The initial and final states, $|i, \vec{k}\rangle$ and $|j, \vec{k}\rangle$, belong to the valence and conduction bands, respectively. The real part of the dielectric function $\varepsilon_1(\omega)$ can be obtained by a Kramers–Kronig transformation.

3. Results and discussion

We first consider the case of bundled armchair CNTs. The total energy per unit cell for the (3, 3), (4, 4), (5, 5) and (6, 6) bundles as a function of the tube-to-tube distance and rotational angle is shown in Fig. 2. The results show that there is a qualitative difference between the (n, n) tubes with $n = 3q$ (q is an integer) and other tubes. The total energy for the (n, n) bundles with $n = 3q$ exhibits conspicuous dependence on the orientation of the tubes. The spacing between neighboring tubes in a bundle affects coupling, which in turn controls the dependence of the total energy on the orientation of the tubes in a quantitative manner. When the wall-to-wall distance is larger than 5 Å, the dependence of the