Electronic band dispersion of vertically aligned multiwall-carbon nanotubes

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Abstract

We have investigated electronic band structure of the vertically aligned multiwall-carbon nanotubes using angle-resolved ultraviolet photoemission spectroscopy and density functional calculations. There exists a finite density of states at the Fermi level, a large one-dimensional subband dispersion, highly degenerate states, and a small momentum periodicity (with a lattice constant of 6.3 Å) in the band dispersion. This strongly suggests that the observed nanotubes are mostly metallic with a chirality of (4k, k), where k is an integer, as predicted from the density functional calculations, although the chirality of the multiwalled nanotubes are likely to be mixed. © 2001 Elsevier Science B.V. All rights reserved.

Carbon nanotubes (CNTs) have unique properties, and especially metallic and semiconducting behaviors depend on the tube chirality [1–4, 49]. The chirality dependent electronic density of states (DOSs) near the Fermi level from a single CNT has been studied using scanning tunneling spectroscopy (STS), showing one-dimensional (1D) subbands of the CNTs in electronic structures [5]. This has also been predicted by the tight-binding calculations by applying periodic boundary condition to the graphitic sheet [1–4, 49]. A self-consistent 1D band dispersion, however, could not be addressed by the STS alone. Although large 1D subband dispersion has been predicted in semiconducting zigzag and especially in metallic armchair along the tube axis from such calculations (expected theoretical band dispersion width is about 3–5 eV) [1–4, 49], more accurate calculations for different chiral CNTs need to be performed in order to fully understand the complicated electronic band structures of CNTs.

Identifying the metallicty of the CNTs is of both fundamental and technological importance, and the first desirable information is the chirality. As an example, applications of single-walled CNTs to transistors [6, 7] and heterojunction devices [8–10] require information of the chirality a priori. In a rope of the CNTs, the metallicity can be affected.
by the intertube interactions [11–16]. Controlling the chirality is not trivial with the current sample-preparation technology. In this Letter, we studied the electronic band structures using angle-resolved photoemission spectroscopy (ARPES) and density functional calculations from vertically aligned multiwalled-CNTs on Si substrates, which were prepared by the microwave plasma-enhanced chemical vapor deposition (MPECVD). The chirality in each wall of the tubes could not be determined in advance. We find, for the first time, 1D dispersions for the bands near the binding energies of −5, −11, −16, and −21 eV at Γ point with band dispersion widths of about 0.6, 0.5, 2, and 1.5 eV, respectively, along the tube axis. 1D subbands at −0.7 eV near the zone edge, and highly degenerate states at around −3 eV, which are easily understood from the metallic tubes, whereas the valence band edge near −0.3 eV at Γ point with relatively low intensity can be understood as the contribution from the semiconducting tubes. We also observe that a finite DOS at the Fermi level strongly indicates that observed tubes are mostly metallic. A small periodicity as a function of wave vector in the band dispersion (with a lattice constant of 6.3 Å) along the tube axis indicates a metallic chirality of (4k, k), although the possibility of the inclusion of the other achiral metallic and semiconducting nanotubes cannot be excluded, as calculated from the density functional calculations.

The aligned multiwall-CNTs were grown on Ni-coated Si substrates using the MPECVD. The diameter, length, growth rate, the number of walls, and the density of the CNTs could be controlled by the grain size and morphology of the nickel thin films that are altered by the radio frequency (RF) power density during the RF-magnetron sputtering process [17]. In this study, three vertically aligned multiwall-CNT films were used with a diameter ranging from 40 to 60 nm, and with 10, 12, and 19 μm long. The angle-resolved photoemission study has been conducted for these three samples in a synchrotron radiation center, Center for Advanced Microstructures and Devices (CAMD) at Louisiana State University. Monochromatic ultraviolet light was obtained from dispersion of 3 m toroidal grating. The combined resolution for the photoemission spectroscopy was 100 meV. The aligned samples are annealed for several stages up to 600 °C in vacuum for the photoemission measurements to remove gas adsorbates. The surface composition was studied using X-ray photoemission spectroscopy using Mg Kα-line (1253.6 eV).

The band structures of various nanotubes were calculated with a commercial CASTEP code for the density functional calculations within the local density approximation (LDA). The ionic potentials are described by a norm-conserving non-local pseudopotential generated by Troullier–Martins [18] in the separable form of Leinman and Bylander [19]. Exchange-correlation functions parameterized by the Perdew–Zunger scheme [20] were used. The energy cutoff for the plane–wave expansion of wavefunctions is 50 Ry. Brillouin zone integrations were done using four special k-points sampling along the tube axis. Using a 50 k-points sampling, the difference in the total energy was less than 0.005 eV/atom. The self-consistent energy was converged to 0.2 × 10⁻⁴ eV/atom. The nanotubes are placed 4.5 Å apart from each other to isolate van der Waals interactions between the tubes. The band dispersion from such separated tube distance was negligible.

Fig. 1a shows the 45° tilted view of the scanning electron microscope (SEM) image of the aligned CNTs with a diameter of 50 nm and a height of ~12 μm. The angular distribution of the aligned CNTs is less than 2° with respect to the surface normal. The aligned CNTs are uniformly distributed over the entire area. High-resolution transmission electron microscope (HRTEM) image of an individual pristine nanotube separated from the raw sample in Fig. 1b shows an encapsulated Ni particle at the tip of the nanotube with some carbonaceous particles on the tube wall. Some crystalline FCC Ni particles are embedded in the capillary, as seen by the HRTEM. This is related to the growth mechanism [21]. In Fig. 1c, the thickness of top graphitic layers is about 10 nm, excluding the possibility for photoelectrons with an energy range 10–110 eV to escape from the encapsulated Ni particles through the tube walls [22]. The interdistance between CNTs is about 100 nm, giving the filling factor of nanotubes about 20% from the top view, which was measured by the HRTEM image.
To study the band dispersion along the nanotubes, the photoemission spectra were taken at normal emission and 45° light incidence at room temperature as a function of photon energy, as shown in Fig. 2. The DOSs near the Fermi level are finite and monotonically increasing with increasing the photon energy. This may result from the existence of metallic nanotubes and/or the large diameter of nanotubes, which eventually give negative or zero-band gap. A non-dispersive strong peak appears near −8 eV, whereas several weak peaks near −5, −11, −16, and −21 eV are dispersive with broad bandwidths. The interpretation of the data is complicated with the possibility of the coexistence of various chiral tubes in the sample, which may give rise to the different subband positions and different band dispersion widths. We deconvoluted the valence band spectra into nine peaks with three different full widths at half maximums (FWHM) (1.2 eV for peak A, B, and C, 2.7 eV for peak D, E, and F, and 3.4 eV for peak G, H, and I), as shown in Fig. 2a. The choice of the number of the peaks and band dispersion widths was determined first by the spectral shape and second by the error minimization of the fitting. We tried different set of fittings but this did not affect the periodicity of the band dispersions of each subband that appear in Figs. 4a and b.

Fig. 2b is the photoemission spectra, which are taken as a function of the emission angle to see the electronic band dispersion perpendicular to the tube axis. There is no binding energy shift with increasing the emission angle. This implies that there is no electronic band dispersion into the perpendicular direction of the tube. This indicates that the intertube interaction is very weak and the resultant band dispersion could be beyond the employed experimental resolution limit. In addition to this, based on the HRTEM study, the interdistance between carbon nanotubes is as large.
as 100 nm. However, we could not exclude the possibility of the no band dispersion due to the disorder of the nanotube distribution along the surface. This clearly indicates that the mean free path of the electron along the tube axis is much larger than the tube diameter (20–60 nm), as expected from other studies [23].

The aligned multiwall-CNTs grown by the CVD could be composed of the CNT walls with different chiralities. In order to fully analyze the experimental PES, we perform LDA calculations for various achiral and chiral nanotubes, as shown in Fig. 3. We choose achiral armchair (10,10) and zigzag (18,0) nanotubes. For band structure calculations, we first chose supercells of two layers with 40 atoms for (10,10) nanotube (periodicity: \( a = 2.46 \text{ Å} \)) and four layers with 64 atoms for (18,0) nanotube (periodicity: \( a' = 4.26 \text{ Å} \)). First of all, the calculated valence bandwidth (\( \approx -20 \text{ eV} \)) of the CNTs is about 13% narrower than the experimental one (\( \approx -23 \text{ eV} \)) as shown in Figs. 2 and 3. Similarly, 11% wider experimental valence bandwidth than the LDA calculated one has also been observed in graphite [24]. Fig. 3a shows the band structure of (10,10) nanotube along the tube axis and the corresponding integrated DOSs. \( \pi \) and \( \pi' \) bands cross the Fermi level at \( K \) point (\( 2\pi/3a \)), resulting in the finite DOSs at the Fermi level. The first 1D subband appears near \(-0.8 \text{ eV} \). Highly degenerate states are formed at the band edge near \(-2.8 \text{ eV} \). Strong peak in the DOS is centered at \(-6.7 \text{ eV} \) with a broad band width. Large s-band dispersion with a bandwidth of 4.1 eV appears below \(-15 \text{ eV} \). The zigzag (18,0) nanotube [Fig. 3b] shows zero gap semiconducting behavior, as expected. The \( \pi \) and \( \pi' \) bands are getting close to the Fermi level with a finite gap at \( \Gamma \) point. The first 1D subband appears at \(-0.9 \text{ eV} \) at \( \Gamma \) point. Strong peak in the DOS centered at \(-6.7 \text{ eV} \) was found, similar to those of armchair nanotube, whereas the bands are spread over the entire band at the band edge, unlike those of highly degenerate bands in the armchair nanotube. We note that the band dispersion of the bottom s-band is 1.3 eV, less severe than that for the armchair nanotube. Another type of zigzag tube with a finite band gap, for instance, (19,0) nanotube gives similar band structure to (18,0) nanotube except the band gap opening of 0.5 eV.

The detailed band dispersion along the tube axis is shown in Fig. 4, obtained as a function of the wave vector based on Fig. 2. The perpendicular component of the momentum to the surface can be represented with an assumption of a free-electron final state [25]. With this assumption, the experimental band dispersion was obtained with \( \approx 6.0 \text{ eV} \) inner potential energy. The feature A in Fig. 4a could come from the contribution of the metallic subband at about \(-0.7 \text{ eV} \) and the semiconducting subband at about \(-0.3 \text{ eV} \), as indicated by the LDA calculations. However, the binding energies of features near D (\(-5 \text{ eV} \)), F (\(-11 \text{ eV} \)), H (\(-16 \text{ eV} \)), and I (\(-21 \text{ eV} \)) are largely shifted with the wave vector. The band dispersion widths of the features, C (\(-3.1 \text{ eV} \)), E (\(-7.8 \text{ eV} \)), and G (\(-13.5 \text{ eV} \)) are less than 0.2 ± 0.1 eV. This is expected from Figs. 3a and b, since many energy bands are overlapped, obscuring the band dispersions of individual subbands. The large band dispersions of the peak D (\(-5.1 \text{ eV} \)) with a band dispersion width of \(-0.5 \text{ eV} \), F (\(-11 \text{ eV} \)) with \(-1 \text{ eV} \), H (\(-16 \text{ eV} \)) with \(-2 \text{ eV} \), and I (\(-21 \text{ eV} \)) with \(-2 \text{ eV} \) are not

\[\text{Fig. 3.} \text{ The calculated electronic band structures along the tube axis and DOSs for (a) armchair (10,10), (b) zigzag (18,0), and (c) chiral (8,2) nanotubes using LDA. Z is (0,0,0/a), where}\ a\ \text{is (a) 2.46, (b) 4.26, and (c) 6.51 Å. Positions of Z and Γ in (a) and (b) are equivalent to the respective positions of Z and Γ in the (8,2) nanotube. The horizontal lines at zero indicate the Fermi level.}\]
Fig. 4. Electronic band dispersion as a function of $k$-parallel momentum to the tube axis for: (a) first four low binding energy features (A, B, C, and D) near Fermi level; (b) the next five higher binding energy features (E, F, G, H, and I); (c) length of a primitive cell as a function of integer $n/m$ in $(n,m)$ nanotubes. Note that the scale of $y$-axis in (a) is different from that of (b).

surprising at all because such bands are much more sensitive to the directional property than the chirality of the CNTs.

The most important feature in Figs. 4a and b is the repetition of the band dispersion with wave vector along the tube axis. The distance from the zone center to the zone center is about $1.00 \pm 0.05$ Å, corresponding to a periodicity along the tube axis of about $6.3 \pm 0.3$ Å. This is much larger than 2.46 and 4.26 Å achiral armchair and zigzag CNTs, respectively. Furthermore, the $s$-band near $-21$ eV has a dispersion width of less than 2 eV, which is smaller than those of achiral tubes, as shown in Fig. 3a. These strongly indicate that the presence of chiral nanotubes in addition to the achiral nanotubes should be taken into account in order to explain such a large cell size and small band dispersion width. Here we estimate the primitive cell size of all classes of chiral nanotubes [26]. Fig. 4c shows the primitive cells along the tube axis as a function of $n/m$ in $(n,m)$, where only those with integers of $n/m$ are shown in the figure.

None of the tubes including non-integer of $n/m$ gives an experimentally observed periodicity of $6.3 \pm 0.3$ Å except $n/m = 4$ or $(4k,k)$, where $k$ is an integer. We therefore chose the $(8,2)$ chiral tube for the band structure calculations, where the primitive cell size, $a' = 6.51$ Å. The band structure of $(8,2)$ tube with 56 atoms in the primitive cell is shown in Fig. 3c.

The $\pi$ and $\pi'$ band cross the Fermi level near $2\pi/3a''$, again revealing metallic properties. However, this differs from the armchair metallic tube in several points:

(i) the Fermi level is shifted towards the conduction band, resulting in the increased 1D subband position ($-1.6$ eV);
(ii) the higher degeneracies are unexpectedly developed at the zone edge states compared to the highly symmetric achiral tubes, resulting in the several discrete peaks in the DOS;
(iii) the overall band dispersion widths are largely depressed and in particular the bottom $s$-band dispersion is 0.3 eV, much smaller than those of achiral nanotubes.

To interpret the PES in Fig. 4, we refer to our LDA calculations in Fig. 3. The A band is a mixture of the $\pi$ band and first 1D subband of all types of nanotubes, where the band dispersion widths are expected to become narrower for large diameters of nanotubes. The A band dispersion is obscured by the band-folding of the chiral tubes (smaller zone width) to achiral tubes (larger zone width), as indicated by the vertical solid lines, as shown in Figs. 4a and b. The B band dispersion near $-2$ eV is negligible, which is a characteristic of the chiral $(8,2)$ tube. The non-dispersive C band is more likely to be a contribution from chiral $(8,2)$ and zigzag nanotubes. The band D, near $-5$ eV, shows the band dispersion width of 0.6 eV. Since the zigzag and chiral $(8,2)$ nanotubes show negligible band dispersions, of the shallow bands, this dispersion may result from nanotubes, in the armchair configuration.

The E, F, and G bands in Fig. 4b heavily overlap, showing negligible band dispersion, although a small dispersion may occur in the F band. The H band near $-16$ eV shows maximum at $\Gamma$ point and decreases with wave vector, which is mostly contributed from the chiral $(8,2)$ nanotube...
with the bandwidth of theoretical value of about 2 eV, in good agreement with the experimental observations. One significant feature of the H and I bands in Fig. 4b is that the H band shows upshift and the I band shows downshift as the wave vector goes from the zone center to the zone edge. The I band dispersion does not agree with the theoretical band dispersion and the origin will be more studied.

In summary, this work shows the first electronic band dispersion studies on aligned multiwall-CNTs using angle-resolved photoemission spectroscopy and the density functional calculations. The multiwall-CNTs with 40–60 nm diameter have 1D electronic band structure; the large band dispersion along the tube and no band dispersion perpendicular to the tube axis. The MPECVD-grown CNTs are metallic with a finite DOS near the Fermi level. The multiwall-CNT has a large unit cell along the tube axis, ~6.3 Å, which corresponds to the chiral \( (4k, k) \) tube. The existence of the finite DOSs at the Fermi level, the large 1D subband dispersion, highly degenerate states, and a small momentum periodicity strongly suggests that the observed nanotubes are mostly metallic with a chirality of \( (4k, k) \), although the contributions from the achiral nanotubes cannot be excluded.

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