Theoretical Study of Carrier Mobility in Two-Dimensional Tetragonal Carbon Allotrope from Porous Graphene *

Song Gao(高松)[1], Hui Xiang(向晖)[1], Bo Xu(徐波)[1**], Yi-Dong Xia(夏奕东)[1**], Jiang Yin(殷江)[1,2], Zhi-Guo Liu(刘治国)[1,2]

[1]*National Laboratory of Solid State Microstructures and Department of Materials Science and Engineering, Nanjing University, Nanjing 210093*

[2]*Collaborative Innovation Center of Advanced Microstructures, Nanjing University, Nanjing 210093*

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The carrier mobility of two-dimensional tetragonal carbon allotrope (T-CA) from porous graphene is investigated by first-principles calculations. T-CA can be constructed from divacancy and Stone–Thrower–Wales defects from graphene. T-CA is a direct semiconductor with a band gap of 0.4 eV at Γ point. T-CA possesses a high carrier mobility of the order of 10^4 $cm^2V^{-1}s^{-1}$. As our study demonstrates, T-CA has potential applications for next-generation electronic materials.

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The discovery of two-dimensional (2D) materials, e.g., graphene,[1–3] has attracted intensive research interests due to their unusual and interesting electronic and mechanical properties. It is well-known that a high-performance device such as a field-effect transistor (FET) requires a moderate electron band gap and reasonably high carrier mobility of the channel material.[4–11] However, pristine graphene offers extremely high carrier mobility, while the absence of a band gap limits its performance in nanotransistors.[4–7]

Great efforts have been devoted to opening the band gap of graphene before its industrial synthesis. The most common strategies use chemical and physical methods, such as oxidation,[12] hydrogenation[13] and fluorination.[14] However, the controlled synthesis of large structures and/or at large scale has been proved to be difficult, and the carrier mobility by these methods is very low owing to their flat bands near the Fermi level. Recently new 2D semiconductors such as transition metal dichalcogenides (TMDs)[15,16] and monolayer black phosphorus (phosphorene)[17] have been developed for this purpose. However, the carrier mobility in TMDs and phosphorene is about two or three orders of magnitude less than that of graphene. Thus the search for 2D planar semiconducting materials with high carrier mobility is still an ongoing task.

An ideal structure would be an allotrope carbon form with an intrinsic good band gap value and electronic bands with good dispersion (electron delocalization and high charge mobility). Numerous carbon allotropes have been proposed.[18–25] For instance, Baughman *et al.*[23] have proposed a novel planar carbon allotrope called graphyne containing both sp and sp^2 hybridized carbon atoms, and the presence of acetylenic linkages in graphyne joining hexagons C_6 together results in a non-zero band gap which is absent in graphene. More recently, Malko *et al.*[24] have examined the electronic properties of these graphyne substructures, so-called α-graphyne, β-graphyne, and 6,6,12-graphyne. It is shown that the existence of Dirac-cone-like features in 2D materials neither depends on a honeycomb structure nor on the hexagonal symmetry. Among these 2D carbon allotropes, most of them are metallic, the semiconductor is scarce. Very recently, Appelhans *et al.*[25] proposed a new 2D tetragonal carbon allotrope (T-CA), constructed from divacancy and Stone–Thrower–Wales defects from graphene, with a band gap of 1.2 eV. Moreover, Nobusue *et al.*[26] succeeded in the synthesis of these kinds of molecular fragments containing octagons, pentagons and hexagons.

In this Letter, we investigate the electronic structure and the carrier mobility of this 2D T-CA based on first-principles calculations. The direct band gap of 0.4 eV is obtained at the Γ point for its monolayer. Our results show that the carrier mobility can reach 10^4 $cm^2V^{-1}s^{-1}$, suggesting that T-graphene would be considered as a good candidate for next-generation electronic materials.

Our density functional theory (DFT) computations are performed by using a plane wave basis set with projector-augmented plane wave (PAW), which is implemented in Vienna ab initio simulation package (VASP).[27–29] The generated gradient approximation (GGA) with the Perdew–Bruke–Ernzerh (PBE) func-

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**Corresponding author. Email: xubonju@gmail.com; xiayd@nju.edu.cn

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tional and a 500 eV cutoff are adopted in all the computations. The vacuum space of 20 Å is large enough to safely avoid the interaction between nanoribbons and their periodic images. All atoms are relaxed and the final force exerted is less than 0.001 eV/Å.

We first characterize the structural and electronic properties of the T-CA, as shown in Fig. 1. The primitive cell of T-CA is tetragonal containing 28 carbon atoms, containing two octagons surrounded by neighboring pentagons and hexagons. The equilibrium primitive cell length a of T-CA is estimated to be 8.774 Å. Therefore, T-CA has an areal density of 0.364 atoms per Å^2, which is slightly less than 0.379 atoms per Å^2 for graphene, while larger than 0.292 atoms per Å^2 for graphyne, and 0.232 atoms per Å^2 for graphdiyne, respectively. There are six distinct bonds in T-CA, ranging from 1.387 to 1.452. All these bond lengths are comparable with 1.420 Å for graphene, suggesting the sp^2-like hybridizing character of T-CA.

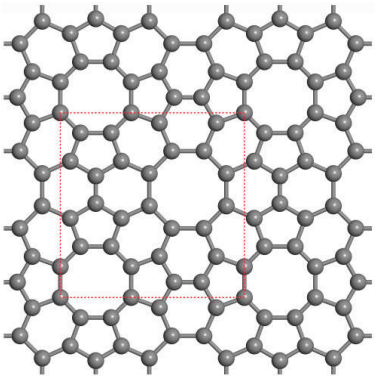

Fig. 1. Optimized crystal structure of 2D T-CA. The square primitive cell is labeled by red dotted lines. It contains two octagons surrounded by neighboring pentagons and hexagons.

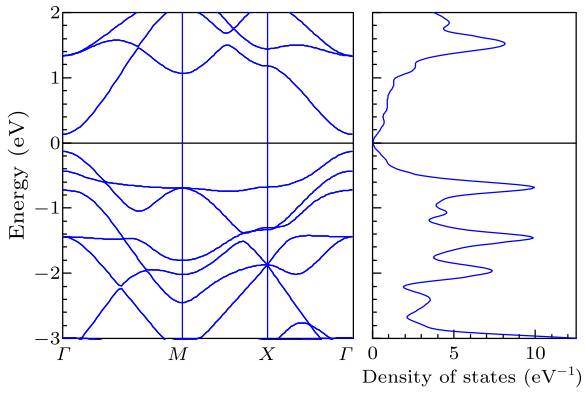

Fig. 2. The band structure and density of states of 2D T-CA.

The calculated electronic band structures, and projected density of states (PDOS) of T-CA are all shown in Fig. 2. It explicitly shows that T-CA is a direct band gap semiconductor at the Γ point. The obtained band gap value of 0.4 eV is also in good agreement with the previous theoretical calculations (0.2 eV).[25] They also predicted that T-CA processes a band gap of 1.2 eV by the GW method, similar to silicon, indicating potential applications for next-generation electronic material. It is clear that both valence band maximum (VBM) and conduction band minimum (CBM) show good dispersion, resulting in low effective mass and large carrier mobility. According to the nearly free electron model fitting those bands, we can estimate the effective mass of the hole as $\sim 0.136 m_0$ (where m_0 is the free electron mass), which is slightly larger than the electron's $0.112 m_0$ for Γ–X direction. The effective masses of hole and electron are, respectively, $0.140 m_0$ and $0.118 m_0$ along the Γ–M direction, which are almost the same as those along the Γ–X direction. To demonstrate their effect on band gap explicitly, we plot spatial distributions of wave functions for VBM and CBM in Fig. 3. It demonstrates clearly that CBM and VBM are localized at pentagons and hexagons, respectively.

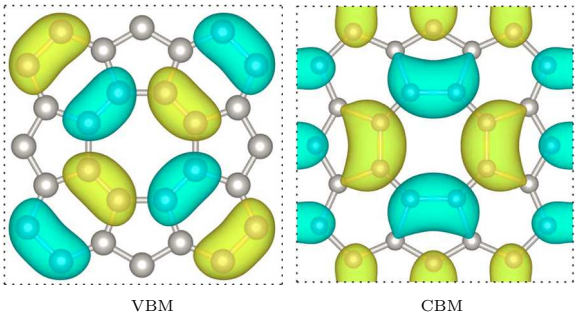

Fig. 3. Spatial distributions of wave functions for VBM and CBM.

Next, we focus our attention on the carrier mobility of T-CA. In 2D materials, the carrier mobility can be calculated by[30,31]

$$\mu = \frac{e\tau}{m^*} = \frac{e\hbar^3 C_{2D}}{k_B T m^* m_a E_1^2}, \tag{1}$$

where e is the electron charge, $\hbar$ is Planck's constant divided by 2π, k_B is Boltzmann's constant, T is the temperature, m^* (m_M^* or m_X^*) is the effective mass in the transport direction, m_a is the averaged effective mass determined by $m_a = (m_M^* m_X^*)^{1/2}$, E_1 is the deformation potential constant of VBM for hole or CBM for electron along the transport direction, defined by $E_1 = \Delta V/(\Delta l/l_0)$, ΔV is the energy change of CBM or VBM under proper cell compression and dilatation, l_0 is the lattice constant in the transport direction, and Δl is the deformation of l_0. The elastic modulus C_{2D} of the longitudinal strain in the propagation directions of the longitudinal acoustic wave is given by $(E - E_0)/S_0 = C_{2D}(\Delta l/l_0)^2/2$, where E is the total energy, and S_0 is the lattice volume at equilibrium for a 2D system. It is noticed that Eq. (1) represents a phonon-limited scattering model.[31]

As described in Eq. (1), the carrier mobility of 2D semiconductor is not completely determined by the effective mass. The other two properties, the deformation potential, E_1, and the 2D elastic modulus, C_{2D}, are also involved. All of these quantities are calculated by the PBE functional, and the corresponding values are summarized in Table 1. For T-CA, the electron mobility is $\sim 3.80 \times 10^4\,\mathrm{cm^2V^{-1}s^{-1}}$ along the Γ–X direction, and $2.69 \times 10^4\,\mathrm{cm^2V^{-1}s^{-1}}$ along the Γ–M direction, the hole mobility is $\sim 1.04 \times 10^4\,\mathrm{cm^2V^{-1}s^{-1}}$ along the Γ–X direction, and $0.97 \times 10^4\,\mathrm{cm^2V^{-1}s^{-1}}$ along the Γ–M direction. Both the electron and hole have very high mobility, only about one order of magnitude less than that of graphene, but two orders of magnitude larger than that of 2D TMDs[15] and phosphorene.[17] The electron mobility is larger than those of holes due to the smaller deformation potential. It is noticed that the directional anisotropy is very weak for both electron and hole, that is, the carrier mobility along the Γ–X direction is slightly larger than that along the Γ–M direction. In T-CA, the high carrier mobility mainly originates from their small effective mass, which is of the order of $0.1m_0$. All of these make T-CA promising for applications in the semiconducting industry.

Table 1. Predicted carrier mobility in T-CA.

Type		Effective mass m^* (m_0)	Elastic modulus C_{2D} (N/m)	Deformation potential E_1 (eV)	Carrier mobility μ ($10^4\,\mathrm{cm^2V^{-1}s^{-1}}$)
Electron	Γ–X	0.112	283.3	−2.90	3.80
	Γ–M	0.118	290.4	−3.4	2.69
Hole	Γ–X	0.136	283.3	−4.75	1.04
	Γ–M	0.140	290.4	−4.90	0.97

In summary, we have investigated the carrier mobility of 2D T-CA from first-principles calculations. Our results show that 2D T-CA possesses high carrier mobilities (around $10^4\,\mathrm{cm^2V^{-1}s^{-1}}$), indicating that 2D T-CA is an ideal semiconducting material that has significant potential for applications in nanoelectronics and optoelectronics.

The calculations were performed on parallel computers at the High Performance Computing Center of Nanjing University.

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