Structural and electronic properties of T graphene nanotubes: a first-principles study

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Abstract

An allotrope of graphene named T graphene was reported to reveal Dirac-like fermions and high Fermi velocity in its buckled phase similar to graphene. However, these Dirac fermions were questioned to be artificial, caused by band folding under the unstable buckling in T graphene. Here, we report first-principles studies on the structural and electronic properties of T graphene nanotubes which are systems rolled up from the two-dimensional planar sheet of T graphene. The ‘artificial’ Dirac fermions in T graphene are turned into reality in the T graphene nanotubes. Two sets of T graphene nanotubes with different diameters were studied. One set of T graphene nanotubes reveals a semi-metallic property and shows an increasing of the number of Dirac points with the diameters. Another set of T graphene nanotubes reveals a metallic property. Our study indicates that rolling up the allotrope of graphene can provide a new avenue for developing new semimetal materials with fascinating properties.

1. Introduction

Carbon, one of the most fascinating element in nature, can form many different crystal structures with diverse properties, such as carbon clusters, carbon nanotubes, graphene, graphite and diamond. Among them, graphene is one of the most amazing two-dimensional (2D) carbon allotrope revealing many unique properties, such as the intriguing band structures, the massless carriers, and the half-integer quantum Hall effect. Graphene is a transparent conductor that holds promise for many material/device applications, including solar cells, light-emitting diodes and field effect transistors in which it can act as an atomically thin channel. Therefore, graphene has been widely studied. Recently, a 2D tetrasymmetrical carbon allotrope named T graphene [1] has been investigated by first-principles calculations. T graphene could be considered to be derived from cleaving two adjacent atomic layers in bcc C8 or bct C4 along (001). It is a 2D sheet constructed by carbon octagons and squares alternately, shown in figure 1.

T graphene has been calculated to be energetically metastable and dynamically stable [1]. Liu et al has also shown that T graphene has Dirac-like fermions and a high Fermi velocity [1], although it has two non-equivalent kinds of bonds and a non-honeycomb structure [2]. Dirac-like fermions were shown to arise from the crossing π and π∗ bands and the two sublattices. Two configurations, i.e. planar T graphene and buckled T graphene, were considered in their calculations [1]. The intriguing electronic structures came out within its buckled phase. The buckled T graphene turned out to have Dirac-like fermions and high Fermi velocity similar to those of graphene. However, Kim et al [3], based on their first-principles calculations, argued that the buckled T graphene did not
exist after a fully relaxation of the buckled T graphene sheet. There was a spontaneous structural transformation from the buckled T graphene to the planar T graphene. The equilibrium lattice constant in their calculations is \( \sim 4.875 \, \text{Å} \), which is in consistent with the previous calculation \( [1] \). However, height difference \( (\Delta z) \) of the fully relaxed buckled T graphene is only \( \sim 0.0002 \, \text{Å} \). Therefore, Kim et al argued that T graphene should not have Dirac-like fermions or the high Fermi velocity since the buckled T graphene would not exist in reality. Their calculations have also been tested in local density approximation and Heyd–Scuseria–Ernzerhof hybrid functional \( [4] \), and the main conclusions are the same as the Perdew–Burke–Ernzerhof (PBE)–generalized gradient approximation (GGA) calculations. Liu et al \( [5] \) admitted that the fully relaxed buckled T graphene will transform into planar T graphene since the formation energy of buckled T graphene is higher than that of planar T graphene. But they argued that the formation energy is not a sufficient criterion for the determination of structural stability. Free energy and phonon spectra also play important roles in this regard. In terms of free energy, buckled T graphene is more stable than other reported carbon allotropes. And all phonon branches of buckled T graphene are positive, suggesting a stable structure as well. Hence, the stability of buckled T graphene (and the existence of Dirac points) need to be further addressed.

Huang et al \( [6] \) also questioned the existence of Dirac-like fermions and high Fermi velocity in the T graphene system, based on the density-functional theory (DFT) calculations. They showed that planar T graphene was normally metallic under the primitive unit cell (see figures 1(a) and (b)), which is in consistent with the previous calculation \( [1] \). However, when a \( \sqrt{2} \times \sqrt{2} \) R-45° supercell (also see figure 1(a)) was used to redraw the band structures of the same planar T graphene, crossing points with linear dispersion relations near the Fermi level appeared, shown in figure 1(c). Such ‘Dirac points’ are then obviously originating from the band folding due to the use of a larger unit cell (i.e. supercell). Therefore, these ‘Dirac points’ are called to be artificial. Importantly, the band structures calculated from the planar T graphene using a supercell were found to be essentially analogous to those calculated from buckled T graphene, despite some differences owing to the corrugation of the buckled T graphene. In the reply to the comment of Huang \( [6] \), Liu et al \( [7] \) argued that although the band structures from a supercell calculation of Huang is similar to that of buckled T graphene, they still have essential distinctions. The assertion by Huang and co-workers \( [6] \) that the metallicity of buckled T graphene is lacking of evidence. Buckled T graphene does have Dirac-like fermions in terms of the linear dispersion, though it is not like graphene in every aspect.

**Figure 1.** (a) Geometrical structure of the planar T graphene. The small black square is the primitive unit cell of the planar T graphene, while the blue dashed lines show the \( \sqrt{2} \times \sqrt{2} \) R-45° supercell of the planar T graphene. (b) The band structures of the primitive unit cell of the planar T graphene. (c) The folded band structures of the \( \sqrt{2} \times \sqrt{2} \) R-45° supercell of the planar T graphene. The band folding is schematically depicted by the green and blue arrows. (d) Brillouin zone of T graphene unit cell (solid line) and T graphene supercell (the blue dashed line). The k-point paths are colored same to the band structures in (b) and (c).
From all these discussions, one can see that the existence of the novel Dirac-like fermions in T graphene relies on the stability of the buckled T graphene. However, the Dirac points in T graphene might be an ‘illusion’ since the stability of the buckled T graphene is still doubtful. In this paper, the planar T graphene sheets are rolled up to form the T graphene nanotubes. The first-principles calculations based on DFT are then performed to study the structural and electronic properties of these T graphene nanotubes. As far as we know, this is the first time that T graphene nanotubes in different topology are studied in their detailed electronic properties, including the zone folding scheme, curvature effect, decomposed charge density and so on. The T graphene nanotubes are shown to have Dirac-like fermions and high Fermi velocity similar to those of graphene. Therefore, the T graphene nanotubes can turn the ‘artificial’ Dirac fermions in T graphene into reality.

2. Method of calculation

The present calculations on graphene nanotubes were performed by using a first-principles method based on the DFT with the GGA in the form of PBE exchange-correlation functional [8], as implemented in the Vienna Ab initio Simulation Package (VASP) [9, 10]. The wave functions are expanded in plane waves up to a kinetic energy cutoff of 520 eV. The Brillouin zone(BZ) integrals were performed using a Monkhorst-Pack [11] sampling scheme with a k-point mesh resolution of 2π × 0.03 Å⁻¹. The unit cell lattice parameters (unit cell shape and size) and atomic coordinates were fully relaxed in each system until the forces on all the atoms were smaller than 0.01 eV Å⁻¹. Phonon calculations were performed by the supercell approach. Force constants of supercells were calculated by DFT implemented in the VASP code, and phonon frequencies were calculated from the force constants using the PHONOPY code [12]. Supercells containing 3 × 1 × 1 unit cells were used in force-constant calculations.

3. Results and discussion

The geometrical structure of T graphene is shown in figure 1(a). In contrast to graphene, T graphene has two types of bonds: (1) those belong to squares named intra-square bonds, (2) those connect the squares named inter-square bonds. Their bond lengths are 1.47 Å and 1.37 Å, respectively. The inter-square bond is shorter than that in graphene (1.42 Å), indicating that the inter-square binding is stronger than that in graphene. For a planar T graphene (a perfect 2D sheet), the primitive unit cell is the small black square shown in figure 1(a), containing four atoms per unit cell. The corresponding band structures of the planar T graphene, shown in figure 1(b), exhibits a metallic character. Four bands cross the Fermi level and exhibit a novel linear dispersion near the Fermi level. The unit cell of the buckled T graphene is the large blue square with dashed lines shown in figure 1(a), i.e. a \( \sqrt{2} \times \sqrt{2} \) R-45° cell. For the buckled T graphene, two adjacent square lattices are not in the same height along the z-axis (i.e. possessing two inter-penetrating square sublattices). Here, we show in figure 1(c) the band structures of a \( \sqrt{2} \times \sqrt{2} \) R-45° supercell by folding the bands of a primitive unit cell, i.e. the bands in figure 1(b). The band folding picture is schematically depicted by the green and blue arrows between the figures 1(b) and (c). Corresponding BZ is shown in figure 1(d). When the bands are folded, the symmetry point X will coincide with \( \Gamma \) in the BZ of T graphene supercell (figure 1(d)). It should be emphasized that the present folded band for the supercell (figure 1(c)) are essentially analogous to those calculated from buckled T graphene [3, 5, 6]. It can be clearly seen that there are two crossing points of bands appearing at the Fermi surface, showing the artificial Dirac points in the figure 1(c) (where the ‘Dirac points’ came from the band folding). A three-dimensional band structure plot, depicted in figure 2(a), reveals the bands intersecting the Fermi level under the \( \sqrt{2} \times \sqrt{2} \) R-45° supercell of T graphene. Two bands intersect with each other and form a corresponding ‘node circle’ on the Fermi surface (a continuous Dirac points at the Fermi level), as presented in figure 2(b). A semimetal having a node circle is named node-line semimetal [13, 14]. Node-line semimetal itself is very interesting, however, as pointed out previously, ‘node circle’ in T graphene under the \( \sqrt{2} \times \sqrt{2} \) R-45° supercell might be an artifact which is a result of band folding. T graphene could be a metal other than a semimetal.

In order to search for real semi-metals as well as Dirac fermions, in this paper, T graphene sheets are rolled up to form T graphene nanotubes. Two kinds of T graphene nanotubes are constructed in this study. As shown in figure 3(a), symbol \( (l, m) n \) [15–18] is used to mark a T graphene nanotube. Tube direction \( (l, m) \) is based on the unit vectors \( a \) and \( b \), and tube diameter is described by \( n \) which is the number of perimeter units used for rolling up a tube. The larger \( n \) employed the bigger the tube will be. Under the four-fold symmetry of the T graphene supercell, the nanotube symbol is confined to \( 0 \leq l \leq m \) to avoid a many-to-one correspondence of the structure. Geometrical structures of a \( (0, 1) 6 \) and a \( (1, 1) 6 \) T graphene nanotubes, as examples, are shown in figures 3(d) and (e).
Curvature energy reveals the energy cost in rolling up a sheet into a tube, which is an important parameter for understanding the stability of a nanotube. The curvature energy, $E_{\text{cur}}$, is defined as:

$$E_{\text{cur}} = E_{\text{tube}}^{\text{at}} - E_{\text{sheet}}^{\text{at}}$$

where $E_{\text{tube}}^{\text{at}}$ is the cohesive energy per atom in the nanotube; $E_{\text{sheet}}^{\text{at}}$ is the cohesive energy per atom in the corresponding 2D sheet. We presented in figure 4 the curvature energies of the $(1, 0)$ $n$ graphene nanotubes, $(0, 1)$ $n$ and $(1, 1)$ $n$ $T$ graphene nanotubes. Compared with the graphene nanotubes, both of the two sets of $T$ graphene nanotubes showed less curvature energies, implying that less energies are needed to roll up $T$ graphene nanotubes than graphene nanotubes, owing to the softer of $T$ graphene sheet as compared with the graphene sheet. Such results also suggest the possibilities in experimental synthesis of the $T$ graphene nanotubes. $T$ graphene has a smaller atomic density than graphene, that is, 0.379 atom Å⁻² for graphene compared with 0.337...
atom Å\(^{-2}\) for \(T\) graphene. The curvature energies for \((0, 1)\) and \((1, 1)\) \(T\) graphene nanotubes are different, owning to the different directions for rolling up the tubes. Bonds along the circumferential direction provide more resistance in rolling. The bond densities along the circumferential direction of \((0, 1)\) and \((1, 1)\) nanotubes are 0.1683 bond Å\(^{-2}\) and 0.0845 bond Å\(^{-2}\), respectively, indicating that \((0, 1)\) tubes bear a bigger resistance in rolling up the \(T\) graphene nanotubes. It should be pointed out that the diameters of \((0, 1)\) and \((1, 1)\) nanotubes are 0.776 Å, and 0.549 Å, respectively. Such diameters are too small to construct nanotubes, because the diameters of these tubes are even smaller than the bond length of carbon.

The differences in the geometrical structures of \(T\) graphene nanotubes have profound effects on the electronic properties of the tubes. Due to periodic boundary conditions along the circumferential direction of the tubes, the allowed wave vectors along the nanotube circumference are quantized [19]: they can take only a set of discrete values. In contrast, the wave vectors along the nanotube axis remain continuous. For the \((0, 1)\) tubes, the continuous wave vectors are along \(\Gamma - M'\) as depicted in figure 5(a) [15]. In figure 5(a), there are 6 \(k\) lines (dashed lines) consisting of \(k\) vectors where \(n\) is equal to 6. The \((0, 1)\) nanotubes are rolled up along the \((0, 1)\) direction, in which the symmetry of \(T\) graphene supercell is preserved in the unit cell of \((0, 1)\) nanotubes. Therefore, the artificial node circle in the BZ of \(T\) graphene supercell should be considered as an origin of the electronic characters of \((0, 1)\) \(T\) graphene nanotubes. When the \(T\) graphene is rolled up into a tube, the 2D BZ of \(T\) graphene degenerate to a 1D BZ. The 2D and 1D BZs are related by the zone-folding approximation. The basic idea behind the zone-folding approximation is that the electronic band structures of a specific nanotube is

Figure 4. Curvature energies of graphene nanotubes and \(T\) graphene nanotubes.

Figure 5. First Brillouin zones of the \(T\) graphene with a $\sqrt{2} \times \sqrt{2}$ R-45° supercell, together with allowed \(k\) lines (dash lines) for (a) the \((0, 1)\) and \((b)\) the \((0, 1)\) 12 \(T\) graphene nanotubes; (c) band structures of \((0, 1)\) 12 and (d) \((0, 1)\) 12 \(T\) graphene nanotubes; (e) Density of states of a \((0, 1)\) 6 \(T\) graphene nanotube. Points \(A, B, C, C', D, D'\) stand for Dirac points.
given by superposition of the $T$ graphene electronic energy bands along the corresponding allowed $k$ lines [19]. As the $k$ wave vectors of the tube $(0, 1) n$ cross over the node circle of the $T$ graphene supercell (see figures 5(a) and (b)), Dirac points, accompanied by Dirac cones around the Fermi level, will appear in the band structures of $T$ graphene nanotubes (see figures 5(c) and (d)). Figures 5(c) and (d) are the calculated band structures of $(0, 1) 6$ and $(0, 1) 12$ tubes to represent the main characteristics of band structures of this set of nanotubes. The bands crossing the Fermi level are linear which is an obvious evidence of Dirac cones and semimetallicity. The semimetal character is also confirmed by the corresponding density of states (figure 5(e)), showing a zero state at the Fermi level. Since the band structures of the nanotubes are calculated under the primitive unit cell of the nanotubes, the points crossing the Fermi level (in figures 5(c) and (d)) are Dirac points. Thus, the artificial Dirac points in $T$ graphene (calculated from a $\sqrt{2} \times \sqrt{2}$ 45° supercell) are turned into real ones in $(0, 1) n T$ graphene nanotubes. These crossing points in the BZ (figures 5(a) and (b)), such as $A, B, B', C, C', D, D', \ldots$, correspond to the Dirac points (marked with same letters) in the band structures in figures 5(c) and (d). The number of Dirac points equals to the number of the crossover points and can be formulated as $[0.321 n] \times 2 + 1$, where $[\ ]$ is the round down sign, 0.32 is the calculated half width of the node circle. The band plot of $(0, 1) 6$ tube (figure 5(c)) has three Dirac cones locating at $A$ (0.326, 0, 0), $B$ and $B'$ (0.233, 0, 0). For all of the $(0, 1) n$ tubes, there is a fixed point $A$ (0.326, 0, 0) which is non-degenerate. Points $B$ and $B'$ (figure 5(a)) are doubly degenerate, leading to two Dirac points at the same position $B$ or $B'$ (see band structures in figure 5(c)). When the $T$ graphene nanotube gets bigger, the crossing points in figure 5(b) increase in pairs, resulting in an increase of doubly degenerate Dirac points in the band structures (figure 5(d)). When the size of the tube increase from $(0, 1) 6$ to $(0, 1) 12$, the number of the crossover points in BZ increases from 3 to 7 (equal to the number of Dirac points). The doubly degenerate Dirac points in the $(0, 1) 12$ tubes are at $D$ and $D'$ (0.126, 0, 0), $C$ and $C'$ (0.229, 0, 0), $B$ and $B'$ (0.292, 0, 0), respectively. The non-degenerate Dirac point is at the $A$ (0.326, 0, 0), which is the same as that in the $(0, 1) 6$ tubes.

We now turn to the $T$ graphene nanotubes rolled up in the $(1, 1)$ direction. The $(1, 1) n$ tubes preserve the symmetry of $T$ graphene unit cell, which is a metal, in the unit cell of $(1, 1) n$ tubes. Hence, the BZ depicted in figures 6(a) and (b) has no node circle inside. Instead of the node circle as in the BZ of $T$ graphene supercell (figures 5(a) and (b)), the circle presented in figures 6(a) and (b) is simply the calculated Fermi surface of the $T$ graphene unit cell. According to the zone-folding approximation, all the intersections (marked with letter $A / A' \sim F / F'$ in figures 6(a) and (b)) between the Fermi surface (solid line) of $T$ graphene and the allowed wave vectors (dash lines) of nanotubes are superposed into the band structure of nanotubes (figures 6(c) and (d)). In figure 6(a), there are 6 $k$ lines (dashed lines) intersecting the Fermi surface. Every intersection point results in a crossing between the energy band and the Fermi level of nanotubes in figure 6(c). Therefore, there are 6 bands crossing the Fermi level in the $(1, 1) 6$ nanotube, revealing a metallic property. Among these crossing points, $A$ and $A'$, $D$ and $D'$ located symmetrically to the $\Gamma$–$M$ (figure 6(a)), respectively, leading to a doubly degeneracy in the band plot. Points $B$ and $C$ are non-degenerate. In the occasion of bigger tubes (figure 6(b)), 12 $k$ lines result in
boundary condition con

more intersection points with the circle. Points B and C are still non degenerate while A and A’, D and D’, E and
E’, F and F’ are doubly degenerate points as shown in BZ (figure 6(d)).

Unless the tube diameter is small, the band structures of the tubes somewhat resemble those of T graphene sheet [15]. The main difference between T graphene sheet and nanotubes lies in the periodic boundary conditions. T graphene has periodic boundary conditions extending infinitely in two-dimensions while T graphene nanotubes have a finite circumference resulting in a one-dimension character. The one-dimension boundary condition confines the electron wave vectors to a certain direction and retain the electronic property of corresponding T graphene cell in this direction. In the (0, 1) n tubes, the electron wave vectors are confined to \(\Gamma – M’\) in the BZ of the T graphene \(\sqrt{2} \times \sqrt{2} \) R-45° supercell. The set of (0, 1) n nanotubes thus exhibit a semi-metallicity when \(n > 3\).

The corresponding Fermi velocities of the Dirac fermions can be evaluated from the gradient of the linear dispersions of the band structures. Based on the band structures of figure 5(c), the Fermi velocities of the cones of (0, 1) 6 are \(7.77 \times 10^5\) m s\(^{-1}\) at B(B’) and \(8.05 \times 10^5\) m s\(^{-1}\) at A, respectively. Tube (0, 1) 12 has four Dirac cones whose Fermi velocities are calculated to be \(7.26 \times 10^5\) m s\(^{-1}\) at D(D’), \(8.32 \times 10^5\) m s\(^{-1}\) at C(C’), \(8.22 \times 10^5\) m s\(^{-1}\) at B(B’) and \(8.28 \times 10^5\) m s\(^{-1}\) at A, respectively. These Fermi velocities are close to \(8.23 \times 10^5\) m s\(^{-1}\) of the Dirac point along \(\Gamma – M’\) in T graphene, while far from \(11.9 \times 10^5\) m s\(^{-1}\) of that along \(\Gamma – X’\), confirming their origination from \(\Gamma – M’\) direction in T graphene with a \(\sqrt{2} \times \sqrt{2} \) R-45° supercell.

Next, the band structures will be discussed by the zone folding scheme. But as a matter of fact, the band structures of nanotubes are different from the ones simply obtained from the band folding. In nanotubes, carbon atoms are placed on a cylindrical wall rather than a sheet which induces a curvature effect. When the diameter of the tubule decreases to \(3 \text{~nm}\) the band structures of the tubes somewhat resemble those of graphene, while far from \(11.9 \times 10^5\) m s\(^{-1}\) of that along \(\Gamma – X’\), confirming their origination from \(\Gamma – M’\) direction in T graphene with a \(\sqrt{2} \times \sqrt{2} \) R-45° supercell.

In T graphene, all the carbon atoms are three-fold coordinated, thus the forth valence electron plays a key role in deciding its conductivity. Figures 9(a) and (b) are the band decomposed charge density describing the bonding electrons at the Fermi surface. Figure 9(a) shows the top view of the charge density of T graphene sheet, indicating a charge density accumulation around the inter-square bonds (at the Fermi surface). In the corresponding side view (figure 9(b)), the charge density indicates a localized \(\pi\) and \(\pi^*\) bonds on the inter-square

**Figure 7.** Evolution of the band structures of (0, 1) n T graphene nanotubes under increasing diameter.
atoms. Similar to the case of graphene [16, 21], the electrons on the Fermi surface are mainly distributed in the $\pi$ states, while the energies of the $\sigma$ bonds located far below the Fermi level, which is not seen in figure 9. The stronger interactions between the inter-square atoms due to the $\pi$ bonding lead to shorter inter-square bond length of 1.37 Å, compared with 1.47 Å of the intra-square bonds. The conductivity of the $T$ graphene comes from the $\pi$ bonds localized on the inter-square bonds. As there are no states on the Fermi level of a semimetal, the charge density of $(0, 1)$ nanotubes is calculated at $\pm 0.1$ eV around the Fermi level to describe the bonded electrons on the Dirac cones (figure 9(c)). The analysis on the electron states of the $(0, 1)$ 6 nanotube (figure 9(c)) indicates that the Dirac cones in the tube is also contributed by $\pi$ bonds. Therefore, the semi-metallicity of $(0, 1)$ nanotubes is associated directly with the localized $\pi$ bonds on the inter-square atoms (figure 9(c)). The enlarged image shown in the figure 9 suggests a possible explanation that all the valence electrons are bounded through the $\pi$ bonds, which leads to the semi-metallic characteristics of the $(0, 1)$ $n$ nanotubes. For the ultra-small nanotubes, the localized $\pi$ bonds are very much deformed. The $\pi$ bonds inside the nanotubes are then all overlapped, making the electronic conducting possible through the interior $\pi$ bonds of the tubes, resulting in the metallicity in the $(0, 1)$ 3 and $(0, 1)$ 2 tubes.

Figures 10(a)–(c) gives the band decomposed charge density at the Fermi surface for the $(1, 1)$ 9 $T$ graphene nanotube. In the $(1, 1)$ $n$ tubes, there are two types of bonds, i.e. the ones parallel to the tube axis and the ones perpendicular to the tube axis. Bonds paralleling to the tube axis are not influenced by the curvature of the nanotubes (figure 10(c)), while the bonds perpendicular to the tube axis deform under the curvature of the tube (figure 10(a)). This deformation may result in a breaking of $\pi$ bonds outside the tube wall as shown in the
in a graphene is a metal in its primitive unit cell, however, it transits into a semimetal under the band-folding effect.

Conclusions

figure 10(a). When the tubes are very small ($n \ll 3$), the electrons inside the tubes are found to be fully bonded under the curvature effect, leading to the semiconducting characteristics of the tubes. For example, in the tubes (1, 1) 2 and (1, 1) 3, electrons are fully bonded (figures 10(d) and (e)), opening band gaps of 1.44 eV and 1.17 eV, respectively. Phonon spectra (see figure 11) of $T$ graphene nanotubes for (0, 1) 2, (0, 1) 3, (0, 1) 4, (0, 1) 6, (0, 1) 12, (1, 1) 2, (1, 1) 3, (1, 1) 4, (1, 1) 6 and (1, 1) 12 are calculated to evaluate the structural stability. The semimetallic tubes of (0, 1) 4, (0, 1) 6 and (0, 1) 12 are shown to be dynamically stable since no imaginary modes are found (see figures 11(c)–(e)). However, two ultra-small tubes (0, 1) 2 and (0, 1) 3 show imaginary modes around $\Gamma$ (figures 11(a), (b)), which indicates a vibrational instability. In another rolling direction, all the phonon spectra for (1, 1) 2, (1, 1) 3, (1, 1) 4, (1, 1) 6 and (1, 1) 12 show no imaginary vibrational modes (figures 11(f)–(j)), indicating that the (1, 1) $n$ nanotubes are all dynamically stable for all the sizes of tubes. Therefore, the prediction of the smallest $T$ graphene nanotubes in the direction of (1, 1) is (1, 1) 2 with a diameter of 2.47 Å, which is much smaller than both the experimental smallest carbon nanotube (about 5 Å [22] or 4.07 Å [23]) and the theoretical smallest diameter of carbon nanotube 4 Å [24]. The smallest $T$ graphene nanotube in the direction of (0, 1) is (0, 1) 4 with a diameter of 6.34 Å.

4. Conclusions

$T$ graphene is a metal in its primitive unit cell, however, it transits into a semimetal under the band-folding effect in a $\sqrt{2} \times \sqrt{2}$ R-45° supercell, where the ‘Dirac points’ are then argued to be ‘artificial’. In this paper, we show that the ‘artificial’ Dirac points in the $T$ graphene supercell can be turned into real ones in the $T$ graphene nanotubes. $T$ graphene nanotubes are rolled up in two directions, i.e. (0, 1) and (1, 1) in this study. The unit cell of (0, 1) $n$ nanotubes exhibits the same symmetry with the $T$ graphene supercell in direction (0, 1), resulting in a semimetallicity with Dirac nodes. The number of these Dirac points increases with $n$ in the (0, 1) $n$ tubes. The Fermi velocities of these Dirac fermions can be higher than those of graphene and graphene nanotubes. In contrast, the (1, 1) $n$ tubes remain the symmetry of the unit cell of $T$ graphene. Thus, the (1, 1) $n$ tubes present a metallic property. The ultra-small tubes ($n \ll 3$) reveal a conductivity change in both the (0, 1) and (1, 1) direction, resulting from a notable curvature effect. Band structures change from semimetal to metal under $n \ll 3$ in the (0, 1) $n$ tubes. The metallicity of (1, 1) $n$ tubes transform into semiconductivity under $n \ll 3$. At last, the curve of curvature energies reveals that rolling up the $T$ graphene into $T$ graphene nanotubes costs less energy than rolling up the graphene, which implies a good stability of $T$ graphene nanotubes. The phonon calculations indicate that all the $T$ graphene nanotubes are dynamically stable except for (0, 1) 2 and (0, 1) 3.
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Figure 11. Calculated phonon spectra of $T$ graphene nanotubes for (a) $(0,1)2$, (b) $(0,1)3$, (c) $(0,1)4$, (d) $(0,1)6$, (e) $(0,1)12$, (f) $(1,1)2$, (g) $(1,1)3$, (h) $(1,1)4$, (i) $(1,1)6$, and (j) $(1,1)12$. 
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