A new 3D metallic carbon allotrope composed of penta-graphene nanoribbons as a high-performance anode material for sodium-ion batteries†

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Three-dimensional (3D) porous metallic carbon allotropes composed of graphene nanoribbons have attracted increasing attention in recent years because of their novel properties, especially due to their potential as anode materials for metal-ion batteries. Here, for the first time, we propose a new 3D porous metallic carbon allotrope consisting of penta-graphene nanoribbons. This material has an orthogonal lattice with its unit cell containing 36 carbon atoms, thus it is named penta-oC36. Based on state-of-the-art first-principles calculations, we show that penta-oC36 is thermally and dynamically stable with a metallic electronic structure. Through a detailed analysis of the intercalation and diffusion processes of Na ions in this structure, we find that penta-oC36 possesses a large reversible capacity of 496.9 mA h g⁻¹, low diffusion energy barrier as low as 0.01 eV, and a low open-circuit voltage of 0.39 V, superior to many other anode materials for sodium-ion batteries (SIBs) reported so far. More importantly, this study expands the penta-carbon family from 2D semiconducting penta-graphene to 3D metallic penta-nanoribbon-based materials with intriguing properties.

1. Introduction

Due to the flexible chemical bonding and orbital hybridization of carbon atoms, a variety of carbon allotropes have been synthesized, ranging from zero-dimensional fullerenes, to one-dimensional graphene nanoribbons and carbon nanotubes, two-dimensional graphene,⁷ graphdiyne⁸ and biphenylenes networks,⁹ and to three-dimensional (3D) graphite and diamond. Meanwhile many carbon allotropes have been theoretically predicted to possess novel properties and potential applications, including topological nodal-line carbon for metal-ion batteries,⁴⁻⁶ 3D metallic carbon allotropes with high stability and potential for lithium ion battery (LIB) anode materials,⁷ magic-angle graphene superlattices with superconductivity,⁸ and graphdiyne for photocatalytic CO₂ reduction.⁹ In particular, motivated by the experimental synthesis of 3D graphene networks,¹⁰,¹¹ great efforts have been devoted to the design and synthesis of 3D porous carbon materials by using graphene nanoribbons as structural units, and the resulting porous structures are favorable for the adsorption and transport of metal-ions, leading to high theoretical specific capacity and fast diffusion dynamics.¹²⁻¹⁶ For instance, by integrating zigzag graphene nanoribbons, a stable graphene monolith, HZGM-42, was theoretically predicted,¹⁷ which exhibits Dirac nodal-line semimetallic properties, and can serve as an anode material for both LIBs¹⁷ and SIBs.¹⁸ Besides, a topological nodal-surface semimetallic carbon allotrope was constructed from assembling graphene nanoribbons,¹⁸ and also shows a high theoretical capacity and low diffusion energy barrier for Na ions.

On the other hand, the derivatives of penta-graphene (PG) have been extensively studied since the prediction of PG, the cousin of graphene, in 2015,¹⁹ and include penta-nanotubes,²⁰,²¹ PG nanoribbons,²²⁻²⁵ surface modification of PG,²⁶,²⁷ multilayer PG,²⁸,²⁹ and pentagon-based 3D diamond-like structures.³⁰,³¹ These materials exhibit interesting properties and have wide applications. In addition, more than a hundred pentagon-based 2D materials have been predicted, and some of them have been experimentally synthesized.³²⁻³⁴ The details of the geometries and properties can be found in the database of pentagon-based 2D structures.³⁵ Parallel to the clue of building 3D porous carbon from graphene nanoribbons, a question arises: is it possible to design a stable 3D metallic carbon allotrope by using PG nanoribbons as the structural units?

In this study, we show that a 3D porous carbon allotrope, penta-oC36, can be directly assembled by using identical copies of a PG nanoribbon as the building blocks without introducing any “glue atoms” that are usually used in integrating graphene nanoribbons into 3D monoliths. We find that, different from...
the semiconducting features of PG and PG derived penta-tubes, pentaoC36 possesses a metallic electronic band structure. The intrinsic metallicity together with the regularly distributed channels and low mass density make penta-oC36 a promising candidate for the anode material of SIBs with good performance.

2. Computational methods

Our calculations within the scheme of density functional theory (DFT) are performed via the Vienna ab initio simulation package (VASP). The generalized gradient approximation is used with the Perdew–Burke–Ernzerhof (PBE) functional is used to treat the exchange–correlation interactions, while the Heyd–Scuseria–Ernzerhof (HSE06) hybrid functional is used for a more accurate calculation of the electronic structure. The projector augmented wave method is used to describe the interaction between valence electrons and ion cores, and plane waves with an energy cutoff of 600 eV are used to expand the basis functions of electrons. The first Brillouin zones of the unit and primitive cells, and the 1 × 1 × 3 supercell of penta-oC36 are sampled by using 5 × 3 × 13, 7 × 7 × 13, and 5 × 3 × 5 k-meshes, respectively. The thresholds for the total energy and the interatomic forces are set to 10⁻⁸ eV and 10⁻⁶ eV·Å⁻¹, respectively. The climbing-image nudged elastic band (CI-NEB) method is used to evaluate the diffusion energy barrier. The temperature fluctuation during ab initio molecular dynamics (AIMD) simulations with the canonical ensemble is controlled by using the Nosé–Hoover thermostat. The phonon band structure is calculated based on the finite displacement method implemented in the Phonopy package.

3. Results and discussion

3.1 Structure and stability

Based on the PG nanoribbon, as shown in Fig. 1a, we assemble a porous carbon allotrope by directly connecting three adjacent nanoribbons in a tip-to-tip manner, where all the tip site atoms on one nanoribbon are saturated by the neighboring atoms on the other two nanoribbons, forming sp³ hybridization, as illustrated in Fig. 1b. Such a structure could be synthesized by the following route: pentalene molecule \( \rightarrow \) bispentalene \( \rightarrow \) penta-graphene nanoribbon \( \rightarrow \) assembled 3D structure. The optimized geometry of this carbon allotrope, as shown in Fig. 1c, possesses an orthogonal symmetry of \( \text{Cmcm} \) (space group no. 63) and contains 36 atoms per unit cell, and thus is named penta-oC36. The optimized lattice parameters of penta-oC36 are \( a = 9.81 \, \text{Å}, b = 14.03 \, \text{Å} \) and \( c = 3.69 \, \text{Å} \). In this structure, there are four chemically nonequivalent carbon atoms, namely, the four-fold coordinated carbon atoms occupying the Wyckoff position 4c (0.500, 0.882, and 0.750), and the other three three-fold coordinated carbon atoms, respectively, occupying the Wyckoff positions 8e (0.626, 0.818, and 0.750), 8f (0.500, 0.952, and 0.065), and 16h (0.693, 0.781, and 0.059), leading to an overall ratio of 1:8 between the three- and four-fold coordinated carbon atoms. The pores with a diameter of 8.6 Å are regularly distributed. Because of its porous structure, penta-oC36 has a low mass density of 1.41 g cm⁻³, which is much lower than that of graphite (2.24 g cm⁻³), and is comparable to that of the previously reported porous carbon allotropes HZGY-42 (1.39 g cm⁻³) and BDL-14 (1.41 g cm⁻³).

We then examine the dynamic stability of penta-oC36 by calculating its phonon spectrum. As shown in Fig. 2a, there are no imaginary modes in the entire first Brillouin zone, confirming that penta-oC36 is dynamically stable. We also verify the thermal stability of penta-oC36 by performing the AIMD simulations at different temperatures for 10 ps with a time step of 1 fs. A 1 × 1 × 3 supercell is used to loosen the constraints associated with the periodic boundary conditions in all the AIMD simulations. The resulting total potential energy spectra during the simulations at 500 and 800 K are plotted in Fig. 2b, showing that the total potential energies fluctuate around constant values, while the geometry of penta-oC36 after the simulations remains almost intact without any breakage and formation of chemical bonds, confirming that penta-oC36 is thermally stable at temperatures up to 800 K.

3.2 Mechanical properties

Next, we calculate the elastic constants of penta-oC36 with orthogonal symmetry. There are nine nonzero independent elastic constants: \( C_{11}, C_{22}, C_{33}, C_{12}, C_{13}, C_{23}, C_{44}, C_{55}, \) and \( C_{66} \) in the Voigt notation as summarized in Table 1. These elastic constants satisfy the Born–Huang criteria for mechanical stability, namely, \( C_{ii} > 0 \) (\( i = 1, 2, 3, 4, 5, 6 \)), \( C_{ii} + C_{jj} = 2C_{ij} > 0 \) (\( i < j; \ i, j = 1, 2, 3 \)) and \( C_{11} + C_{22} + C_{33} + 2(C_{12} + C_{13} + C_{23}) > 0 \).

![Fig. 1](image-url) (a) PG nanoribbon. (b) Schematic diagram of assembling the PG nanoribbons into penta-oC36. (c) Optimized geometry of penta-oC36.
We then calculate the Young's moduli of penta-oC36 along different directions based on the elastic constants and the following equation,

\[
Y = \frac{\left( l_1^4 s_{11} + l_2^4 s_{22} + l_3^4 s_{33} + 2l_1^2 l_2^2 s_{12} + 2l_1^2 l_3^2 s_{13} + 2l_2^2 l_3^2 s_{23} + l_2^2 l_3^4 s_{44} + l_1^2 l_3^2 s_{55} + l_1^2 l_2^2 s_{66} \right)}{C_0} \tag{1}
\]

where \( s_{ij} \) is the elastic compliance constant determined by the matrix equation \( \left( s_{ij} \right)_{ij} = \left( C_{ij} \right)_{ij} = -1 \), and \( l_i \) (\( i = 1, 2, \) and \( 3 \)) represents the cosine of the angle between the given direction and the lattice vector \((a, b, c)\), respectively. The Young's moduli of penta-oC36 along \( a, b, \) and \( c \) are calculated to be 18.91, 23.51 and 649.36 GPa, respectively. It is obvious that the value of the Young's modulus along the lattice vector \( c \) is much larger than that along the other two directions, showing high anisotropy. We note that this value is close to that of a graphene monolith HZGM-42 (646.7 GPa),\(^ {17} \) indicating moderate mechanical strength of the PG-nanoribbon-based 3D structure. Since the difference in the values of Young's moduli along the lattice vectors \( a \) and \( b \) is small, we further study the Young's moduli along different directions in the \( a-b \) plane, as plotted in Fig. 3a. The results indicate that the local minima are located on the lattice \( a \) and \( b \) axes, whereas the maximum value of 54.2 GPa is on the axis close to the angular bisector between \( a \) and \( b \) (47.6° to \( a \)).

We also calculate the ideal tensile strength of penta-oC36 along the lattice vectors \( a, b, \) and \( c \), i.e., the crystallographic orientations [100], [010], and [001], respectively. In the calculation, small strain increments along different directions are applied to simulate the effect of external stress, and the stress–strain curves under tensile strain are plotted in Fig. 3b. The fracture strain under the uniaxial loading condition is 0.25, 0.24, and 0.19, while the ideal tensile strength is 14.06, 16.10, and 21.37 GPa along the [100], [010], and [001] directions, respectively.

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**Table 1** Elastic constants of penta-oC36 (in GPa)

<table>
<thead>
<tr>
<th>( C_{11} )</th>
<th>( C_{22} )</th>
<th>( C_{33} )</th>
<th>( C_{12} )</th>
<th>( C_{13} )</th>
<th>( C_{44} )</th>
<th>( C_{55} )</th>
<th>( C_{66} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>123.37</td>
<td>153.41</td>
<td>673.13</td>
<td>126.57</td>
<td>51.92</td>
<td>57.94</td>
<td>106.21</td>
<td>68.24</td>
</tr>
</tbody>
</table>

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**Fig. 2** (a) Phonon spectrum of penta-oC36. (b) Total potential energy fluctuation during the AIMD simulations at 500 and 800 K, and geometry (insets) of penta-oC36 at the end of the simulation at 800 K.

**Fig. 3** (a) Variation of the Young's modulus with respect to the crystalline directions in the \( a-b \) plane, and (b) variation of stress with axial tensile strain in penta-oC36.
3.3 Electronic structure

To study the electronic properties of penta-oC36, we first calculate the electronic band structure of penta-oC36. As shown in Fig. 4a, the partially occupied energy bands cross the Fermi level in the high-symmetry k-paths R → S, Γ → Z, and T → Y at the HSE06 level, showing that penta-oC36 is metallic. The first Brillouin zone of the primitive cell is plotted in Fig. 4b. An analysis of the bands crossed over the k-paths reveals that they are all aligned in the [001] direction. We then calculate the electron localization function (ELF)\(^{31}\) for penta-oC36, which is a dimensionless parameter normalized in the range (0, 1), where ELF = 0, 0.5, and 1 corresponds to very low charge density, fully delocalized electrons, and fully localized electrons, respectively. The metallicity of penta-oC36 is further confirmed by the formation of metallic channels along the [001] direction on the two crystalline planes, as shown in Fig. 4c, where the ELF values are close to 0.5 not only around three-fold coordinated carbon atoms but also in the pentagonal \( \text{C}_5 \) rings, forming the channels of delocalized valence electrons along the [001] direction.

3.4 Application as an anode material for SIBs

Based on the intrinsic metallicity of penta-oC36 and its large pores with regularly distributed channels for the adsorption and transport of Na ions, we calculate the parameters that measure the performance of penta-oC36 as an anode material for SIBs, i.e., reversible capacity, diffusion energy barriers for Na migration, and voltage profile.

First, we investigate the binding of a single Na atom in penta-oC36. A \( 1 \times 1 \times 3 \) supercell is used to prevent the interaction between the Na atom and its periodic images. We search for all possible adsorption sites for Na atoms, including three top sites on the top of each nonequivalent three-fold coordinated carbon atom, three hollow sites above the center of the five- and eight-membered rings, and six bridge sites on the top of the nonequivalent C-C bonds. We calculate the Na binding energy \( E_b \) to check the feasibility of these adsorption sites. The average Na binding energy in penta-oC36 is defined as:

\[
E_b = \frac{E_{\text{Na}_{x}, \text{penta-oC36}} - E_{\text{penta-oC36}} - x\mu_{\text{Na}}}{x},
\]

Here \( x \) is the Na concentration in the chemical formula \( \text{Na}_x\text{C}_{4.5} \), \( x = 1/24 \) corresponds to one Na atom in the supercell, \( E_{\text{Na}_{x}, \text{penta-oC36}} \) is the total energy of the system with Na concentration \( x \) without Na on the per \( \text{C}_{4.5} \) basis, and \( \mu_{\text{Na}} \) is the energy of one Na atom in its bulk phase. After geometry optimization, three stable adsorption sites are identified, i.e., the top site T, hollow site H, and bridge site B, as shown in Fig. 5a, and their corresponding binding energies are \(-0.64, -0.57, \) and \(-0.56 \text{ eV} \), respectively. Thus, the top site T is the most favorable adsorption site for Na, while sites H and B are almost degenerate in binding energy. We also check the electron transfer profiles via Bader charge analysis\(^{32,33} \) and find a charge transfer of over 0.993e from Na to the carbon framework of penta-oC36 for all the three adsorption sites, confirming the thorough ionic nature of the adsorbed Na.

Next, we evaluate the reversible capacity of penta-oC36 together with its open circuit voltage (OCV) by gradually increasing the Na concentration \( x \) in the chemical formula \( \text{Na}_x\text{C}_{4.5} \), where \( x = 0.125, 0.25, 0.375, 0.5, 0.625, 0.75, 0.875, \) and 1. For each Na concentration \( x \) in the range \( (0, 1) \), 15 different geometries are generated for identifying the most stable adsorption configuration, and the relative stabilities of these structures are evaluated from their formation energy \( E_f \) defined as

\[
E_f = E_{\text{Na}_{x}, \text{penta-oC36}} - (1 - x)E_{\text{penta-oC36}} - xE_{\text{Na}, \text{penta-oC36}}.
\]

Here \( E_{\text{Na}, \text{penta-oC36}} \) is the total energy of the most stable configuration with the chemical formula of \( \text{NaC}_{4.5} \). The fully Na-intercalated configuration is given in Fig. 5b, where all the T sites and every other B site along the [001] direction are occupied by Na ions, while the H sites are not occupied, and all the adsorbed Na ions are slightly deviated anticlockwise from their ideal sites when viewed along the [001] direction. Using the calculated formation energy, we plot the energy convex hull, as shown in Fig. 5c, which suggests four stable Na-intercalated configurations with \( x = 0.125, 0.25, 0.375, \) and 0.75. As the Na concentration increases, the metallicity enhances as the Fermi level shifts upward, as seen in the band structures shown in Fig. S1 in the ESI.\(^{1} \) The OCV, as one of the most important factors to characterize battery performances, is then calculated in the half-cell reaction vs. Na/Na\(^+ \), described as

\[\text{Li}^+ + \text{e}^- + \text{Na} \rightarrow \text{Li} + \text{Na}^+ \]
When neglecting the effects of volume, pressure and entropy, the average voltage $V$ of $Na^x$-penta-oC36 in the concentration range $(x_1, x_2)$ (0 < $x_1$ < $x_2$ < 1) can be evaluated using the following formula:

$$V(x) = \frac{E_{Na^x \text{-penta-oC36}} - E_{Na_{x_1} \text{-penta-oC36}} + (x_2 - x_1)\mu_{Na}}{(x_2 - x_1)e}. \quad (4)$$

The resulting voltage profile is presented in Fig. 5d, and is positive throughout the [0, 1] range of Na concentration $x$ with a monotonous decline in voltage as $x$ increases. More specifically, the OCV drops rapidly from 0.61 to 0.35 V within the range 0.25 < $x$ < 0.375, whereas it drops slowly in the ranges 0 < $x$ < 0.25 and 0.375 < $x$ < 1. The low-lying energy configuration with a Na concentration of $x = 1/24$ leads to a negative voltage of −0.87 V in the range $\left(1, 1^{1/24}\right)$, indicating an instability at this concentration. Thus, the reversible capacity of penta-oC36 for Na adsorption is 496.9 mA h g$^{-1}$, which is the highest value that can be achieved in penta-oC36, and is about 2 times larger than that of hard carbon (~250 mA h g$^{-1}$) and defective hard carbon (274 mA h g$^{-1}$).

We also calculate the average binding energies of all the Na-intercalated configurations using eqn (2). As shown in Fig. 5e, the average binding energy for the fully Na-intercalated Na-penta-oC36 configuration is −0.39 eV, whereas the most stable Na intercalated configuration at each concentration possesses considerable binding energy, indicating that the clustering of Na ions is avoided, leading to an average OCV of 0.39 V.

Next, we study the energy barrier for the migration of Na ions in penta-oC36. Based on the CI-NEB method, the diffusion energy profiles for Na-ion diffusion in mono-sodium and mono-vacancy models are both calculated for the evaluation of the energy barrier at low and high Na concentrations, respectively. In the mono-sodium case, we consider four migration paths in the channel along the [001] direction between every two neighboring adsorption sites among T, B and H. The optimized diffusion energy profiles and the corresponding migration pathways are shown in Fig. 6a and b, respectively. The paths I, II, III and IV represent the migration of Na ions along the channel from a T site to its nearest equivalent site, to the nearest B site and to the nearest H site, and from a B site to its nearest H site, respectively. The diffusion barrier ($E_a$) along the paths I, II, III and IV is calculated to be 0.010, 0.244, 0.240 and 0.059 eV, respectively. The low diffusion barriers for paths I and IV indicate that Na ions can migrate easily on these two paths directly along the [001] direction at low Na concentrations, according to the Arrhenius equation $D \propto \exp(-E_a/k_BT)$. On the other hand, in the mono-vacancy case with a Na ion removed from the fully Na-intercalated configuration of penta-oC36, we consider four migration paths between neighboring Na vacancies on the T and B sites in the channel along the [001] direction. The optimized diffusion energy profiles and the corresponding migration pathways are plotted in Fig. 7a and b for the migration of Na vacancies from a T site to its nearest B site (path I), from a T site to its nearest equivalence (path II), from...
a B site to its nearest equivalent site (path III), and from a B site to its second-nearest T site (path IV), and the corresponding diffusion barriers are 0.067, 0.058, 0.062 and 0.118 eV, respectively. Intriguingly, the diffusion barriers for Na vacancies tend to be lower than those for Na ions in most cases. As a result, besides the regular direct migration of Na vacancies along the [001] direction in paths I and II, diffusions in paths III and IV also make contributions for enhancing the transport of Na ions in penta-oC36 at high Na concentrations.

For clarity, a comparison is made for the performances of the penta-oC36 anode with some other previously reported structures, as listed in Table 2. It is obvious that for the capacity, diffusion energy barrier, and OCV, penta-oC36 exhibits better overall performance, specifically it possesses the largest theoretical reversible capacity and the lowest OCV among all of them.

### 4. Conclusions

Different from the widely reported 3D graphene monoliths formed by graphene nanoribbons, for the first time, we propose a new 3D porous carbon allotrope, penta-oC36, which is constructed from identical copies of PG nanoribbons without introducing any extra atoms for cross-linkage. Penta-oC36 is dynamically, thermally and mechanically stable. More importantly, penta-oC36 is metallic, which comes mainly from the three-coordinated carbon atoms, and is completely different from the semiconducting PG sheet and penta-tubes, exhibiting the variety of electronic properties of penta-carbon allotropes. When used as an anode material for SIBs, penta-oC36 shows advantages in the capacity and rate performance: a high reversible capacity of 496.9 mA h g\(^{-1}\) with an ultralow energy barrier down to 0.01 eV, and a low average OCV of 0.39 V. These theoretical findings clearly show the flexibility and

### Table 2

Reversible capacity (in mA h g\(^{-1}\)), diffusion barrier (in eV), open-circuit voltage (in V), and electronic properties of penta-oC36 and some previously studied anode materials for SIBs

<table>
<thead>
<tr>
<th>Materials</th>
<th>Reversible capacity</th>
<th>Diffusion barrier</th>
<th>OCV</th>
<th>Electronic property</th>
</tr>
</thead>
<tbody>
<tr>
<td>Penta-oC36</td>
<td>496.9</td>
<td>0.010</td>
<td>0.39</td>
<td>Metallic</td>
</tr>
<tr>
<td>T-C(_{24}) (ref. 19)</td>
<td>232.65</td>
<td>0.053</td>
<td>0.54</td>
<td>Semimetallic</td>
</tr>
<tr>
<td>ISN (ref. 57)</td>
<td>159.5</td>
<td>0.005</td>
<td>1.35</td>
<td>Semimetallic</td>
</tr>
<tr>
<td>2H-MoS(_{2}) (ref. 58)</td>
<td>146</td>
<td>0.680</td>
<td>0.75</td>
<td>Semiconducting</td>
</tr>
<tr>
<td>1T-MoS(_{2}) (ref. 58)</td>
<td>86</td>
<td>0.280</td>
<td>1.25</td>
<td>Metallic</td>
</tr>
<tr>
<td>YS(_{2}) (ref. 59)</td>
<td>350</td>
<td>0.240</td>
<td>1.44</td>
<td>Metallic</td>
</tr>
<tr>
<td>Ti(<em>{5})Pte(</em>{2}) (ref. 60)</td>
<td>280.72</td>
<td>0.22</td>
<td>0.31</td>
<td>Metallic</td>
</tr>
<tr>
<td>HZGM-42 (ref. 18)</td>
<td>318.5</td>
<td>0.080</td>
<td>0.43</td>
<td>Semimetallic</td>
</tr>
</tbody>
</table>
effectiveness of using pentagonal carbon units for tuning the geometrical configuration, physical properties and electrochemical performance of carbon materials. We hope that this study could stimulate more experimental efforts in developing new strategies for synthesizing pentagon-based 3D porous metallic carbon materials for batteries, catalysis and microelectronics.

Conflicts of interest
There are no conflicts of interest to declare.

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