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Computational Prediction of a Novel Superhard sp^3 Trigonal Carbon Allotrope with Bandgap Larger than Diamond

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Searching for new carbon allotropes with superior properties has been a longstanding interest in material sciences and condensed matter physics. Here we identify a novel superhard carbon phase with an 18-atom trigonal unit cell in a full-sp^3 bonding network, termed tri-C_{18} carbon, by first-principles calculations. Its structural stability has been verified by total energy, phonon spectra, elastic constants, and molecular dynamics simulations. Furthermore, tri-C_{18} carbon has a high bulk modulus of 400 GPa and Vickers hardness of 79.0 GPa, comparable to those of diamond. Meanwhile, the simulated x-ray diffraction pattern of tri-C_{18} carbon matches well with the previously unexplained diffraction peaks found in chimney soot, indicating the possible presence of tri-C_{18} carbon. Remarkably, electronic band structure calculations reveal that tri-C_{18} carbon has a wide indirect bandgap of 6.32 eV, larger than that of cubic diamond, indicating its great potential in electronic or optoelectronic devices working in the deep ultraviolet region.

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Carbon is capable of forming different kinds of allotropes with remarkable properties due to its *sp*-, sp^2- and sp^3-hybridized states.[1] Graphite consisting entirely of sp^2-bonded networks exhibits a good ductility and electrical conduction. In contrast, because of the complete sp^3 bonds, diamond possesses many extraordinary properties such as the highest hardness, wide bandgap, high carrier mobility, chemical inertness and unmatched thermal conductivity, presenting fascinating applications in various fields.[2–6] The discoveries of fullerenes,[7] carbon nanotubes,[8] graphene[9] and C_{18} carbon rings[10] have triggered enormous interest in designing and synthesizing other carbon materials in recent years. The quest for novel carbon polymorphs with desired structure and properties has always been a very intriguing and long-standing pursuit.

Carbon allotropes consisting of fully sp^3-hybridized bonds have attracted increasing attention experimentally and theoretically, which show superior mechanical and electrical properties and are expected to offer opportunities in electronic or optoelectronic devices. In this pursuit, it has been shown that cold compression of raw carbon precursors that completely converted their sp^2 to sp^3 bonds is a particularly appealing approach to synthesizing such allotropes that are different from diamond.[11–25] For example, cold-compressed graphite and carbon nanotubes have been reported to produce sp^3-rich superhard phases,[11,12] while their structures are difficult to identify due to the inadequate quality of the experimental diffraction data. This leads to much theoretical efforts to solve the puzzling structures and several superhard sp^3-hybridized structural models (i.e., bct C_4, *M*-carbon, *W*-carbon, Cco-C_8 and *R*/*P* carbon) have been proposed.[26–33] Meanwhile, various carbon forms are also proposed as candidate structures for unsolved carbon crystals discovered in previous experiments, including body-centered cubic carbon (BC12),[34] R16,[35] simple cubic carbon (C20-sc),[36] C14 carbon,[37] T carbon.[38] Recently, a fully sp^3-hybridized *V*-carbon with high hardness comparable to diamond was identified by cold-compressed C_{70} peapods with the assistance of computational prediction.[39] These advances indicate that theoretical predictions are necessary as a powerful tool for explaining experimental observations or predicting novel carbon phases. However, these proposed sp^3 carbon structures are mostly confined to potential applications within the visible or near infrared light region resulting from their narrow bandgaps. Novel energetically stable carbon allotropes with intrinsic

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wide bandgap working in the ultraviolet region have great potential in deep ultraviolet electronic or optoelectronic devices, but have been rarely reported.[40]

In this work, based on an unbiased structure searching method, we predict a novel all-sp^3 hybridized carbon allotrope in $P3_221$ symmetry. The newly identified carbon structure that has been checked by the SACADA database[41] contains eighteen atoms in its trigonal unit cell, hereafter referred to as tri-C_{18} carbon. Total energy calculations show that it is energetically favorable in comparison with those metastable carbon allotropes previously predicted, and the dynamic stability is carefully verified by phonon and molecular dynamics simulations. In addition, the calculated bulk modulus and Vickers hardness indicates that tri-C_{18} carbon is a superhard material. The excellent match between the simulated and measured x-ray diffraction (XRD) patterns indicates the possible presence of tri-C_{18} carbon in chimney soot samples. Electronic band structure results reveal that tri-C_{18} carbon possesses a wide indirect bandgap of 6.32 eV. These findings establish a new carbon phase and provide insight into its attractive structural and electronic properties.

Computational Methods. Crystal structure search via the particle swarm optimization as implemented in the CALYPSO code was performed with cell size up to 18 carbon atoms in the pressure range of 0–100 GPa.[42–47] First-principles calculations based on density functional theory were carried out by the Vienna *ab initio* simulation program package (VASP).[48] The generalized gradient approximation (GGA) in the form of Perdew–Burke–Ernzerhof (PBE)[49] function was used to describe the electron exchange-correlation potential. The energy cutoff for the plane-wave basis was set to 500 eV for all calculations. The electronic self-consistent relaxation and ionic relation of 10^{-8} eV and 10^{-3} eV/Å for energy and force were employed to guarantee well converged total energies. A resolution of 0.2 $Å^{-1}$ for the Monkhorst–Pack Brillouin zone sample grids was tested to ensure the accuracy. A hybrid density functional method based on the Heyd–Scuseria–Ernzerhof scheme (HSE06)[50] was also used for improving the accuracy of electronic structure calculations. A $2 \times 2 \times 2$ supercell containing 144 atoms was created to calculate the phonon dispersion curves under 0 GPa and 90 GPa using the phonon package[51] with the forces calculated from VASP. The elastic constants and the bulk modulus were calculated using Voigt–Reuss–hill (VRH) approximations.[52] The Vickers hardness was estimated using the model reported by Chen *et al.*[53] The first-principles molecular dynamic (MD) simulations in the canonical (NVT) ensemble were performed to examine the thermal stability at temperatures of 300 and 1000 K.

Results and Discussion. Figure 1 shows the optimized crystal structure of the tri-C_{18} carbon at zero pressure with the lattice parameters $a = b = 5.9597$ Å, $c = 3.4775$ Å, respectively. The covalent network contains a complex carbon rings topology pattern, which is different from other reported sp^3 carbon structures that usually comprise of $5 + 6 + 7$ or $4 + 6 + 8$ ring patterns.[32] Four types of inequivalent carbon atoms C_1, C_2, C_3 and C_4 occupy the Wyckoff positions at 6c (0.8103 0.6745 0.1072), 6c (0.7858 0.3674 0.6332), 3b (0.6217 0.0000 0.1667) and 3a (0.8982 0.0000 0.6667), respectively. All carbon atoms of the tri-C_{18} structure are bonded to each other with tetrahedral coordination, forming pure sp^3-hybridized bonds. The calculated average C–C bond length is about 1.58 Å, which is slightly larger than that of diamond (1.54 Å).

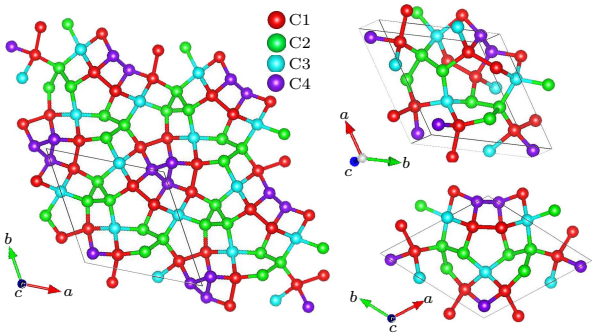

Fig. 1. (a) Crystal structure of the tri-C_{18} carbon in $2 \times 2 \times 1$ supercell. (b) Three-dimensional view and (c) view along the c axis of the tri-C_{18} carbon in its unit cell.

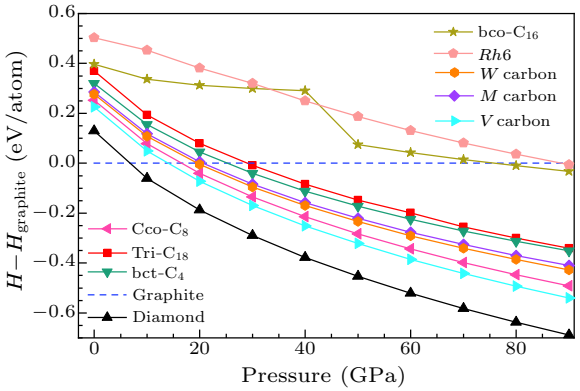

Fig. 2. Enthalpy per atom, H, for tri-C_{18} carbon and previously predicted carbon allotropes versus pressure relative to graphite-2H.

Figure 2 displays the calculated enthalpy per atom for tri-C_{18} carbon compared with graphite, diamond and some previously predicted carbon allotropes. It is clearly seen that tri-C_{18} carbon is energetically comparable to previously reported M carbon,[27] W carbon[29] and V carbon,[39] but more favorable than bco-C_{16} carbon[54] and $Rh6$ carbon.[55] Note that when the pressure exceeds about 28.9 GPa, tri-C_{18} carbon becomes stable with respect to graphite, suggesting that it could be synthesized under high pres-

sure. To examine the dynamic stability of the tri-C_{18} carbon, its phonon spectra at zero and 90 GPa have been calculated, as shown in Figs. 3(a) and 3(b). No imaginary frequencies throughout the entire Brillouin zone exist in both phonon dispersion curves, thus confirming that the tri-C_{18} carbon is dynamically stable. The highest phonon frequency of C–C bond stretching mode in tri-C_{18} carbon at ambient pressure reaches about 43 THz, close to that in diamond (40 THz), which means relatively strong C–C bonds in the tri-C_{18} structure. To further verify the thermodynamic stability of tri-C_{18} carbon, we have performed molecular dynamics simulations. A $2 \times 2 \times 2$ supercell containing 144 carbon atoms with a time step of 1 fs during the simulation was used. Figures 3(c) and 3(d) show the fluctuations of potential energy as a function of simulation time. It can be seen that the skeleton of the tri-C_{18} carbon remains nearly intact at 300 and 1000 K after 8000 steps, respectively, indicating the thermal stability of the tri-C_{18} carbon even at high temperature up to 1000 K. Therefore, once synthesized under appropriate experimental conditions, it can remain stable under ambient conditions.

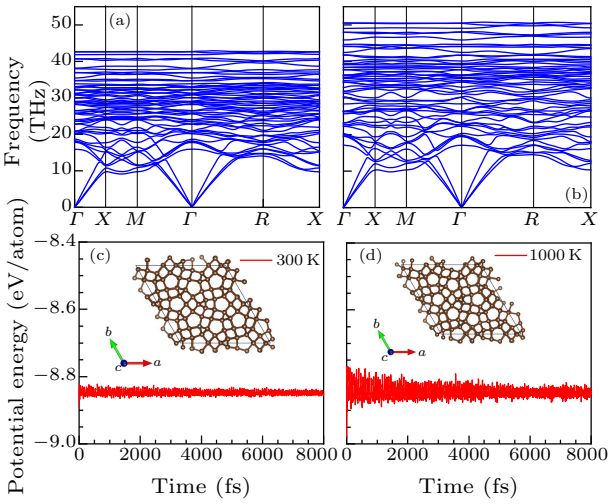

Fig. 3. Calculated phonon dispersion curves of tri-C_{18} carbon at (a) 0 and (b) 90 GPa. The energy fluctuations of tri-C_{18} carbon as a function of the molecular dynamic simulation step at (a) 300 and (b) 1000 K, respectively. The inset shows the snapshot of tri-C_{18} structure after 8000 steps.

Table 1. Calculated equilibrium density ρ, bulk modulus B_0, shear modulus G_0, Vickers hardness H_v, and bandgap E_g for tri-C_{18} carbon, diamond, M-carbon, W-carbon, bct C_4, Cco-C_8, and V carbon at zero pressure, in comparison with available experimental data and other theoretical values.

Structure	Method	ρ (g/cm^3)	B_0 (GPa)	G_0 (GPa)	H_v (GPa)	E_g (eV)
Diamond	This work	3.50	435.0	516.0	92.6	5.29
	GGA[38]	3.52	464.0		93.7	4.16
	Exp.[56]	3.52	443.0	538.0	96 ± 5	5.47
bct C_4	This work	3.31	402.3	475.0	86.4	2.51
	GGA[38]		409.0		92.2	2.47
M-carbon	This work	3.41	412.5	478.7	85.0	3.49
	GGA[38]	3.45	420.0		91.5	3.56
	LDA[27]		431.2		83.0	3.60
W-carbon	This work	3.35	399.0	477.1	87.9	4.37
	GGA[57]	3.35	401.0	452.1	89.5	
Cco-C_8	This work	3.38	409.3	475.0	84.6	3.33
	GGA[57]	3.40	410.0	470.7	90.2	
V carbon	This work	3.41	420.8	475.8	82.0	4.50
	GGA[39]	3.41	411.0		89.4	4.48
Tri-C_{18}	This work	3.36	400.0	449.9	79.0	6.32

The elastic constants C_{ij} of the tri-C_{18} carbon have been calculated to evaluate its mechanical stability. For a stable trigonal lattice, six independent elastic constants should obey the Born stability criteria:[58] $C_{11} - C_{12} > 0$, $(C_{11} + C_{12})\, C_{33} > 2C_{13}^2$, $(C_{11} - C_{12})\, C_{44} > 2C_{14}^2$, $C_{44} > 0$. Our calculated elastic constants C_{11}, C_{12}, C_{13}, C_{14}, C_{33} and C_{44} are 994.6, 90.2, 139.6, −11.9, 877.0 and 487.5 GPa, respectively. These values obviously satisfy all the above conditions, confirming the mechanical stability of the tri-C_{18} carbon. The calculated data of tri-C_{18} carbon at zero pressure are summarized in Table 1, for comparison, with the corresponding data of diamond and several other carbon allotropes also listed. The density of the tri-C_{18} carbon is 3.36 g/cm^3, which is comparable to diamond (3.50 g/cm^3). Using the Voigt–Reuss–Hill approximations, the bulk modulus (B_0) and shear modulus (G_0) are estimated to be 400 and 445 GPa, respectively. The B/G value of the tri-C_{18} carbon is 0.90, revealing its brittle character. It is known that the bulk modulus and shear modulus govern the indentation hardness of a structure. According to the hardness model demonstrated by Chen *et al.*,[53] we obtained a Vickers hardness (H_v) of 79.0 GPa. Therefore, the tri-C_{18} carbon is a potential superhard phase of carbon allotrope.

Figures 4(a) and 4(b) show the electronic band structures and density of states (DOS) for tri-C_{18} carbon from the PBE and HSE06 methods. It can be seen that the valence band maximum (VBM) and conduc-

tion band minimum (CBM) of the tri-C_{18} carbon are located at the L and the A points, respectively. It has an indirect PBE bandgap of 5.01 eV and its corresponding HSE06 gap is 6.32 eV, which is larger than that of diamond (5.29 eV using HSE06). The HSE06-based largest bandgap is 7.25 eV in the known carbon allotrope family.[40] This makes it a potential candidate material in the field of future electronic or optoelectronic devices working in the deep ultraviolet region. Meanwhile, from the projected density of states and band-decomposed partial charge density distribution [Figs. 4(c) and 4(d)], one can see that the states around the CBM and VBM points mainly stem from the C_1 and C_2 atoms.

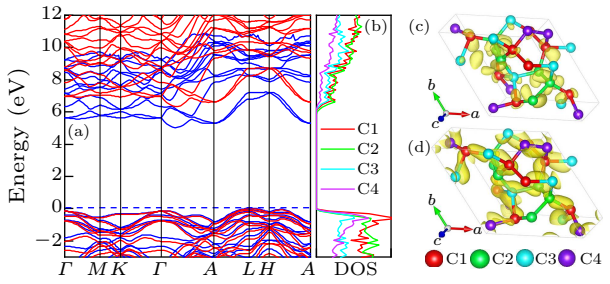

Fig. 4. (a) Electronic band structures and (b) density of states of tri-C_{18} carbon at zero pressure using PBE (blue lines) and HSE06 (red lines) functional at ambient temperature. Partial charge density distribution of the (c) downmost conduction band and (d) topmost valence band with an isosurface value of 0.075 $e/Å^3$, mainly coming from the C_1 and C_2 atoms.

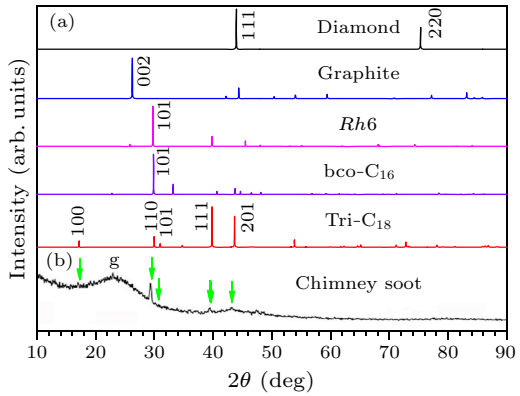

Fig. 5. (a) Simulated XRD patterns for diamond, graphite, *Rh*6,[35] bco-C_{16}[54] and tri-C_{18} carbon. The x-ray wavelength is 1.5406 Å. (b) Experimental XRD pattern for the chimney soot samples.[59] Arrows indicate the peaks of the tri-C_{18} carbon observed in the experiment, and g denotes graphite.

Finally, to further provide structural information for the identification of tri-C_{18} carbon in experiment, we compared its simulated XRD pattern, along with those of graphite, diamond, *Rh*6, and bco-C_{16} carbon, with the experimental data from the chimney soot of a domestic fireplace,[59] as shown in Fig. 5. Five main peaks of tri-C_{18} carbon appear at 17.16°, 29.96°, 30.98°, 39.80° and 43.64°, which are very close to the experimental diffraction peaks of the chimney soot sample, and their peaks are located at around 17.15°, 29.46°, 30.22°, 39.45° and 43.19°, respectively. Note that two carbon structures *Rh*6 and bco-C_{16} have been suggested as candidates since the prominent (101) peak of each is close to the strong peak at 30° in the measured XRD spectra, but determining the crystal structure through only one peak remains controversial. Meanwhile, tri-C_{18} carbon is energetically more stable than *Rh*6 and bco-C_{16} (see Fig. 2). Therefore, the good match between the simulated and experimental XRD patterns suggests that tri-C_{18} carbon is a most likely candidate structure for the yet unidentified carbon phase observed in the chimney soot samples.

In conclusion, we have predicted a novel carbon phase named tri-C_{18} carbon. First principles calculations show that the tri-C_{18} carbon is dynamically, mechanically and thermally stable. Computational predication reveals that the tri-C_{18} carbon has a Vickers hardness of 79.0 GPa and a bulk modulus 400 GPa, which are comparable to those of diamond. The wide bandgap of 6.32 eV makes it a promising candidate for the future electronic or optoelectronic devices working in the deep ultraviolet region. Simulated XRD patterns show a favorable match between this carbon structure and the unidentified carbon phase found in chimney soot. Our results resolve the yet unknown carbon phase produced in chimney soot and may stimulate further exploration of the unique properties and potential applications of this kind of novel carbon allotrope.

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