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The thermoelectric performance of bulk three-dimensional graphene

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HIGHLIGHTS

- There exist Dirac cones in three-dimensional (3D) graphene.
- The thermoelectric performance of 3D graphene is excellent.
- The defective 3D graphene has better thermoelectric performance.

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ABSTRACT

The electronic and thermoelectric properties of a new carbon bulk material, three-dimensional (3D) graphene, are investigated in this study. Our results show that 3D graphene has unique electronic structure, i.e., near the Fermi level there exist Dirac cones. More importantly, the thermoelectric performance of 3D graphene is excellent, at room temperature the thermoelectric figure of merit (ZT) is 0.21, an order of magnitude higher than that of graphene. By introducing line defects, the ZT of 3D graphene could be enhanced to 1.52, indicating 3D graphene is a powerful candidate for constructing novel thermoelectric materials.

1. Introduction

Thermoelectric materials have aroused widespread interest from both theoretical and technological researchers due to their ability to directly convert industrial waste heat into useful electricity, which could provide an important solution to today's energy challenges [1]. In the evaluation of thermoelectric materials, a parameter usually employed is the figure of merit (ZT), which measures the energy conversion efficiency of thermoelectric materials. Here, $ZT = S^2\sigma T/k$, where S is the Seebeck coefficient, σ is the electrical conductance, T is the absolute temperature and k ($k = k_{el} + k_{ph}$) is the thermal conductance composed of the contributions from electrons (k_{el}) and phonons (k_{ph}).

An excellent thermoelectric material requires a large electrical conductance like a metal, a high Seebeck coefficient like an insulator and a low thermal conductance like a glass. Because of these seemingly contradicting requirements, it is often believed that high thermoelectric performance is difficult to achieve in a conventional bulk material. Hicks and his coworkers, in their work in 1993, predicted that nanomaterials. May have large ZT values [2], which suggests a new route to obtain excellent thermoelectric materials. Since then different nanomaterials have been intensively investigated with the hope to develop and design possible thermoelectric materials with high conversion efficiency.

Among various nanomaterials studied, one particular category is carbon nanomaterials. However, these carbon nanomaterials possess quite different thermoelectric properties. For example,

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although the electronic properties of famous two-dimensional (2D) graphene are excellent, the ZT value is only 0.01 at room temperature [3], primarily owing to its extremely high thermal conductance. Graphyne [4], another well-known 2D carbon allotrope, has become a more interesting topic in the carbon material research community recently. Different from graphene, graphyne contains both sp and sp^2 hybridized bonds and holds four typical geometrical structures, namely, α-, β-, γ- and (6, 6, 12)-graphyne. For the different structures of graphyne, γ-graphyne is found to have the largest thermoelectric conversion efficiency at room temperature [3], ZT = 0.15, which is about 15 times higher than that in graphene.

More recently, a new carbon allotrope, which is called three-dimensional (3D) graphene, was synthesized in experiment [5]. 3D graphene is fully constructed by sp^2 hybridized carbon atoms but, unlike the 2D counterpart, it is a typical bulk material. According to the experimental observation, the structures of 3D graphene can be both periodic and random, and hold very high stabilities. A representative periodic structure of 3D graphene is shown in Fig. 1a. The structure can be viewed as three flat graphitic sheets, which are known to be the most stable carbon form with sp^2 bonds, are joined together at an angle 120° between two sheets along a straight line.

So far, the geometric structures of 3D graphene have been reported, but the corresponding electronic structures, to our knowledge, are still limited [6]. More importantly, as mentioned before, the thermoelectric performance of graphene is very low, this drawback may be overcome in 3D graphene since it has unique structure. Therefore, the study on the electronic and thermoelectric properties of 3D graphene should be interesting and important. In this study, we theoretically discuss these issues.

2. Models and methods

All the calculations were performed by using Atomistic ToolKit (ATK) package [7]. Density functional theory (DFT) was employed to optimize the structure of 3D graphene. The exchange-correlation functional was treated within the generalized gradient approximation proposed by Perdew, Burke and Ernzerhof (PBE) [8]. Double-ζ plus polarization (DZP) basis sets were used in the calculation. Careful and extensive convergence tests were performed. Finally, the cutoff energy was set to 200 Ry and a 15 × 15 × 25 k-point grid was adopted.

After structural optimization, the electronic band structure and density of states (DOS) of the system were calculated at DFT level. Furthermore, we employed the second-generation Brenner potential to simulate the thermal properties of 3D graphene [9], such as phonon DOS. The advantage of classical potential, when compared with DFT, is its accuracy and efficiency in the calculation of systems with large unit cells. The Brenner potential has been used to explore the thermal properties of β-graphyne nanoribbons

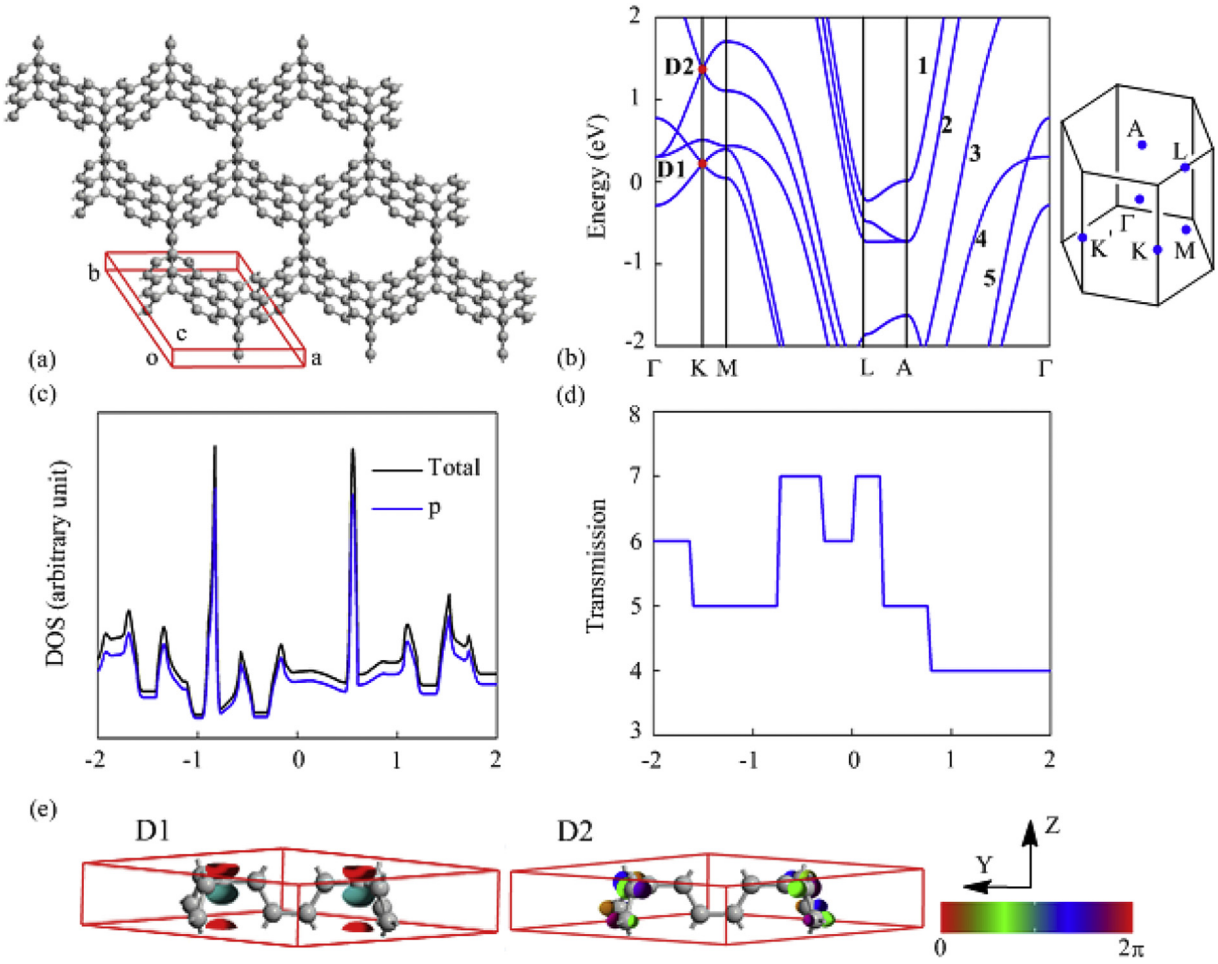

Fig. 1. (a) The periodic structure of 3D graphene. The red box represents the unit cell. (b) The electronic band structure of 3D graphene. The red dots D1 and D2 indicate the Dirac cones. Along the transport direction, five energy bands are labeled by numbers. The Brillouin zone is also given. (c) The DOS and (d) the zero-bias electronic transmission spectrum of 3D graphene. (e) The Bloch states at D1 and D2. In (b), (c) and (d), the Fermi level is set as zero. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article).

and other carbon materials [10–14]. The combination of DFT and classical potential has been successfully applied to investigate the thermoelectric properties of materials [15].

With the optimized 3D graphene, one can design nanodevices. It should be pointed out that, similar to previous treatment [10], the whole nanodevice is divided into three parts: left lead, right lead and central region, and during the nanodevice simulation the transport direction is along *oc* (see Fig. 1a). The electron (phonon) transport properties of the nanodevice were then studied by combining the real-space nonequilibrium Green's function (NEGF) with DFT (Brenner potential). The NEGF method is a very powerful tool for simulating transport properties. The electron and phonon transmission spectra were firstly calculated from NEGF, and then other physical quantities such as S, σ, k_{el} and k_{ph} were obtained from the corresponding transmission spectra. Finally, using the above physical quantities, we easily achieved the ZT values of 3D graphene.

3. Results and discussion

The calculated electronic band structure, DOS and electronic transmission spectrum are plotted in Fig. 1. Our results show that 3D graphene is a typical metal and, more interestingly, in the band structure near the Fermi level there exist Dirac cones. At K point in the Brillouin zone (BZ), two different types of Dirac cones, which are denoted as D1 and D2, are observed (since the K and K′ points in BZ are related by symmetry, only one representative is shown in the figure). Both D1 and D2 are located slightly above Fermi level but the slopes, i.e. the first derivative of the band energies of the two involved bands in reciprocal space, are different.

For D1, it is a direction-independent isotropic Dirac cone and the slopes along KΓ and KM directions are the same, ±30 eVÅ. However, different from D1, D2 is a direction-dependent anisotropic Dirac cone, the corresponding slopes along the two directions are ±44 and ±39 eVÅ, respectively. Therefore, by exciting electrons from Fermi level to D1 or D2, one can obtain two types of Dirac electrons in 3D graphene and they will have different properties. Furthermore, the example of 3D graphene also suggests that the existence of Dirac cones is not a unique feature of 2D carbon allotropes.

The origination of the two Dirac cones can be explained from the DOS and the corresponding Bloch states. The electronic structure of 3D graphene near the Fermi level is dominated by the p states of carbon atoms. More specifically, the Bloch state at D1 consists of p_z orbitals (see Fig. 1e), which is very similar to the case in graphene. As a result, the Dirac cone is isotropic. As to D2, the Bloch state comes from the hybridization of p_x and p_y orbitals, leading to the direction-dependent slopes. To our knowledge, for carbon allotropes, only in 3D graphene the Dirac cone could be constructed by p_x and p_y states and exhibits anisotropic characteristics.

The metallicity of 3D graphene could be further understood from its transmission spectrum. From Fig. 1d, one can see that, along the *oc* direction, there are six transport channels at Fermi level. The six transport channels arise from five energy bands in the band structure (see Fig. 1b). Note that the second band is double degenerate and it will split into two non-degenerate bands along A to L point, as a result of symmetry decrease. So the intersection of the second band and Fermi level can provide two transport channels. As will be discussed latter, the unique electronic properties of 3D graphene is very important for the thermoelectric performance.

To analyze the thermal properties of 3D graphene, we calculated its phonon DOS and thermal conductance, as shown in Fig. 2a and b. The phonon frequencies of 3D graphene are all positive, suggesting

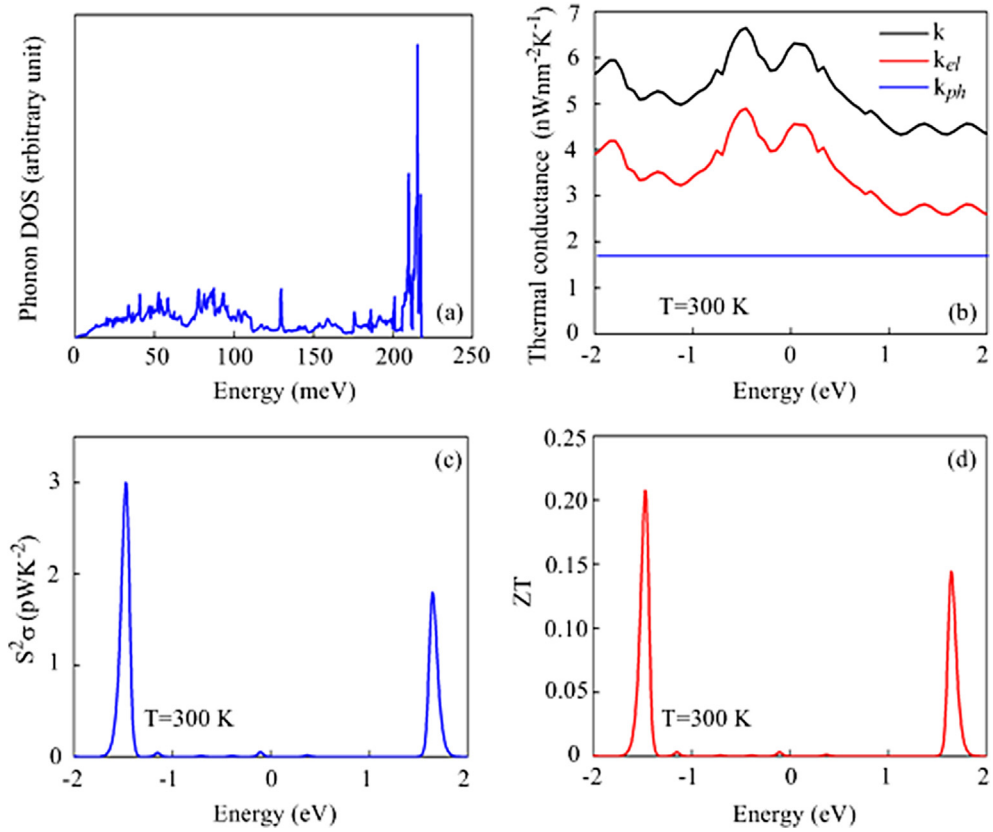

Fig. 2. (a) The phonon DOS, (b) the thermal conductance, (c) the thermal power factor $S^2\sigma$ and (d) the ZT of 3D graphene. In (b), (c) and (d), the temperature is 300 K and the Fermi level is set as zero.

this new carbon allotrope is indeed dynamically stable. At a certain temperature, k_{ph} and k_{el} have different characteristics, i.e. the former is a constant while the latter is a function of energy. Furthermore, our results show that k_{el} is always larger than k_{ph} at 300 K, and similar phenomenon is observed for other temperatures as well. Although at 300 K the k_{ph} of 3D graphene is only 1.79 $nWnm^{-2}\ K^{-1}$, much smaller than that of graphene, the k_{el} is very large, finally leading to the total thermal conductance of 3D graphene close to that of graphene [3].

Large thermal conductance is, of course, undesirable for the thermoelectric conversion efficiency. However, the thermoelectric performance of 3D graphene is surprisingly excellent owing to the unique electronic properties. To understand this, the thermal power factor $S^2\sigma$ and the ZT values are displayed in Fig. 2c and d, respectively. It is very interesting that the two curves exhibit very similar trends, and such phenomena were also found in graphene and graphyne [3]. The similarity suggests the electronic properties play a key role in the thermoelectric performance of the system, since both S and σ were obtained from the electronic transmission spectrum. At 300 K, the predicted maximal ZT is 0.21, which is much larger than the values of graphene (ZT = 0.01) and graphyne (ZT = 0.15) at the same temperature [3].

As mentioned before, bulk materials often have low conversion efficiencies. On the contrary, our results verify that 3D graphene, as a typical bulk material, holds outstanding thermoelectric performance. This finding is very interesting and will greatly extend the applications of carbon materials in thermoelectrics, since in many cases the properties of nanomaterials may be unstable or easily affected by external environment.

The thermoelectric conversion efficiency of 3D graphene could be enhanced by introducing defects. These defects will cause additional scattering for phonons and thermal electrons, thus may decrease the thermal conductance and simultaneously increase ZT. Recently, Zhou et al. found the ZT of defective β-graphyne nanoribbon can reach 1.64 at 800 K, which is about six times larger than that of perfect β-graphyne nanoribbon [10]. In addition, in our recent study [16], we found that the thermoelectric performance of γ-graphyne nanoribbon is enhanced by point defects. It is worthy to note here we considered several typical defects, including point defects, line defects and planar defects, to improve ZT. The calculated results show that most of the defects indeed influence the ZT of the system, especially the line defects do effectively enhance the thermoelectric properties of 3D graphene.

Among the defective structures studied here, the one with the best thermoelectric conversion efficiency is given in Fig. 3a. In the structure there exist several line defects and, to stabilize the system, all the dangling bonds of carbon atoms around the line defects are saturated by hydrogen atoms. The thermal stability of the defective 3D (D-3D) graphene has been confirmed by calculating the phonon DOS (see Fig. 3a). The calculated maximal ZT values under different temperatures are shown in Fig. 3b. It is obvious that the ZT becomes much larger if the line defects are introduced. At high temperature 800 K, the maximal ZT is as high as 1.52, very close to the result of defective β-graphyne nanoribbon (ZT = 1.64) at the same temperature [10]. By doping B or N atoms, Muley and Ravindra pointed out that the peak ZT value of armchair graphene

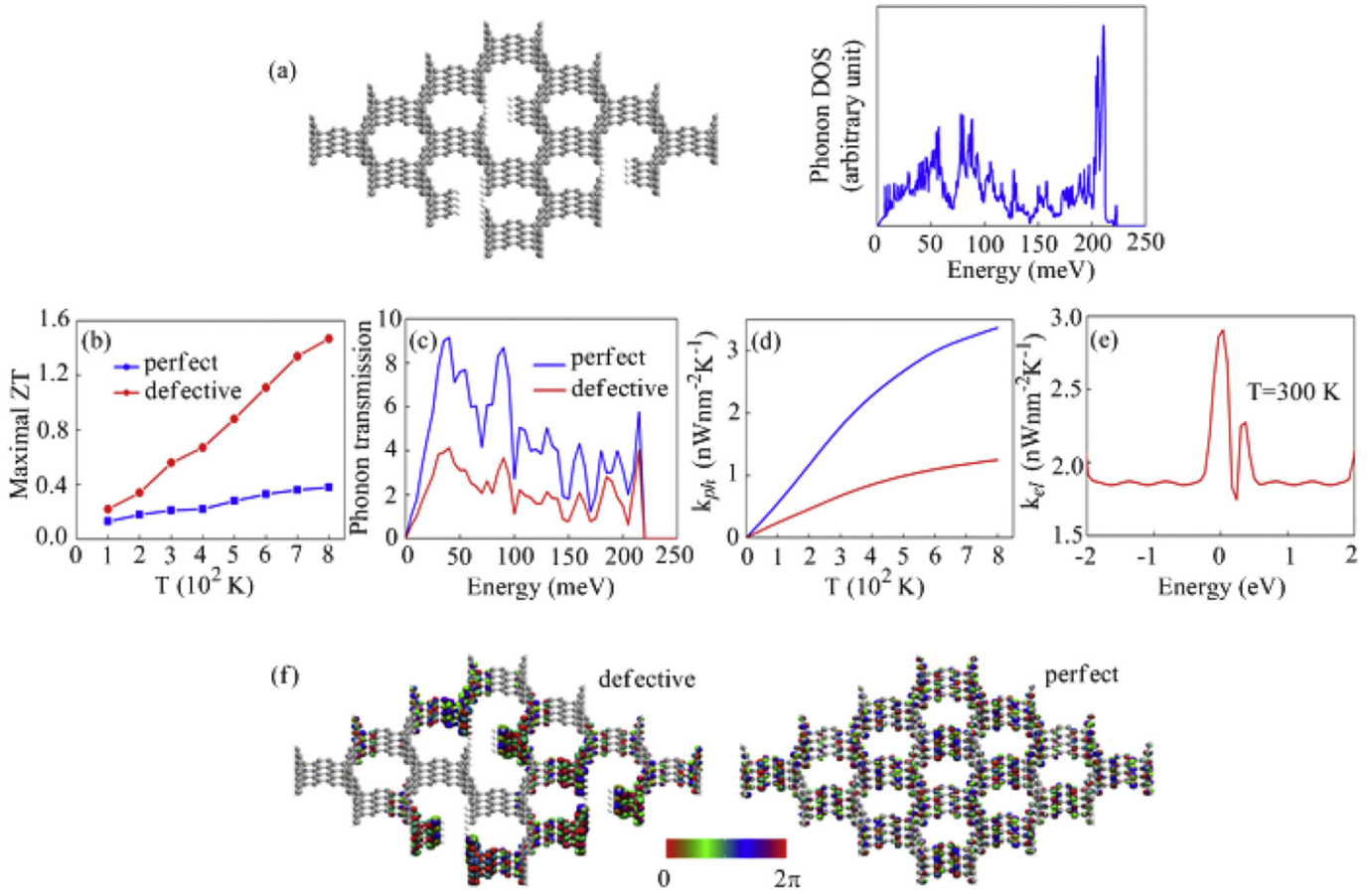

Fig. 3. (a) The structure and phonon DOS of D-3D graphene. (b) The maximal ZT, (c) the phonon transmission spectra, and (d) the phononic thermal conductance of the 3D graphene and D-3D graphene. (e) The electronic thermal conductance of D-3D graphene at 300 K. The Fermi level is set as zero. (f) The transmission eigenstates of the 3D graphene and D-3D graphene.

nanoribbon is about 1.6 [17,18]. Therefore, our results suggest that D-3D graphene has outstanding thermoelectric performance.

The origination of the high thermoelectric conversion efficiency of D-3D graphene is easy to understand. Because the line defects form new scattering centers, the phonons in 3D graphene and D-3D graphene have quite different transport behaviors. As can be seen from Fig. 3c and d, all the phonon transport channels of D-3D graphene are depressed and the k_{ph} notably decreases in a wide temperature range.

At the same time, the defects have a huge influence on the k_{el} as well. To illustrate this, the k_{el} of D-3D graphene at 300 K is shown in Fig. 3e. It is obvious that, compared with that of 3D graphene (see Fig. 2b), the k_{el} curve of the defective structure has quite different trend. Generally speaking, for a given energy, the k_{el} becomes smaller when the line defects are introduced and similar phenomenon is also observed for other temperatures. In a word, these line defects could scatter both phonons and thermal electrons, leading to a decrease in k ($k = k_{el} + k_{ph}$) and enhancement in ZT.

More importantly, when ZT reaches the maximal value, we find the line defects have little negative effect on the electronic properties. This is a very important reason why the ZT of the defective structure can be very high. For example, at 800 K, although the defects could effectively scatter thermal electrons, for the maximal ZT the corresponding transmission eigenstates in 3D graphene and its defective structure are both delocalized (see Fig. 3f), thus the large thermal power factor $S^2\sigma$ keeps nearly unchanged in the two structures. The excellent electronic properties of 3D graphene can be kept in D-3D graphene.

According to the above discussion, present study indicates that the appearance of 3D graphene will provide more opportunities to design carbon-based thermoelectric materials in the near future.

4. Conclusions

In conclusion, the electronic and thermoelectric properties of a new kind of carbon allotrope, 3D graphene, are investigated in present study. Our results show that, near the Fermi level, there exist Dirac cones in this bulk material. More importantly, the thermoelectric properties of 3D graphene are excellent. By introducing line defects, the figure of merit of the defective structure could be enhanced to 1.52, indicating that 3D graphene is a powerful candidate for constructing novel carbon-based thermoelectric materials.

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