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Full paper

A new metallic carbon allotrope with high stability and potential for lithium ion battery anode material

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ABSTRACT

Metallic carbon has been extensively studied for its potential novel applications in catalysis, superconductivity, and electronic devices. Currently, the design of metallic carbon is mainly by educated intuition which could miss some more stable allotropes. Here we carry out a global structure search on the potential energy surface, and identify a new three-dimensional (3D) metallic carbon phase, termed Hex-C_{18}, which is energetically more favorable than most of the previously identified 3D metallic carbon allotropes. Using state-of-the-art theoretical calculations, we show that Hex-C_{18} not only possesses a high thermodynamic stability, large heat capacity, high Debye stiffness, anisotropic elasticity, and super hardness, but also is a promising anode material for lithium ion batteries (LIBs). As compared to graphite commercially used in LIBs, Hex-C_{18} exhibits a lower Li diffusion energy barrier and a higher Li capacity because of its intrinsic metallicity and regular porosity. In addition, the simulated x-ray diffraction of Hex-C_{18} matches well with a previously unidentified low-angle diffraction peak in experimental XRD spectra of detonation soot, implying the possibility of its existence in the specimen. This study expands the family of metallic carbon, and may open a new frontier in design of high performance anode materials for LIBs as well.

1. Introduction

With versatile flexibilities of bonding in *sp*-, sp^2- and sp^3-hybridizations, carbon exhibits an amazing ability to form a tremendous number of allotropes with many unique physical and chemical properties [1,2]. Among the rich carbon phases, metallic carbon has attracted increasing interest in recent years because of its fascinating properties. It was found that metallic carbon displays a superior catalytic effect [3] attributed to its high density of states (DOS) at the Fermi level. For instance, metallic carbon nanotubes have been used as electrodes for electrocatalysis [4], and metallic carbon nanotube networks can dramatically increase the electrocatalytic activities of an enzyme-based electrode [4]. It was reported that metallic carbon can be magnetic when the Stoner-like criterion is satisfied [5]. In addition, it has been demonstrated, both theoretically and experimentally, that metallic carbon can exhibit strong phonon-plasmon coupling [6], negative differential resistance [7], and superconductivity [8,9]. Therefore, besides the *conventional* semiconducting or insulating carbon structures, metallic carbon has significantly broadened the application of carbon materials.

Since the pioneering work of Hoffmann and his colleagues [10,11], further exploration of three-dimensional (3D) metallic carbon allotropes has received considerable attention either for fundamental research or practical applications. All 3D metallic carbon structures studied thus far can be classified into three groups based on the nature of their bonding: all-sp^2 structures [10,12,13], sp^2-sp^3 hybrid structures [11,14–17], and all distorted sp^3 structures [18–20]. Recently two new 3D metallic carbon structures, H_{18} carbon [17] and Tri-C_9 carbon [20], have been predicted. The former has a hexagonal primitive cell containing 18 carbon atoms with an sp^2-sp^3 hybrid bonding network, while the latter is a trigonal system composed solely of distorted sp^3 hybridized carbon atoms. They have lower binding energy than some previously studied 3D metallic structures such as T6 carbon [17,20]. However, these two structures are constructed by physical and chemical intuition. Thus, some low-energy allotropes can be easily missed because of the complex potential energy surface. Here, based on the particle swarm optimization method combined with first principles calculations, we find a new 3D metallic carbon allotrope, Hex-C_{18}, which is thermodynamically more stable than both H_{18} carbon and Tri-C_9 carbon, and many other previously identified

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metallic carbon phases. We also demonstrate that Hex-C_{18} exhibits interesting thermodynamic, mechanical, and electronic properties, in particular, its potential as an anode material for Li-ion batteries.

2. Computational methods

We employ the efficient particle swarm optimization (CALYPSO) code [21,22] to search for low-energy 3D metallic carbon structures at ambient pressure. This efficient structure prediction method is specially designed to search for stable or metastable structures with only the knowledge of chemical composition at given external pressures. The successful applications and the details of the method are described elsewhere [23,24], The unit cell we used contains eighteen carbon atoms compatible with the size of the recently reported Tri-C_9 carbon and H_{18} carbon allotropes. Lattice parameters and atomic positions of the searched structures are further relaxed using density functional theory (DFT) within the generalized gradient approximations (GGA) [25] and the projector augmented wave (PAW) method [26], as implemented in the Vienna *Ab initio* Simulation Package (VASP) [27]. The electronic exchange-correlation interaction is incorporated using Perdew-Burke-Ernzerhof (PBE) functional [25]. The effect of van der Waals (vdW) interaction is taken into account using the semi-empirical long-range dispersion correction by Grimme (PBE-D2 method) [28]. The Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional [29,30] are also used for the high accuracy of electronic structure calculations. The plane-wave cutoff energy for wave function is set to 500 eV. For structure optimization, the convergence thresholds are set to 10^{-4} eV and 10^{-3} eV/Å for total energy and force component, respectively. Monkhorst-Pack k-mesh of 7×7×21 for Hex-C_{18} is adopted to represent the first Brillouin zone. *Ab initio* molecular dynamics (AIMD) simulations at different temperatures are performed using the canonical ensemble (NVT) with the Nosé thermostat [31] to examine thermal stability. Phonon spectrum calculation is carried out using the linear response method within density functional perturbation theory [32] as implemented in the Phonopy code [33].

3. Results and discussion

3.1. Structure and stability

By CALYPSO search, the recently reported H_{18} carbon with $P6/mmm$ (D^1_{6h}) symmetry [17] is reproduced, and an energetically more stable hexagonal structure with space group $P6_3/mcm$ (D^3_{6h}) is discovered, which contains 18 atoms per unit cell, thus named Hex-C_{18}. As show in Fig. 1, there are two chemically nonequivalent carbon atoms in the primitive cell: one is the sp^3-hybridized carbon atoms at the 6 g (0.000, 0.555, 0.250) site, denoted as C1, colored in yellow, and the other is the sp^2-hybridized carbon atoms occupied the 12j (0.255, 0.429, 0.250) site, denoted as C2, colored in dark red. This structure can be considered as a 3D assembly of the sp^3 and sp^2 carbon chains, as shown in Fig. 1c. The optimized lattice constants of Hex-C_{18} are $a = b$ =8.36 Å, and c =2.46 Å. This unique configuration of Hex-C_{18} forms a porous structure with a density of 2.41 g/cm^3 (see Table 1) which is comparable to that of graphite (2.24 g/cm^3). The nanopores could accommodate other species such as atoms or molecules for further functionalization [34].

To study the effect of the van der Waals (vdW) interaction on the geometry of Hex-C_{18}, we recalculate the lattice parameters and its relative energy with respect to graphite by using the PBE functional with semiempirical vdW correction [28]. For comparison, the calculations for diamond and graphite are also carried out. The calculated results are given in Table S1 as Supplementary information, which shows that the lattice parameters and relative energies calculated with and without the semiempirical vdW correction are almost same, suggesting that the effect of vdW interaction on the geometry of Hex-C_{18} is subtle and negligible. Therefore, the following computations of the thermodynamic and mechanical properties of Hex-C_{18} are carried out using the standard PBE functional.

To further investigate the energetic stability of Hex-C_{18}, we calculate its total energy as a function of the volume. For comparison, calculations are also carried out for graphite, diamond, bct-C_4 [35], and the recently predicted metallic carbon phases, including T6 [15], H_{18} [17], K_6 [19] and Tri-C_9 [20] carbons. The results are given in Fig. 2a and Table 1, which shows that except for graphite and diamond, Hex-C_{18} has the lowest energy. In particular, it is energetically more favorable than the recently identified 3D metallic carbon allotropes (the T6, H_{18}, K_6 and Tri-C_9 carbon phases). To understand the origin of the high energetic stability of this new phase, we investigate its bonding feature. The calculated bond length of the sp^2-sp^2 bond in the sp^2-hybridized zigzag chains is 1.41 Å, which is very close to that of graphene (1.42 Å). For the sp^3-sp^3 bond in the sp^3-hybridized chains, the calculated bond length is 1.54 Å, very close to that of diamond (1.53 Å). The average bond angle of the sp^2-hybridized carbon atoms is 120.5°, while average bond angle of the sp^3-hybridized carbon atoms is 110.5°. These are respectively quite close to the ideal bonding angles of 120° and 109.5° in graphene and diamond, thus leading to the high energetic stability of Hex-C_{18}.

To examine the stability of Hex-C_{18}, we first calculate its phonon band structure. As shown in Fig. 2b, the absence of imaginary modes in the whole Brillouin zone confirms that Hex-C_{18} is dynamically stable. We then perform AIMD simulation at 300 K to verify the thermal stability of Hex-C_{18} at room temperature. We use a 2×2×4 large supercell to minimize the constraint of periodic boundary condition. The simulated results are plotted in Fig. 3, which clearly shows that the skeleton of this structure remains almost intact after heating for 8 ps (*ps*) with a time step of 1 femtosecond (*fs*), and the average value of the total potential energy remains almost constant during the whole simulation, confirming that Hex-C_{18} is thermally stable at room temperature. We further increase the heat bath temperature to 600 K, and then to 1200 K, respectively. As shown in the snapshots of Fig. 3, the atomic configuration at the end of the MD simulation at 1200 K has no obvious distortions, and the potential energy fluctuates around its average value. Hence, the structure is confirmed to be thermally stable even at high temperatures (1200 K). We recall that the two previously proposed 3D metallic carbon structures, T6 [15] carbon and K_6 [19] carbon, become unstable when heated to above 500 K [17], suggesting that Hex-C_{18} can withstand much higher temperatures compared to the other metallic carbon structures. The favorable thermal stability of Hex-C_{18} implies that this new carbon allotrope is separated by high energy barriers from other local minima on the potential energy surface (PES).

To verify the mechanical stability, we calculate the elastic constants of Hex-C_{18}. The calculated results are listed in Table 2. In general, for a hexagonal lattice, only C_{11}, C_{33}, C_{44}, C_{12}, and C_{13} are independent. Also, the linear elastic constants of a mechanically stable 3D hexagonal lattice have to obey the Born-Huang criteria: $C_{44} > 0$, $C_{11} > C_{12}$, $(C_{11} + 2C_{12})C_{33} > 2C_{13}^2$ [36]. We find that the calculated constants of Hex-C_{18} satisfy all of the criteria, hence the Hex-C_{18} is mechanically stable.

3.2. Thermodynamic properties

Based on the calculated phonon spectrum, a series of thermodynamic properties can be derived. Here we concentrate on the constant volume lattice heat capacity (denoted as lattice capacity for convenience of discussion without ambiguity) and Debye temperature of Hex-C_{18}. The calculated phonon heat capacity with respect to temperature is plotted in Fig. 4a. The heat capacity can also be expressed as a function of phonon DOS [37]. The Debye temperature $\Theta_D = h\nu_D/k_B$ is determined by fitting the calculated C_V-T curve using Debye model. The fitted Debye temperature Θ_D (T) is given in Fig. 4b, which shows that the Θ_D (T) is as high as 1600 K at room temperature. Since the vibrational frequency is proportional to the square root of the stiffness