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Low-energy electronic structures of nanotube–graphene hybrid carbon systems

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ABSTRACT

Electronic structures of nanotube–graphene hybrid carbon systems are calculated by the tight-binding model. The Lennard-Jones potential is used to determine the optimal geometry between nanotubes and a monolayer graphene. The periodic alignment of nanotubes on graphene results in quasi-one-dimensional physical phenomena. The low-frequency energy dispersions are significantly influenced by the interlayer interactions, such as the removal of subband degeneracy, creation of extra band-edge states, and modulation of energy gaps. The composite systems could be either metals or semiconductors according to the alignment and geometry of nanotubes.

Carbon-based nanosystems have been the technologically attractive materials in recent years ascribing to their various kinds of dimensionality [1–4] and extraordinary physical properties. Single graphene sheet, a monolayer of carbon atoms packed into a dense honeycomb crystal structure, could be regarded as an ideal two-dimensional nanosystem which behaves as the zero-gap semiconductor. Depending on how a monolayer graphene is rolled into seamless cylinder, the one-dimensional nanotubes could be metallic or semiconducting [5,6]. To measure their electronic and transport properties, nanotubes are, in general, supported by certain substrates [7,8], and some interfacial interactions would inevitably occur. Nanotubes could exhibit the acceptor- or donor-doped behavior due to the charge transfer from substrate. However, the interlayer couplings are relatively weak while the graphene sheet is regarded as substrate. In Falvo's recent experimental studies, the nanometer-scale motion of nanotubes on graphene sheets was controllable by the atomic force microscopy tips. The in-registry position between them can be determined [9–11]. The conductance measurements were also achieved to observe how the electrons go through the nanotube–graphene interface [10]. The control over the tunable electronic properties suggests the potential application of electronic nano-devices. Thus, in this work, the electronic structures of the nanotube–graphene composite systems are investigated.

From the theoretical aspect, many studies focused on how the band structures of carbon nanotubes are influenced by the substrate, such as silicon, indium arsenide, and other III–V semiconductors [12–17]. The work function difference between nanotubes and these substrates might make charge carriers transfer across the interface. Free carriers might accumulate at the interface to form the shorter and stronger chemical bonds. The Fermi level (E_F), energy dispersions, and charge distributions are significantly modified by the substrates. In the case of nanotubes deposited onto a graphene sheet, they possess the similar chemical potential. The main interactions are the weak van der Waals force [18,19]. Nevertheless, the atomic hoppings between them would substantially induce the overlap of low energy bands [20]. The changes in band-edge states, energy gap, and subband degeneracy would systematically rely on the nanotube geometry and the nanotubes alignment on graphene.

In this work, we mainly focus on the non-chiral nanotubes periodically adsorbed on a monolayer graphene. The optimal interfacial geometry are determined by the Lennard-Jones potential. The tight-binding model, containing the intralayer and interlayer atomic hoppings, is utilized for the band structure calculations. The low energy dispersions, density of states, and energy gaps are examined in detail for the different nanotube sizes, interfacial geometry, and periodic alignments. The experimental measurements of scanning tunneling spectroscopies could be useful in determining the geometric configurations of these hybrid systems [17,21–23].

The armchair (m,m) (zigzag $(m,0)$) nanotubes are periodically aligned along the zigzag (armchair) direction of graphene sheet. They possess the commensurate interfacial geometry. A partial geometry of the armchair system is illustrated in Fig. 1(a). The van der Waals interactions between the two objects are characterized

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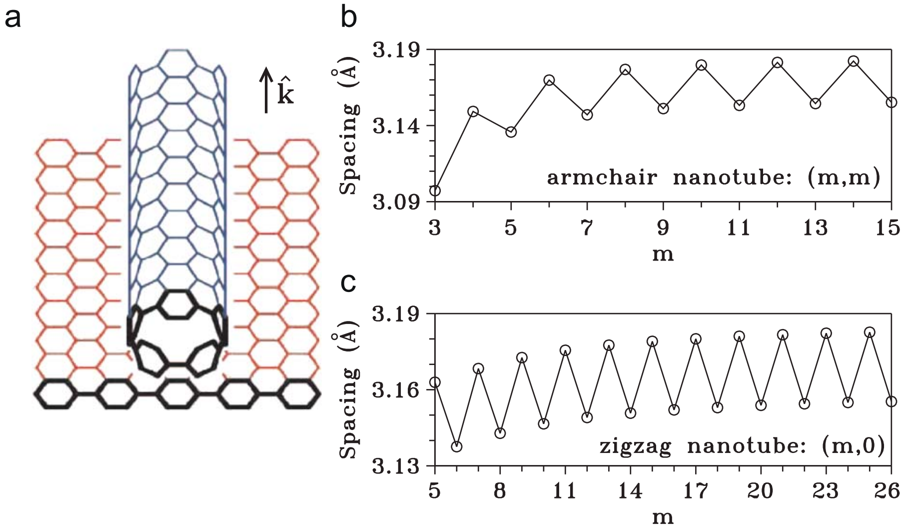

Fig. 1. (a) Geometric configuration of a (5, 5) armchair nanotube placed on a monolayer graphene with stable lattice registry. The optimal nanotube–graphene spacings as a function of nanotube size for the (b) armchair and (c) zigzag composite systems.

by the Lennard-Jones potential, $V(r)=4\varepsilon\{-(\sigma/r)^6+(\sigma/r)^{12}\}$, with parameters $\varepsilon=2.968$ meV and $\sigma=3.407$ Å [24]. The small nanotubes employed in this work (radius less than 5.5 Å) would avoid the effects of radial deformation [8,25]. The stable in-registry position can be determined, as well as the rotational and translational energy barriers between nanotube and graphene. In the case of (5,5) nanotube on graphene, the rotation and translation periods are 72° and $\sqrt{3}b$ (intralayer C–C bond length $b=1.42$ Å); the corresponding barriers are about 0.30 and 0.29 meV, respectively. The stable lattice registry is similar to the AB-stacking sequence between graphene layers. The interfacial spacings (a's) are about 3.1–3.2 Å, as sketched in Figs. 1(b)–(c), which are smaller than those of graphene layers and multiwall nanotubes. It is noticeable that (m,m) nanotubes with odd m ($(m,0)$ nanotubes with even m) have the smaller interlayer spacings than those with even (odd) m. With the increasing nanotube size, the nanotube–graphene spacing will become larger and closer to that of multilayer graphene.

Each carbon atom has three sp^2 planar orbitals and one 2p$_z$ orbital normal to the graphene surface. The 2p$_z$ electrons mainly contribute to the low energy states. The tight-binding Hamiltonian is written as

$$H=\sum_{i,i'}h(\theta_{i,i'})c^{\dagger}_{i'}c_i+\gamma_0\sum_{l,l'}c^{\dagger}_{l'}c_l-W\sum_{i,l}h(\theta_{i,l})e^{a-d_{i,l}/\delta}c^{\dagger}_{l}c_i, \tag{1}$$

where c_i and $c^{\dagger}_i$ (c_l and $c^{\dagger}_l$) denote the creation and annihilation operators for the i th (l th) atom on nanotube (graphene). The first term in Eq. (1) is the intralayer atomic hoppings in nanotubes, and the second is in graphene. Only the nearest neighboring atomic hoppings are considered. The weak interlayer couplings are expressed in the third term; the hoppings are taken into consideration only when the interatom distance $d_{i,l}$ is less than 3.9 Å. Their hopping intensity, resembling those in multiwall nanotubes [26–31], increase with reducing interatom distances in the exponential form, while W and δ are fitted as $\frac{1}{8}$ and 0.45 Å [26–28]. The parallel 2p$_z$ orbitals in graphene form the π bondings ($V_{pp\pi}=-3.16\,\text{eV}=\gamma_0$). $h(\theta_{i,i'})$ and $h(\theta_{i,l})$ in the first and third terms describe the misorientation of 2p$_z$ orbitals, where $\theta_{i,i'}$'s and $\theta_{i,l}$'s are the relative angle differences between two orbitals. The intralayer hoppings in nanotubes and the nanotube–graphene hoppings are simultaneously constructed by the π bondings ($V_{pp\pi}=-2.66$ eV) and σ bondings ($V_{pp\sigma}=6.38$ eV). The former are mainly dominated by π bondings while the latter by σ bondings. The electron energy $E^{c,v}(k)$, as a function of wave vector k, is obtained through diagonalizing the tight-binding Hamiltonian. The information about electronic structures are directly reflected in the density of states, which is given by

$$D(\omega)=\int_{1stBZ}\frac{dk}{(2\pi)^2}\frac{\Gamma}{[\omega-E^{c,v}(k)]^2+\Gamma^2}, \tag{2}$$

where $\Gamma=10^{-3}\gamma_0$ is the broadening parameter.

Through the periodic arrangement of one-dimensional nanotubes on graphene sheet, nanotube–graphene composites can be regarded as the one-dimensional systems while the period is sufficiently long [32]. Carbon atoms in both nanotube and graphene sheet construct the primitive unit cell, which relate to the nanotube size and the alignment period. In Fig. 2(a), the blue and red curves, respectively, illustrate energy bands of the non-interacting (5,5) nanotubes and graphene with 512 atoms in a unit cell (~ 545.28 Å in period). The difference in Fermi momenta k_F's is ascribed to the curvature effect in nanotubes. For the non-interacting graphene, the k-dependent subbands derive from the two-dimensional graphene subbands. With the extension of graphene unit cell, more one-dimensional subbands along discrete wave vectors k's are extracted from the two-dimensional energy bands. That is to say, each subband originates from the energy dispersion along specific k-line. In another aspect, the folding of graphene subbands due to periodic alignment is analogous to the circumferential boundary condition of nanotubes [3,5,33]. The linear band and parabolic band result in the finite plateau and asymmetric divergence in the density of states, respectively, as shown in Fig. 2(d). The carrier concentration around E_F is closely related to the atom number in a graphene unit cell. As the alignment period expands to infinity, the charge density at $E_F=0$ would eventually fall to zero. In this situation, the monolayer graphene resumes the two-dimensional nature with zero-gap semiconducting characteristics.

Fig. 2(b) depicts the electronic structures of (5,5) nanotubes lying in registry with a graphene sheet. Low-energy subbands of graphene and nanotube substantially couple with each other. Some intersecting linear bands are transformed into parabolic bands with extra band-edge states. The parabolic bands of non-interacting graphene are doubly degenerate with different quantum numbers. Such subband degeneracy is destroyed; one of each paired degenerate bands effectively couples with the energy states which are mainly contributed by nanotubes. The