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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 onedimensional graphene nanoribbons and carbon nanotubes, two-dimensional graphene,1 graphdiyne2 and biphenylene networks,3 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 metalion 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

A new 3D metallic carbon allotrope composed of penta-graphene nanoribbons as a highperformance 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.

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,¹⁹ 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 2015,²⁰ and include penta-nanotubes,^{21,22} PG nanoribbons,²³⁻²⁵ 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.³²⁻³⁵ The details of the geometries and properties can be found in the database of pentagon-based 2D structures.³⁶ 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

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the semiconducting features of PG and PG derived penta-tubes, penta-oC36 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).^{37,38} The generalized gradient approximation³⁹ with the Perdew-Burke-Ernzerhof (PBE) functional⁴⁰ is used to treat the exchange-correlation interactions, while the Heyd-Scuseria-Ernzerhof (HSE06) hybrid functional^{41,42} is used for a more accurate calculation of the electronic structure. The projector augmented wave method⁴³ 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 $1 \times 1 \times 3$ supercell of penta-oC36 are sampled by using $5 \times 3 \times 13$, $7 \times 7 \times 13$, and $5 \times 3 \times 5$ kmeshes, respectively. The thresholds for the total energy and the interatomic forces are set to 10^{-8} eV and 10^{-6} eV \mathring{A}^{-1} , respectively. The climbing-image nudged elastic band (CI-NEB) method⁴⁴ 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.45 The phonon band structure is calculated based on the finite displacement method implemented in the Phonopy package.46

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 sp^3 hybridization, as illustrated in Fig. 1b. Such a structure could be synthesized by the following route: pentalene molecule \rightarrow bispentalene⁴⁷ \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 *Cmcm* (space group no. 63) and contains 36 atoms per unit cell, and thus is named penta-oC36. The optimized lattice parameters of pentaoC36 are a = 9.81 Å, b = 14.03 Å and c = 3.69 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 threefold 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, pentaoC36 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 HGZM-42 $(1.39 \text{ g cm}^{-3})^{17}$ and BDL-14 $(1.41 \text{ g cm}^{-3})^{.13}$

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 $1 \times 1 \times 3$ 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,⁴⁸ as summarized in Table 1. These elastic constants satisfy the Born–Huang criteria for mechanical stability,⁴⁹ 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 (a) PG nanoribbon. (b) Schematic diagram of assembling the PG nanoribbons into penta-oC36. (c) Optimized geometry of penta-oC36.



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.

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C ₁₁	C_{22}	C ₃₃	C_{12}	C_{13}	C_{23}	C_{44}	C_{55}	C_{66}
123.37	153.41	673.13	126.57	51.92	57.94	106.21	68.24	15.09

We then calculate the Young's moduli of penta-oC36 along different directions based on the elastic constants and the following equation,⁵⁰

$$Y = (l_1^4 s_{11} + l_2^4 s_{22} + l_3^4 s_{33} + 2l_1^2 l_2^2 s_{12} + 2l_1^2 l_3^2 s_{13} + 2l_2^2 l_3^2 s_{23} + l_2^2 l_3^2 s_{44} + l_1^2 l_3^2 s_{55} + l_1^2 l_2^2 s_{66})^{-1},$$
(1)

where s_{ij} is the elastic compliance constant determined by the matrix equation $(s_{ij})_{6\times 6} = (C_{ij})_{6\times 6} - 1$, and l_i (i = 1, 2, and 3) represents the cosine of the angle between the given direction and the lattice vector (a, b, or 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 \boldsymbol{a} and \boldsymbol{b} is small, we further study the Young's moduli along different directions in the $\boldsymbol{a}-\boldsymbol{b}$ plane, as plotted in Fig. 3a. The results indicate that the local minima are located on the lattice \boldsymbol{a} and \boldsymbol{b} axes, whereas the maximum value of 54.2 GPa is on the axis close to the angular bisector between \boldsymbol{a} and \boldsymbol{b} (47.6° to \boldsymbol{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.



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.



Fig. 4 (a) Electronic band structure calculated at the HSE06 level, (b) high-symmetry *k*-paths in the first Brillouin zone, and (c) ELF of given crystalline planes of 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 is shown in Fig. 4a, the partially occupied energy bands cross the Fermi level in the high-symmetry *k*-paths $R \rightarrow S$, $\Gamma \rightarrow Z$, and T \rightarrow 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)⁵¹ 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 C₅ 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 pentaoC36. 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 eightmembered 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:

$$E_{\rm b} = \frac{E_{\rm Na_x-penta-oC36} - E_{\rm penta-oC36} - x\mu_{\rm Na}}{x}.$$
 (2)

Here *x* is the Na concentration in the chemical formula Na_xC_{4.5}, x = 1/24 corresponds to one Na atom in the supercell, $E_{\text{Na}_x\text{-penta-oC36}}/E_{\text{penta-oC36}}$ is the total energy of the system with Na concentration *x*/without Na on the per C_{4.5} basis, and μ_{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 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,^{52,53} and find a charge transfer of over 0.993*e* 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 Na_xC_{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 $E_{\rm f}$ defined as

$$E_{\rm f} = E_{\rm Na,-penta-oC36} - (1 - x)E_{\rm penta-oC36} - xE_{\rm Na-penta-oC36}.$$
 (3)

Here $E_{\text{Na-penta-oC36}}$ is the total energy of the most stable configuration with the chemical formula of NaC_{4.5}. The fully Naintercalated 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.† 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



Fig. 5 (a) Optimized Na adsorption sites. (b) Geometry of the fully Na-intercalated penta-oC36. Variation of (c) the formation energy, (d) voltage, and (e) binding energy with Na concentration in Na-intercalated penta-oC36 configurations.

$$(x_2 - x_1)$$
Na⁺ + $(x_2 - x_1)$ e⁻ + Na_{x1}-penta-oC36 \leftrightarrow Na_{x2}-penta-oC36.

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) ($0 \le x_1 < x_2 \le x$) can be evaluated using the following formula:

$$V(x) \approx \frac{E_{\text{Na}_{x_1}\text{-penta-oC36}} - E_{\text{Na}_{x_2}\text{-penta-oC36}} + (x_2 - x_1)\mu_{\text{Na}}}{(x_2 - x_1)e}.$$
 (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 $x = 1^{1/2}4$ 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)⁵⁴ and defective hard carbon (274 mA h g⁻¹).⁵⁵

We also calculate the average binding energies of all the Naintercalated configurations using eqn (2). As shown in Fig. 5e, the average binding energy for the fully Na-intercalated Napenta-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,44 the diffusion energy profiles for Na-ion diffusion in mono-sodium and monovacancy 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 $D \propto \exp(-E_{\rm a}/k_{\rm B}T)$.⁵⁶

On the other hand, in the mono-vacancy case with a Na ion removed from the fully Na-intercalated configuration of pentaoC36, 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



Fig. 6 (a) Diffusion energy profiles, and (b) optimized geometry of migration pathways for Na ions in penta-oC36.



Fig. 7 (a) Diffusion energy profiles, and (b) optimized geometry of migration pathways for Na vacancies. Vacancies are represented by the green spheres.

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.

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

Materials	Reversible capacity	Diffusion barrier	OCV	Electronic property
Penta-oC36	496.9	0.010	0.39	Metallic
T-C ₂₄ (ref. 19)	232.65	0.053	0.54	Semimetallic
ISN (ref. 57)	159.5	0.005	1.35	Semimetallic
2H-MoS ₂ (ref. 58)	146	0.680	0.75	Semiconducting
1T-MoS ₂ (ref. 58)	86	0.280	1.25	Metallic
YS ₂ (ref. 59)	350	0.240	1.44	Metallic
Ti_2PTe_2 (ref. 60)	280.72	0.22	0.31	Metallic
HZGM-42 (ref. 18)	318.5	0.080	0.43	Semimetallic

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. PentaoC36 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, pentaoC36 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 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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References

- K. S. Novoselov, A. K. Geim, S. V. Morozov, D. Jiang, M. I. Katsnelson, I. V. Grigorieva, S. V. Dubonos and A. A. Firsov, Two-dimensional gas of massless Dirac fermions in graphene, *Nature*, 2005, 438, 197–200.
- 2 G. Li, Y. Li, H. Liu, Y. Guo, Y. Li and D. Zhu, Architecture of graphdiyne nanoscale films, *Chem. Commun.*, 2010, **46**, 3256–3258.
- 3 Q. T. Fan, L. H. Yan, M. W. Tripp, O. Krejci, S. Dimosthenous, S. R. Kachel, M. Y. Chen, A. S. Foster, U. Koert, P. Liljeroth and J. M. Gottfried, Biphenylene network: a nonbenzenoid carbon allotrope, *Science*, 2021, **372**, 852–856.
- 4 J. T. Wang, H. M. Weng, S. M. Nie, Z. Fang, Y. Kawazoe and C. F. Chen, Body-centered orthorhombic C16: A novel topological node-line semimetal, *Phys. Rev. Lett.*, 2016, **19**, 195501.
- 5 J. Liu, S. Wang and Q. Sun, All-carbon-based porous topological semimetal for Li-ion battery anode material, *Proc. Natl. Acad. Sci. U. S. A.*, 2017, **114**, 651–656.
- 6 H. H. Xie, Y. Qie, M. Imran and Q. Sun, Topological semimetal porous carbon as a high-performance anode for Li-ion batteries, *J. Mater. Chem. A*, 2019, 7, 14253–14259.
- 7 J. Liu, T. Zhao, S. Zhang and Q. Wang, A new metallic carbon allotrope with high stability and potential for lithium ion battery anode material, *Nano Energy*, 2017, **38**, 263–270.
- 8 Y. Cao, V. Fatemi, S. Fang, K. Watanabe, T. Taniguchi, E. Kaxiras and P. Jarillo-Herrero, Unconventional superconductivity in magic-angle graphene superlattices, *Nature*, 2018, **556**, 43–50.
- 9 F. Y. Xu, K. Meng, B. C. Zhu, H. B. Liu, J. S. Xu and J. G. Yu, Graphdiyne: a new photocatalytic CO₂ reduction cocatalyst, *Adv. Funct. Mater.*, 2019, **29**, 1904256.
- 10 Z. P. Chen, W. C. Ren, L. B. Gao, B. L. Liu, S. F. Pei and H. M. Cheng, Three-dimensional flexible and conductive

interconnected graphene networks grown by chemical vapour deposition, *Nat. Mater.*, 2011, **10**, 424–428.

- 11 N. V. Krainyukova and E. N. Zubarev, Carbon honeycomb high capacity storage for gaseous and liquid species, *Phys. Rev. Lett.*, 2016, **116**, 055501.
- 12 L. Shi, A. Xu and T. S. Zhao, Three-dimensional carbonhoneycomb as nanoporous lithium and sodium deposition scaffold, *J. Phys. Chem. C*, 2018, **122**, 21262–21268.
- 13 X. Li, J. Liu, F. Q. Wang, Q. Wang and P. Jena, Rational design of porous nodal-line semimetallic carbon for K-ion battery anode materials, *J. Phys. Chem. Lett.*, 2019, **10**, 6360–6367.
- 14 J. P. Hu, W. K. Wu, C. Y. Zhong, N. Liu, C. Y. Ouyang, H. Y. Yang and S. Y. A. Yang, Three-dimensional honeycomb carbon: Junction line distortion and novel emergent fermions, *Carbon*, 2019, **141**, 417–426.
- 15 W. Zhou, H. Xie, S. Wang, Q. Wang and P. Jena, A 3D porous honeycomb carbon as Na-ion battery anode material with high capacity, excellent rate performance, and robust stability, *Carbon*, 2020, **168**, 163–168.
- 16 S. W. Wang and B. C. Yang, Dirac nodal line semimetal of three-dimensional cross-linked graphene network as anode materials for Li-ion battery beyond graphite, ACS Appl. Energy Mater., 2021, 4, 2091–2097.
- 17 J. Liu, X. Li, Q. Wang, Y. Kawazoe and P. Jena, A new 3D Dirac nodal-line semi-metallic graphene monolith for lithium ion battery anode materials, *J. Mater. Chem. A*, 2018, **6**, 13816– 13824.
- 18 Y. Shen, Q. Wang, Y. Kawazoe and P. Jena, Potential of porous nodal-line semi-metallic carbon for sodium-ion battery anode, *J. Power Sources*, 2020, **478**, 228746.
- 19 Y. Qie, J. Y. Liu, S. Wang, Q. Sun and P. Jena, Tetragonal C_{24} : a topological nodal-surface semimetal with potential as an anode material for sodium ion batteries, *J. Mater. Chem. A*, 2019, 7, 5733–5739.
- 20 S. Zhang, J. Zhou, Q. Wang, X. Chen, Y. Kawazoe and P. Jena, Penta-graphene: a new carbon allotrope, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 2372–2377.
- 21 Z. Wang, X. Cao, C. Qiao, R. J. Zhang, Y. X. Zheng, L. Y. Chen, S. Y. Wang, C. Z. Wang, K. M. Ho, Y. J. Fan, B. Y. Jin and W. S. Su, Novel penta-graphene nanotubes: strain-induced structural and semiconductor-metal transitions, *Nanoscale*, 2017, **9**, 19310–19317.
- 22 M. Chen, H. Zhan, Y. Zhu, H. Wu and Y. Gu, Mechanical properties of penta-graphene nanotubes, *J. Phys. Chem. C*, 2017, **121**, 9642–9647.
- 23 B. Rajbanshi, S. Sarkar, B. Mandal and P. Sarkar, Energetic and electronic structure of penta-graphene nanoribbons, *Carbon*, 2016, **100**, 118–125.
- 24 P. F. Yuan, Z. H. Zhang, Z. Q. Fan and M. Qiu, Electronic structure and magnetic properties of penta-graphene nanoribbons, *Phys. Chem. Chem. Phys.*, 2017, **19**, 9528–9536.
- 25 C. He, X. F. Wang and W. X. Zhang, Coupling effects of the electric field and bending on the electronic and magnetic properties of penta-graphene nanoribbons, *Phys. Chem. Chem. Phys.*, 2017, **19**, 18426–18433.

- 26 X. Li, S. Zhang, F. Q. Wang, Y. Guo, J. Liu and Q. Wang, Tuning the electronic and mechanical properties of pentagraphene via hydrogenation and fluorination, *Phys. Chem. Chem. Phys.*, 2016, **18**, 14191–14197.
- 27 H. J. Jia, H. M. Mu, J. P. Li, Y. Z. Zhao, Y. X. Wu and X. C. Wang, Piezoelectric and polarized enhancement by hydrofluorination of penta-graphene, *Phys. Chem. Chem. Phys.*, 2018, **20**, 26288–26296.
- 28 Z. Y. Wang, F. Dong, B. Shen, R. J. Zhang, Y. X. Zheng, L. Y. Chen, S. Y. Wang, C. Z. Wang, K. M. Ho, Y. J. Fan, B. Y. Jin and W. S. Su, Electronic and optical properties of novel carbon allotropes, *Carbon*, 2016, **101**, 77–85.
- 29 F. Q. Wang, J. Liu, X. Li, Q. Wang and Y. Kawazoe, Weak interlayer dependence of lattice thermal conductivity on stacking thickness of penta-graphene, *Appl. Phys. Lett.*, 2017, **111**, 192102.
- 30 X. Zhu and H. Su, Chiral pentagon only diamond-like structures, J. Phys. Chem. C, 2017, **121**, 13810–13815.
- 31 Z. H. Li, Y. J. Wu, S. S. Zhang, Y. Zhang, Y. F. Gao, K. Luo, Z. S. Zhao and J. L. He, Pentadiamond-like metallic hard carbon nitride, *J. Phys. Chem. C*, 2020, **124**, 24978–24983.
- 32 A. D. Oyedele, S. Yang, L. Liang, A. A. Puretzky, K. Wang, J. Zhang, P. Yu, P. R. Pudasaini, A. W. Ghosh, Z. Liu, C. M. Rouleau, B. G. Sumpter, M. F. Chisholm, W. Zhou, P. D. Rack, D. B. Geohegan and K. Xiao, PdSe₂: pentagonal two-dimensional layers with high air stability for electronics, *J. Am. Chem. Soc.*, 2017, 139, 14090–14097.
- 33 M. Bykov, E. Bykova, A. V. Ponomareva, F. Tasnadi, S. Chariton, V. B. Prakapenka, K. Glazyrin, J. S. Smith, M. F. Mahmood, I. A. Abrikosov and A. F. Goncharov, Realization of an ideal cairo tessellation in nickel diazenide NiN₂: high-pressure route to pentagonal 2D materials, *ACS Nano*, 2021, **15**, 13539–13546.
- 34 J. I. Cerda, J. Slawinska, G. Le Lay, A. C. Marele, J. M. Gomez-Rodriguez and M. E. Davila, Unveiling the pentagonal nature of perfectly aligned single-and double-strand Si nanoribbons on Ag(110), *Nat. Commun.*, 2016, 7, 13076.
- 35 W. L. Chow, P. Yu, F. Liu, J. Hong, X. Wang, Q. Zeng, C. H. Hsu, C. Zhu, J. Zhou, X. Wang, J. Xia, J. Yan, Y. Chen, D. Wu, T. Yu, Z. Shen, H. Lin, C. Jin, B. K. Tay and Z. Liu, High mobility 2D palladium diselenide fieldeffect transistors with tunable ambipolar characteristics, *Adv. Mater.*, 2017, **29**, 1602969.
- 36 Y. P. Shen and Q. Wang, Database for pentagon-based sheets, http://www.pubsd.com/.
- 37 G. Kresse and J. Furthmuller, Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1996, 54, 11169–11186.
- 38 G. Kresse and J. Furthmuller, Efficiency of ab-initio total energy calculations for metals and semiconductors using a plane-wave basis set, *Comput. Mater. Sci.*, 1996, **6**, 15–50.
- 39 M. P. Teter, M. C. Payne and D. C. Allan, Solution of Schrodinger-equation for large systems, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1989, **40**, 12255–12263.

- 40 J. P. Perdew, K. Burke and M. Ernzerhof, Generalized gradient approximation made simple, *Phys. Rev. Lett.*, 1996, 77, 3865–3868.
- 41 J. Heyd, G. E. Scuseria and M. Ernzerhof, Hybrid functionals based on a screened Coulomb potential, *J. Chem. Phys.*, 2003, 118, 8207–8215.
- 42 J. Heyd, G. E. Scuseria and M. Ernzerhof, Erratum: "hybrid functionals based on a screened Coulomb potential", *J. Chem. Phys.*, 2006, **124**, 219906.
- 43 P. E. Blöchl, Projector augmented-wave method, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1994, **50**, 17953–17979.
- 44 G. Henkelman, B. P. Uberuaga and H. Jonsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, *J. Chem. Phys.*, 2000, **113**, 9901–9904.
- 45 S. Nosé, A unified formulation of the constant temperature molecular dynamics methods, *J. Chem. Phys.*, 1984, **81**, 511–519.
- 46 A. Togo and I. Tanaka, First principles phonon calculations in materials science, *Scr. Mater.*, 2015, **108**, 1–5.
- 47 J. Cao, G. London, O. Dumele, M. V. Rekowski, N. Trapp, L. Ruhlmann, C. Boudon, A. Stanger and F. Diederich, The impact of antiaroniatic subunits in [4n+2] π-systems: bispentalenes with [4n+2] π-electron perimeters and antiaromatic character, *J. Am. Chem. Soc.*, 2015, **137**, 7178–7188.
- 48 Y. Le Page and P. Saxe, Symmetry-general least-squares extraction of elastic data for strained materials from ab initio calculations of stress, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2002, **65**, 104104.
- 49 M. Born and K. Huang, *Dynamical theory of crystal lattices*, Clarendon press, 1954.
- 50 J.-W. Yang and J.-J. Zheng, Electronic properties, anisotropic elasticity, theoretical strengths, and lattice vibrational mode of orthorhombic YSi, *Solid State Commun.*, 2020, **321**, 114029.
- 51 A. D. Becke and K. E. Edgecombe, A simple measure of electron localization in atomic and molecular systems, *J. Chem. Phys.*, 1990, **92**, 5397–5403.
- 52 G. Henkelman, A. Arnaldsson and H. Jónsson, A fast and robust algorithm for Bader decomposition of charge density, *Comput. Mater. Sci.*, 2006, **36**, 354–360.
- 53 W. Tang, E. Sanville and G. Henkelman, A grid-based Bader analysis algorithm without lattice bias, *J. Phys.: Condens. Matter*, 2009, **21**, 084204.
- 54 S. Komaba, W. Murata, T. Ishikawa, N. Yabuuchi, T. Ozeki, T. Nakayama, A. Ogata, K. Gotoh and K. Fujiwara, Electrochemical Na insertion and solid electrolyte interphase for hard-carbon electrodes and application to Na-ion batteries, *Adv. Funct. Mater.*, 2011, **21**, 3859–3867.
- 55 Z. Li, Y. Chen, Z. Jian, H. Jiang, J. J. Razink, W. F. Stickle, J. C. Neuefeind and X. Ji, Defective hard carbon anode for Na-ion batteries, *Chem. Mater.*, 2018, **30**, 4536–4542.
- 56 C. Uthaisar and V. Barone, Edge effects on the characteristics of Li diffusion in graphene, *Nano Lett.*, 2010, **10**, 2838–2842.
- 57 Y. Qie, J. Y. Liu, X. Y. Li, S. Wang, Q. Sun and P. Jena, Interpenetrating silicene networks: a topological nodal-line semimetal with potential as an anode material for sodium ion batteries, *Phys. Rev. Mater.*, 2018, 2, 084201.

Paper

- 58 M. Mortazavi, C. Wang, J. K. Deng, V. B. Shenoy and N. V. Medhekar, Ab initio characterization of layered MoS₂ as anode for sodium-ion batteries, *J. Power Sources*, 2014, 268, 279–286.
- 59 Y. H. Guo, T. Bo, Y. Y. Wu, J. R. Zhang, Z. S. Lu, W. D. Li, X. P. Li, P. Zhang and B. T. Wang, YS_2 monolayer as

a high-efficient anode material for rechargeable Li-ion and Na-ion batteries, *Solid State Ionics*, 2020, **345**, 115187.

60 J. Liu, M. Qiao, X. Zhu, Y. Jing and Y. Li, Ti₂PTe₂ monolayer: a promising two-dimensional anode material for sodium-ion batteries, *RSC Adv.*, 2019, **9**, 15536–15541.