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T-Carbon: An Amazing Carbon Allotrope

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A structurally stable crystalline carbon allotrope is predicted by means of the first principles calculations. This allotrope can be derived by substituting each atom in diamond with a carbon tetrahedron, and possesses the same space group $Fd\bar{3}m$ as diamond, which is thus coined as T-carbon. The calculations on geometrical, vibrational and electronic properties reveal that T-carbon, with a considerable structural stability and a much lower density 1.50 g/cm^3, is a semiconductor with a direct band gap about 3.0 eV, and has a Vickers hardness 61.1 GPa lower than diamond but comparable with cubic boron nitride. Such a form of carbon, once obtained, would have wide applications in photocatalysis, adsoption, hydrogen storage and aerospace materials.

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Carbon is the element that plays a fundamental role for life on Earth. As it can form sp^3-, sp^2- and sp-hybridized chemical bonds, carbon has strong ability to bind itself with other elements to generate countless organic compounds with chemical and biological diversity, resulting in the present colorful world. In nature, elemental carbon has three best-known allotropes, say, graphite, diamond and amorphous carbon. These forms have been long studied, and their chemical and physical properties are well disclosed nowadays. Since 1980s, people have great interest in synthesizing new allotropes of elemental carbon. The most successful examples include fullerenes [1], carbon nanotubes [2], and graphene [3]. These synthesized allotropes give rise to enormous scientific and technological impacts in relevant areas of chemistry, physics, materials and information sciences, leading to many derivatives, devices and products. With advances of synthetic tools, a variety of elusive carbon allotropes such as one-dimensional sp-carbyne, two-dimensional sp-sp^2-graphyne, and three-dimensional (3D) sp-sp^3-yne-diamond, were also obtained or predicted (for review see e.g. Refs. [4, 5]). Recently, an allotrope of carbon has been obtained by compressing graphite with pressure over 17 GPa, whose hardness is even larger than diamond [6], while its structure is unknown so far. Several carbon crystalline phases, e.g., monoclinic M-carbon [7] and bct C$_4$ carbon [8], were therefore proposed to simulate this synthesized phase. Moreover, there are still other experimental and theoretical efforts paid on carbon (e.g. [9, 10]). It appears that we might enter into the era of carbon allotropes [5].

In this Letter, by means of the first principles calculations we predict a new allotrope of elemental carbon that has very intriguing physical properties. This structure can be obtained by substituting each atom in diamond by a carbon tetrahedron, forming a 3D cubic crystalline carbon that possesses the same space group $Fd\bar{3}m$ as diamond. This form is thus dubbed as the T-carbon. The calculated results show that T-carbon, kinetically stable and with a much lower density 1.50 g/cm^3, has a Vickers hardness 61.1 GPa smaller than diamond (93.7 GPa) but comparable with the cubic boron nitride. Electronic structures reveal that it is a semiconductor with a direct band gap around 3.0 eV. The possibility of hydrogen storage in T-carbon is also examined.

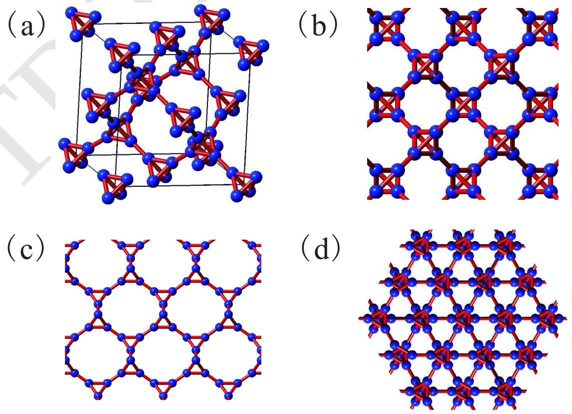

FIG. 1: (Color online) Schematic depiction of the structure of T-carbon. (a) The cubic crystalline structure of T-carbon that is obtained by replacing each atom in diamond by a carbon tetrahedron, where the lattice constant is 7.52 Å; (b)-(d) are views from [100], [110] and [111] directions of T-carbon, respectively.

Most calculations were performed within the density-functional theory [11, 12] as implemented within the Vienna *ab initio* simulation package (VASP) [13, 14] with the projector augmented wave (PAW) method [15]. Both local density approximation (LDA) in the form of Perdew-Zunger [16] and generalized gradient approximation (GGA) developed by Perdew and Wang [17] were adopted for the exchange correlation potential. The plane-wave cutoff energy is taken as 400 eV. The Monkhorst-Pack scheme was used to sample the Brillouin zone [18], and a mesh of 8×8×8 k-point sampling was used for the calculations. The geometries were opti-

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TABLE I: The lattice constant (l), equilibrium density (ρ), bond length (d), cohesive energy (E_{coh}), energy gap (E_g), bulk modulus (B) and Vickers hardness (H_v) at zero pressure of cubic diamond (c-diamond), hexagonal diamond (h-diamond), graphite, M-carbon, bct C_4, and T-carbon.

Structure	Method	l (Å)	ρ (g/cm^3)	d (Å)	E_{coh} (eV/atom)	E_g (eV)	B (10^2 GPa)	H_v (GPa)
c-diamond	GGA	3.566	3.52	1.544	7.761	4.16	4.64	93.7
c-diamond	LDA	3.529	3.63	1.529	8.859	4.22	5.05	99.0
c-diamond	Exp [20, 21]	3.567	3.52	1.54	7.37	5.45	4.43	96±5
h-diamond	GGA	2.506,4.169	3.52	1.539,1.561	7.732	3.13	4.30	92.8
Graphite	Exp [22]	2.46,(c=2.7a-2.73a)	2.27-2.28	1.42	7.374	-	2.86-3.19	
Graphite	GGA	2.462,6.849	2.22	1.422	7.891	-	2.94	
M-Carbon	GGA	9.09,2.50,4.10	3.45	1.488-1.607	7.636	3.56	4.20	91.5
Bct C_4	GGA	4.33,2.48	3.35	1.507,1.561	7.533	2.47	4.09	92.2
T-carbon	GGA	7.52	1.50	1.502,1.417	6.573	2.25	1.69	61.1
T-carbon	LDA	7.45	1.54	1.488,1.404	7.503	2.22	1.75	63.7

mized when the remanent Hellmann-Feynman forces on the ions are less than 0.01 eV/Å. The calculations of phonon spectra and electronic structures were performed using Quantum-ESPRESSO package [19], where 8×8×8 k-mesh was used.

Inspired by the structural connection between methane and tetrahedrane, where the latter can be obtained by replacing each carbon atom in methane with a carbon tetrahedron, we may construct, likewise, a new allotrope of carbon by substituting each carbon atom in diamond by a carbon tetrahedron, as indicated in Fig. 1. Luckily, the stability of such a structure was verified and optimized by the first principles calculations. In this new structure, each unit cell contains two tetrahedrons with eight carbon atoms, and the lattice constant is about 7.52 Å. The three unit vectors are $\vec{a} = l/2(1,1,0)$, $\vec{b} = l/2(0,1,1)$ and $\vec{c} = l/2(1,0,1)$. The carbon atoms occupy the Wyckoff position 32e (x,x,x) with $x = 0.0706$. The lattice constant (l), equilibrium density (ρ), bond length (d), cohesive energy (E_{coh}), energy gap (E_g) between valence and conduction bands, bulk modulus (B) and Vickers hardness (H_v) at zero pressure of cubic and hexagonal diamond, graphite, M-carbon, bct C_4, and T-carbon are computed and summarized in Table I for a comparison. Note that all data presented here, apart from the sources indicated, were obtained by ourselves using the same method as the T-carbon, which can thus be compared reasonably at the same level. It is seen that there exist two distinct bonds with length 1.502 Å (intra-tetrahedron) and 1.417 Å (inter-tetrahedron) for T-carbon, respectively, both of which are smaller than those of diamond. There are also two different bond angles, 60° in tetrahedron, and 144.74° between two inequivalent bonds. The former is much less than that in diamond (109.5°), implying that a strain exists in T-carbon higher than that in diamond, which probably leads to the raise of the total energy. Indeed, our calculations confirm that the cohesive energy per atom of the T-carbon is 6.573 eV, around 1 eV/atom smaller than other forms of carbon at the GGA level, suggesting that this structure might be less thermodynamical stable against those allotropes at zero pressure. The remarkable feature is that the equilibrium density (ρ) of T-carbon is the smallest (1.50 g/cm^3) among diamond, graphite, M-carbon and bct C_4. This is conceivable, because T-carbon, if compared with other forms of carbon, has large interspaces between carbon atoms along certain directions (Fig. 1), and the volume per atom is about twice larger than those of diamond, M-carbon and bct C_4, or 1.5 times larger than graphite, while its bulk modulus is only 36.4% of cubic diamond. Owing to the large interspaces between atoms, the hydrogen storage in T-carbon may be expected. Our computations show that it is indeed possible to store hydrogen molecules into the T-carbon, and the gravimetric and volumetric hydrogen capacities are calculated to be around 7.7 wt % and 0.12 Kg H_2/l, respectively.

Similar to c-diamond, T-carbon has also three elastic constants, C_{11}, C_{12} and C_{44}, which are calculated with GGA to be 225 GPa, 141 GPa and 89 GPa, respectively. With the Voigt-Reuss-Hill approximation [23], we can acquire the bulk and shear modulus of T-carbon, say 169 GPa and 70 GPa, respectively. The Vickers hardness H_v of T-carbon is 61.1 GPa that is obtained from an empirical formula [24] $H(GPa) = 350[(N_e^{2/3})e^{-1.191f_i}]/d^{2.5}$, where N_e is the electron density of valence electrons per Å^3, d is the bond length, and f_i is the ionicity of the chemical bond in a crystal scaled by Phillips [25]. Following the same settings, the Vickers hardness of diamond is obtained to be 93.7 GPa (in comparison to the experimental value 96 ± 5 GPa). In this sense, T-carbon is around 1/3 softer than diamond, and is comparable with the c-BN (whose H_v is 64 GPa [24]). These above features together with a much lower density suggest that the T-carbon, once synthesized, might have broad applications.

Fig. 2 plots the total energy per atom against the volume per atom for the T-carbon, hexagonal diamond, cubic diamond, graphite, M-carbon and bct C_4 allotropes. It can be observed that the total energy of T-carbon as a function of volume per atom has a single minimum, showing that the geometrical structure would be stable. For a comparison, we also calculate the total energies per atom for other allotropes of carbon, and observe that the minimum total energy per atom of graphite is the lowest, and the other allotropes bear higher minimum total energies per atom, while that of T-carbon is the highest, say -7.92 eV/atom, suggesting that T-carbon could be a thermodynamically metastable phase against diamond, graphite, M-carbon and bct-C_4 allotropes.

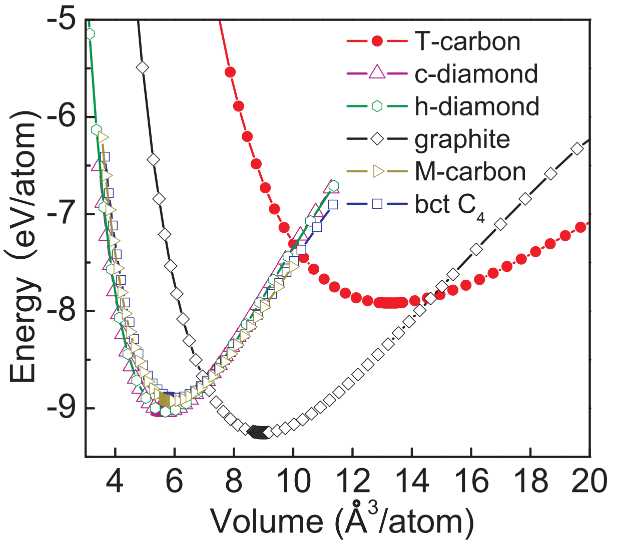

FIG. 2: (Color online) The total energy per atom as a function of volume per atom for T-carbon, cubic diamond (c-diamond), hexagonal diamond (h-diamond), graphite, M-carbon and bct C_4 allotropes.

To confirm further the mechanical stability, the phonon spectra of T-carbon are calculated, as shown in Fig. 3. No imaginary phonon modes in T-carbon are found, implying again the kinetical stability of T-carbon. The highest phonon frequency of T-carbon is about 1760 cm^{-1}, larger than that of diamond (1303 cm^{-1}). It is instructive to note that there exists a wide direct band gap (325 cm^{-1}) of phonons between the frequency 739 - 1064 cm^{-1} at Γ point.

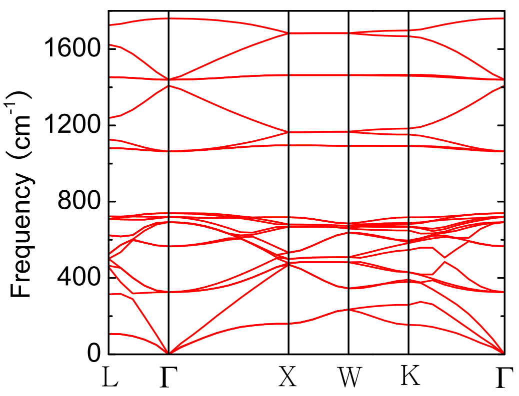

FIG. 3: (Color online) Phonon band structure of T-carbon.

To provide more information and characters for possible experimental observation, we also simulate the X-ray diffraction (XRD) spectra of T-carbon and c-diamond with wavelength 1.54059 Å. The results are presented in Fig. 4. Different from diamond where the peaks of (111) at $2\theta = 43.94°$, (022) at 75.31° and (113) at 91.51° are observed obviously, only one sharp XRD peak of (111) at 20.44° with a strong intensity is seen for T-carbon, and the peaks of (022) at 33.68°, (222) at 39.72°, (133) at 50.7°, (115) at 61.35° are negligibly small. This is very similar to graphite, where a sharp XRD peak of (002) appears with several other small peaks. These features may be helpful for identifying the T-carbon in experiments.

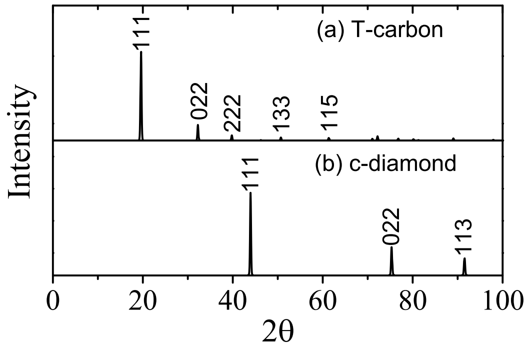

FIG. 4: (Color online) Simulated XRD patterns of T-carbon and c-diamond. The X-ray wavelength we use is 1.54059 Å.

Now let us look at the electronic structures and density of states (DOS) of T-carbon, as given in Fig. 5. One may see that at the GGA level there is a direct band gap 2.25 eV at Γ point, suggesting that the T-carbon is a direct-band-gap semiconductor. From the DOS, the band gap is also clearly indicated. To calculate the band gap more accurately, the B3LYP (Becke, three-parameter, Lee-Yang-Parr) exchange-correlation functional [26, 27] is used. The band gap of T-carbon is obtained to be 2.968 eV. We also note that the band gap of T-carbon can be manipulated by doping, which would be useful for photocatalysis. With the same method, the band gap of c-diamond is calculated to be 5.799 eV, being comparable with its experimental value 5.45 eV. In addition, the computations on the projected DOS (PDOS) of each carbon atom show that the PDOS for $2p_x$, $2p_y$ and $2p_z$ orbitals are the same, much larger than that of $2s$ orbitals, illustrating that the wave functions of valence electrons in the T-carbon are recombined, leading to extreme anisotropic sp^3-hybridized bonds. Particularly, the charge population analysis reveals that the electron density around the inter-tetrahedron bonds is much higher than that on the intra-tetrahedron bonds, showing that the inter-tetrahedron bonds are relatively strong, which are also consistent with their short bond length, and can balance the strain of the carbon tetrahedron cage, thereby making the whole structure stable.

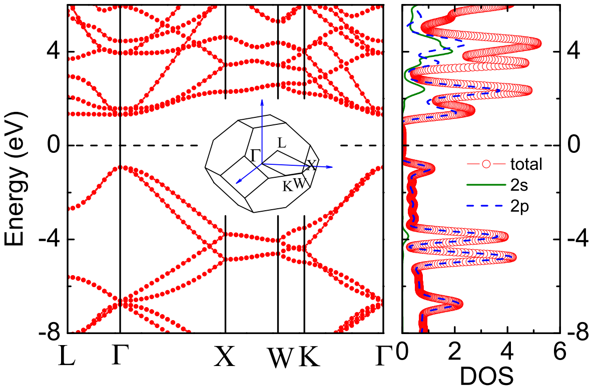

FIG. 5: (Color online) Electronic band structures and density of states (DOS) of T-carbon.

In summary, we have predicted a novel carbon allotrope dubbed as T-carbon that has the same space group $Fd\bar{3}m$ as diamond by means of the first-principles calculations. This new structure can be derived by substituting each atom in diamond with a carbon tetrahedron, and its structural stability is checked and optimized at both LDA and GGA levels. The calculations on the mechanical and electronic properties of T-carbon show that it is, with a much lower density and a bulk modulus than diamond, a semiconductor with a direct band gap about 3.0 eV. The Vickers hardness of T-carbon is found 35% smaller than cubic diamond but comparable with that of cubic boron nitride. The XRD pattern is observed to have features similar to that of graphite. The possibility of hydrogen storage in T-carbon is also attested. Upon obtained, the amazing T-carbon would have wide applications in photocatalysis, adsorption, hydrogen storage, and aerospace materials.

All calculations are completed on the supercomputer NOVASCALE7000 in Computer Network Information Center (Supercomputing center) of Chinese Academy of Sciences (CAS) and MagicCube (DAWN5000A) in Shanghai Supercomputer Center. This work is supported by the National Science Foundation of China (Grant Nos. 90922033, 10934008, 10974253, and 11004239), and the CAS.

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