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Recent advances of novel ultrathin two-dimensional silicon carbides from a theoretical perspective

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Compared to graphene with semimetallic features, two-dimensional (2D) silicon carbide (Si–C) materials constitute another highly promising family for opto-electronic applications owing to their intrinsic electronic gaps. Recent theoretical studies of 2D Si–C materials thoroughly investigated their structure and properties. Herein, we overview these high-throughput approaches aiming to theoretically design 2D Si–C crystals. Graphene-like siligraphene and non-siligraphene are described in terms of morphology, physicochemical properties and potential applications based on the insights provided by simulations. In addition, the current progress of experimental exploration of 2D Si–C materials and underlying challenges are assessed as well.

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1. Introduction

Two-dimensional (2D) materials, such as graphene and silicene, show very attractive physical and chemical properties, which are highly promising for the next generation of faster and smaller electronic devices.¹ However, their intrinsic semimetallicity significantly limits their applications to (opto)electronic devices frequently requiring tunable band-gaps.² Consequently, numerous efforts have been devoted to opening the band gaps, including approaches such as substrate-induced gaps,^{3,4} fluorination⁵ or hydrogenation,⁶ application of an external gate,⁷ fabrication of graphene nanoribbons,⁸ doping,⁹ *etc.* However, using most of these approaches, the opening of the band gap has proved difficult to attain in experiments. The feasibility challenges include well-controlled adsorption sites,⁶ width of nanoribbons⁸ and doping concentrations,⁹ and thus altogether lead to high cost in experimental realization. Moreover, they usually produce either too small (tenths of eV),^{3,4} or too large band gaps (>5 eV)⁶ or chirality and width dependent gaps of nanoribbons.^{2,8} Considering the compatibility in the modern industry, the exploitation of 2D C- and/or Si-based crystals beyond graphene and silicene is a desirable direction which could greatly expand the family of

2D materials. 2D SiC in the hexagonal phase is the most well-known representative of this material class: it has an experimentally verified direct band gap of ~3.72 eV (ref. 10) and has been extensively investigated theoretically. However, for opto-electronic applications such as field effect transistors and photovoltaics, medium band gaps (*i.e.*, 1.0–2.0 eV) are in a high demand. Moreover, intrinsic graphene and silicene sheets are typically poorly suited catalysis or gas sensing due to the absence of active sites. This altogether triggers further theoretical and experimental studies of 2D Si–C materials beyond the 1:1 elemental composition targeting wider applications. With different Si/C ratios and various geometries, the newly designed or predicted 2D Si–C materials could attain novel electronic, optical, mechanical, and chemical properties that go beyond those of graphene, silicene, and their allotropes.

The high-throughput simulations of materials using density functional theory (DFT) methods are matured and promising approaches to computationally investigate possible tunability of novel 2D crystals. The first principles DFT calculations frequently utilizing screened exchange hybrid density functionals Perdew, Burke, and Ernzerhof (PBE)¹¹ and Heyd–Scuseria–Ernzerhof (HSE06)^{12,13} provide semi-quantitative accuracy for structural and electronic properties of these materials. The PBE functional usually underestimates the band gap while the HSE06 level can be utilized to achieve more accurate band gap values. Furthermore, structural search and conformational optimizations include a variety of techniques such as (adaptive) genetic algorithms,^{14,15} inverse design *via* multi-objective differential evolution,¹⁶ Particle Swarm Optimization (PSO),¹⁷ Cluster Expansion (CE) methods,¹⁸ *etc.* Among them, PSO and CE methods have been

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used to explore 2D Si-C crystals. For example, by using PSO, Zhou *et al.* reported a novel 2D Si-C material adopting the honeycomb lattice of pristine graphene (aka siligraphene), SiC₂.² Following this study, a series of 2D siligraphenes, SiC₃,¹⁹ SiC₅,²⁰ and SiC₇^{21,22} proposed *via* mainly high-throughput DFT calculations, were systematically investigated in terms of geometry, electronic, optical, topological and magnetic properties, as well as their potential applications. Besides C-rich siligraphenes, their Si-rich counterparts, such as g-Si_nC for $n = 3, 5$ and 7 , were reported as well using the PSO technique.²³ These studies brought out other low-dimensional systems and suggested enrichment of carbon chemistry. What is more, a recent discovery of non-siligraphene crystals exposed a new opportunity to seek novel Si and/or C-based 2D Si-C materials with structures beyond the hexagonal lattice. These new predicted non-siligraphene structures include planar tetra-coordinated SiC₂ (pt-SiC₂),²⁴ penta-SiC₂,²⁵ SiC₆,²⁶ α -SiC₇,²² SiC₈,²⁷ t -SiC,²⁸ t -Si₂C,²⁸ γ -siligraphyne,²⁸ *etc.* These theoretical findings disclosed extraordinary properties and new potential applications, thus triggering experimental exploration in this field towards desired functionalities.

In this mini-review, we focus on the modeling advances of the ultra-thin 2D Si-C crystals with a particular emphasis on the materials design approaches and the connections between morphology, physicochemical properties and potential applications. We outline a systematic categorization for various 2D Si-C materials according to structural motifs and then discuss their structural, mechanical, electronic, magnetic, and optical properties as well as possible future applications. Finally, we elaborate the current status and existing potential challenges in experiment and theory for the 2D Si-C material family and assess prospects of new opportunities for their future research and development. We further refer an interested reader to recent reviews overseeing development of materials design²⁹ and related 2D carbon-based materials including graphene/SiC heterostructures,³⁰ transition metal carbides,³¹ B₂C,³² *etc.*

2. Materials design approaches for 2D silicon carbide crystals

In recent years, the rapid development of 2D material prediction has been fueled by high-throughput calculations.^{14,15,17,18} Here, PSO and CE methods have been utilized to predict the 2D Si-C crystals. Due to the fact that Si and C have the preference of sp³ and sp² hybridizations, respectively, the mix of Si and C atoms provides a versatile composition space to generate novel 2D Si-C crystals, including C-rich (flat) and Si-rich (low-buckled) siligraphene and non-siligraphene structures.

2.1. Particle swarm optimization

The PSO algorithm has been proven to be an efficient tool for the structural prediction of 2D crystals since the first realization of 2D B-C crystals in 2011.³³ The evolution of the structures in the PSO algorithm^{17,33,34} is inspired by the social behavior of flocking birds and is designed to solve problems

related to a multidimensional optimization. Within this scheme, a structure in the search space is regarded as a particle. A set of particles is called a population or a generation. For 2D systems, all the structures are constrained in a plane. However, the atoms in layered materials may shift out of the plane, resulting in quasi-2D structures. To avoid the occurrence of instability of structure and to capture this feature of 2D materials, the atoms in the perpendicular direction within a certain range of $\pm\Delta z$ (*e.g.*, $\Delta z \sim 0.1$ Å) are allowed to relax in the DFT optimizations, so that the 2D nature of the structure in question is retained. The PSO technique is instrumental for the prediction of many siligraphene and non-siligraphene structures as exemplified in Fig. 1a. Zhang *et al.* have verified

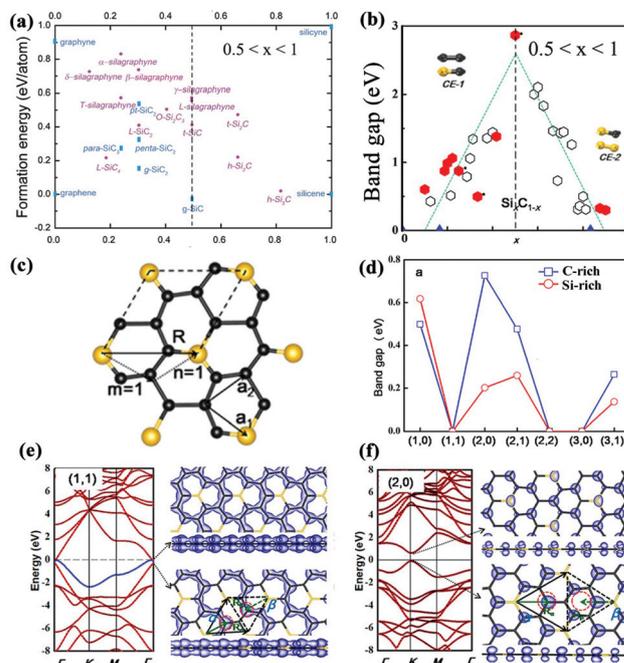


Fig. 1 (a) The calculated formation energies (E_f) of 2D $\text{Si}_x\text{C}_{1-x}$ compounds with respect to elemental decomposition into graphene and silicene. When $x = 0$ (or $x = 1$), the calculated E_f values for graphene (or silicene) are 0 eV per atom. Reproduced with permission from ref. 28. Copyright 2017 Royal Society of Chemistry. (b) Calculated band gaps of 2D $\text{Si}_x\text{C}_{1-x}$ as a function of x based on the PBE functional. Insets: The top and side views of the primitive cell adopted in CE-1 (planar) and CE-2 (buckling) calculations, respectively. Reproduced with permission from ref. 36. Copyright 2015 American Chemical Society. (c) The (1, 1) homogeneous structure characterized by the superlattice vector $\mathbf{R} = 1\mathbf{a}_1 + 1\mathbf{a}_2$. Reproduced with permission from ref. 36. Copyright 2015, American Chemical Society. (d) Band gaps of representative homogeneous $\text{Si}_x\text{C}_{1-x}$ structures as a function of the superlattice vector ranging from (1,0) to (3,1). Reproduced with permission from ref. 36. Copyright 2015, American Chemical Society. (e and f) Band structures of the (1,1), and (2,0) structures and the partial charge densities of the states near the Fermi level. The superatom models are illustrated in each plot of the charge density of valence band maximum (VBM). A vector dependence of the classification is identified by defining vectors \mathbf{R}_α and \mathbf{R}_β (green arrow in e and f) connecting the vertex and the center (red dashed circle) of the superatoms α and β , respectively. Reproduced with permission from ref. 36. Copyright 2015, American Chemical Society.

the existence of a series of 2D Si–C siligraphenes using the PSO.³⁵ The obtained band gaps in these sheets vary from 0 to 2.5 eV based on the PBE functional. It should be noted that all these stable monolayers possess a honeycomb lattice. Next, Fan *et al.* found that a new type of 2D tetragonal inorganic material containing tetracoordinate silicons, named *t*-SiC and *t*-Si₂C siligraphene, maintained both thermodynamic and mechanical stabilities predicted with the aid of the PSO.²⁸ More interestingly, six different siligraphyne sheets with higher pore sizes and higher Poisson's ratios are also determined. These siligraphyne sheets were suggested as potential candidates for separation membranes and catalytic materials.²⁸

2.2. Cluster expansion methods

First principles calculations combined with the CE approach¹⁸ were used by Shi *et al.* to perform high-throughput calculations to explore the configuration space and describe the relationships between the structure and properties, as well as limits of electronic tunability in 2D Si–C materials.³⁶ The CE method is established in the theory of alloys, where the alloy Hamiltonian is mapped onto a generalized Ising Hamiltonian.¹⁸ When applying to the predictions of the 2D Si–C monolayer, the 2D system is considered as an alloy. Here the CE is defined by first assigning the occupation variables σ_i to each site *i* of the parent lattice: σ_i takes the value -1 or $+1$ due to the existing two atom types occupying the site, *i.e.*, Si and C atoms. The CE calculations are divided into two parts: CE-1, from graphene to Si_{0.5}C_{0.5}, and CE-2, from Si_{0.5}C_{0.5} to silicene. It is suggested that Si doping can effectively engineer the band gap of a graphene monolayer (Fig. 1b) thus enabling optoelectronic device applications.

Importantly, ref. 36 reported the existence of two distinct structural phases, a homogeneous phase and in-plane hybrid phase with Si–C domains. The in-plane hybrid phase shows uniform semiconducting properties with widely tunable band gaps due to the quantum confinement effect imposed by these domains. Nonetheless, either semiconducting or semimetallic traits can be achieved within homogeneous structures depending on a superlattice vector $\mathbf{R} = n\mathbf{a}_1 + m\mathbf{a}_2$ connecting two neighboring dopants Si or C, where \mathbf{a}_1 and \mathbf{a}_2 are the primitive lattice vectors of graphene, as illustrated in Fig. 1c. Notably, all predicted siligraphenes with $(n - m) \bmod 3 = \pm 1$ possess sizable energy gaps ranging from 0.137 to 0.726 eV, while the rest with $(n - m) \bmod 3 = 0$ remain semimetallic (Fig. 1d). This seems to be a universal rule similar to gap-chirality relationships in carbon nanotubes.³⁷

The mechanism underpinning the structure–electron property relationships is clarified *via* analyzing the energy-resolved charge density and stems from the ionic potential difference between Si and C atoms (Fig. 1e and f). Additionally, the origin of this rule is further explained by the superatom model proposed using group theory by Shima and Aoki.³⁸ In this model, the unit cell of the homogeneous sheet is considered as a supercell consisting of two superatoms, denoted as α and β (Fig. 1e and f). The superatoms are further classified into

type A_0 when there exists a hexagon in the center of each superatom and type A_C when an atom resides in such a center (see the right panels of Fig. 1e and f). Then the triangular lattices of the semimetallic sheets are constituted by two A_C superatoms, while those of semiconducting sheets comprise the mixture of A_0 and A_C superatoms.³⁶

3. 2D Si–C materials: structures, electronic properties and potential applications

Due to their higher structural stability and attractive electronic and optical properties, the 2D Si–C sheets with a higher ratio of C/Si were studied frequently. It was found that both mechanical properties and anisotropy of 2D Si–C sheets are essentially associated with the presence and dispersion of Si atoms.³⁹ The Young's modulus and fracture stress generally decrease when the Si concentration increases from 0 to 0.2, and then slightly increase when Si concentration varies from 0.3 to 0.5.

Among the 2D Si–C crystals, graphene-like siligraphenes have received special attention due to their figures of merit making them particularly suitable for optoelectronics, energy storage and catalysis. Thus, we divided the scope of 2D Si–C materials into siligraphenes and non-siligraphenes. For siligraphenes, we further split them into two parts, C-rich (with a higher ratio of C atoms) and Si-rich (with a higher ratio of Si atoms) materials, according to the ratio of C/Si. Thus, we discuss next C-rich, and Si-rich siligraphenes as well as non-siligraphenes in terms of structures, electronic properties and potential applications.

3.1. C-rich siligraphenes

The C-rich siligraphene (*g*-SiC_{*x*}) is formed by incorporating Si atoms into a honeycomb lattice of graphene. The *g*-SiC_{*x*} structures are strictly planar with hexagonal symmetry. The ratio of Si atoms in siligraphene ranges from 0 to 50%, and the hexagonal single-layer SiC (*g*-SiC) could be viewed as a special example of siligraphene. Isomorphous transformation has been demonstrated to be able to tune the electronic structures and even achieve the formation of Dirac cones (DCs) when *g*-SiC siligraphenes feature C–C and Si–Si atom pairs.⁴⁰ This has been confirmed in the two isomorphous tetragonal phases, *i.e.*, one with all C–C and Si–Si pairs aligning parallel to each other^{40,41} and the other one with both pairs distributing more isotropically⁴⁰ of *g*-SiC siligraphene. When we expand to other siligraphenes with stoichiometry beyond 1 : 1, although there exists obvious similarity in the structure, entirely different mechanical, electronic and optical properties could be exhibited compared to those of the parent graphene.

With respect to mechanical properties, the *g*-SiC_{*x*} sheets preserve rigorous isotropic Young's moduli and Poisson's ratios. In view of its robust mechanical performances, the C-rich siligraphene family may facilitate the design of

advanced 2D materials to meet demands for practical mechanical engineering applications.⁴² Additionally, electronic properties of the g-SiC_x show great variability. g-SiC₂, g-SiC₃, g-SiC₅, and g-SiC₇ have been extensively investigated in theory, with reported promising characteristics making them suitable for photovoltaic, electrocatalysis, energy storage, spintronics, and gas sensor technologies, which will be discussed next in detail.

3.1.1. g-SiC siligraphene. The g-SiC siligraphene possesses a planar geometry with a hexagonal space group of *P62m* (Fig. 2a). The optimized lattice parameter *a* = 3.07 Å and the Si–C bond length of 1.77–1.79 Å are predicted. Compared to graphene and silicene, the degeneracy of valence and conduction bands at the K point is lifted out and a direct energy gap of 2.55 eV is opened (Fig. 2b).^{43,47} This originates from the charge transfer from Si to C atoms and preferential location of p^z orbital electrons on C atoms. Controlling the hydrogenation modes on g-SiC siligraphene is a promising approach to modulate the magnetic properties: a ferromagnetic semiconductor upon semi-hydrogenation over Si atoms and an antiferromagnetic semiconductor upon semi-hydrogenation over C atoms. Upon full hydrogenation, the chair-like and boat-like conformers are confirmed to be stable and are calculated to be nonmagnetic semiconductors with direct band gaps of 3.84 and 4.29 eV, respectively, both greatly larger than that of pristine g-SiC sheet (2.55 eV). Furthermore, new magnetic and electronic properties in the g-SiC monolayer can be attained *via* the formation of substitutional impurities, and vacancies and adatom decoration.⁴⁷

Due to the reduced charge screening and the enhanced electron correlation in the low-dimensional system, g-SiC is

expected to exhibit a significant excitonic effect on the optical properties. Fig. 2c presents the optical spectra obtained from the Greens function and the screened Coulomb interaction (GW approximation) combining with the RPA or BSE calculations.⁴⁴ The onset energy of the GW corrected electron–hole continuum confirms the quasiparticle gap to be 4.42 eV, a large GW correction of 1.86 eV to the DFT band gap.⁴⁴ The lowest bright exciton wave function is located at about 3.25 eV rooting to the excitation between the π and the π* states at the K point. This exciton with the π character is mainly distributed on the nearest-neighbor Si atoms around the hole (Fig. 2d),⁴⁴ indicating a localized exciton with a large exciton binding energy of 1.17 eV, strongly confining the quasiparticles.

The g-SiC siligraphene has been proposed as a metal-free oxygen reduction reaction (ORR) electrocatalyst to replace Pt-based catalysts due to its high concentrations of active reaction sites within a pure sheet. Zhang *et al.* reported that in an acidic environment, the g-SiC sheet exhibits an ORR catalytic activity comparable to that of Pt-based catalysts.⁴⁵ Importantly, g-SiC sheets possess better catalytic activity in alkaline media when compared with Pt-based catalysts. As shown in Fig. 2e, the ORR in the Langmuir–Hinshelwood mechanism in alkaline media is divided into two elemental steps: O₂* + H₂O* → O* + 2OH* and O* + H₂O* → 2OH* (* denotes the g-SiC₂ surface). These two steps have small activation energies being 0.11 and 0.23 eV, respectively. The second elemental step on g-SiC sheets is an exothermic process with a reaction energy of nearly 0.40 eV, while it is endothermic by 0.51 eV on the Pt (111) surface. Surprisingly, the g-SiC catalyst does not have a CO poisoning phenomenon which is a major obstacle in the conventional Pt-based catalysts. The above advantages suggest

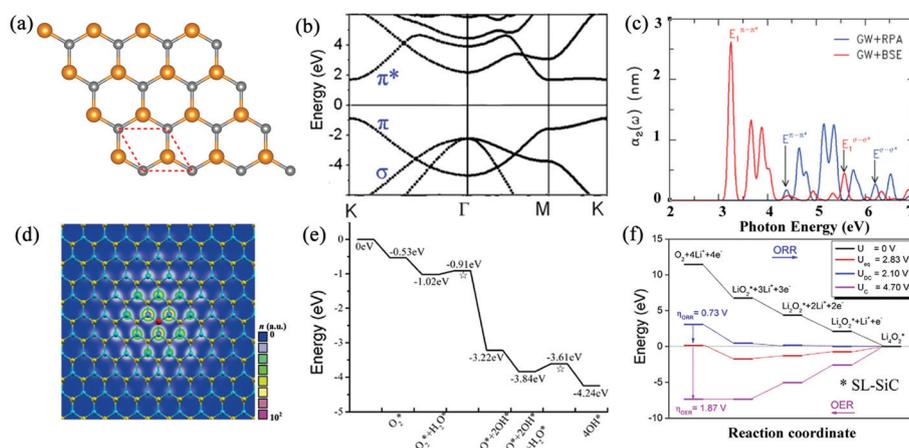


Fig. 2 (a) The crystalline structure of g-SiC, with red dash lines marking the unit cell. (b) The band structure of g-SiC calculated by the PBE level. Reproduced with permission from ref. 43. Copyright 2011 Elsevier B.V. (c) Optical polarizability per unit area obtained from GW combined with random phase approximation (RPA) (blue) and BetheSalpeter equation (BSE) calculations. The theoretical spectra are broadened with a Gaussian smearing width of 0.15 eV. Reproduced with permission from ref. 44. Copyright 2011 American Physical Society. (d) The lowest bright exciton wave function of the SiC sheet. The hole is fixed at the top of a C atom (yellow sphere) and the electron amplitudes in arbitrary units are mainly distributed on Si atoms (cyan spheres) next to the hole. Reproduced with permission from ref. 44. Copyright 2011 American Physical Society. (e) Schematic energy profile for ORR elemental steps in alkaline media on g-SiC. Reproduced with permission from ref. 45. (f) The calculated free energy diagrams for the ORR/OER catalyzed by g-SiC at zero potential (*U* = 0 V), equilibrium potential (*U*_{eq}), discharge potential (*U*_{DC}) and charge potential (*U*_c). Reproduced with permission from ref. 46. Copyright 2018 Elsevier B.V.

the g-SiC siligraphene as a feasible metal-free ORR electrocatalyst in fuel cells.

Moreover, the electro-catalytic performance of g-SiC in non-aqueous lithium–oxygen (Li–O₂) batteries has also been theoretically investigated.⁴⁶ The reaction steps of the discharge process follow the sequence (a) (Li⁺ + e⁻) + 2O* → LiO₂*, (b) (Li⁺ + e⁻) + LiO₂* → Li₂O₂*, (c) (Li⁺ + e⁻) + Li₂O₂* → Li₃O₂*, and (d) (Li⁺ + e⁻) + Li₃O₂* → Li₄O₂*, with Li₂O acting as the discharge product. As depicted in Fig. 2f, the free energy diagrams for the ORR/OER catalyzed by g-SiC at different potentials illustrate both the evaluated discharge ($\eta_{\text{ORR}} = 0.73$ V) and charge ($\eta_{\text{OER}} = 1.87$ V) overpotentials which make g-SiC suitable to act as a cathode catalyst in non-aqueous Li–O₂ batteries.⁴⁶

Besides these theoretical investigations of a single-layer structure, multilayers of g-SiC were also theoretically studied. Xu *et al.* found that the band structure varies dramatically from the monolayer to 3-layers, but remains essentially the same when going from 4 to 6-layers.⁴⁸ Unlike a monolayer, multilayer g-SiC exhibits an indirect band gap. The indirect-to-direct band-gap transition indicates that a single-layer g-SiC is more suitable for optoelectronic applications. A further theoretical study revealed that for a bilayer g-SiC, the AB stacking wherein Si(C) atoms are positioned over C(Si) atoms is the most stable arrangement.⁴⁹ In addition, when multilayered g-SiC is examined for catalysis applications, an increase of the layer number merely changes the adsorption, activation and reaction energies of reaction intermediates, inferring similar ORR catalytic activities.⁴⁵

3.1.2. g-SiC₂ siligraphene. The graphene-like g-SiC₂ sheet is the first siligraphene structure theoretically predicted in 2013,² which became the most well-studied siligraphene. The unit cell of g-SiC₂ exhibits a hexagonal space group of *P62m* with the optimized lattice parameter of $a = b \approx 5.02$ Å. The structure of g-SiC₂ can be envisioned when two *meta*-positioned C atoms in the graphene unit cell are replaced with Si atoms, as shown in Fig. 3a. Thus, there are two types of C atoms: the C1 atoms connected directly with one C2 atom and two Si atoms, and C2 atoms bonded with three C1 atoms. Obviously, due to different bond lengths between Si–C and C–C bonds and the electronegativity difference between Si and C atoms, there exists a small distortion of the hexagon. The degree of these distortions ultimately generates the variability in electronic structures. The DFT calculations indicate that g-SiC₂ is a direct band gap semiconductor with a gap of 1.09 eV (HSE06 level). Surprisingly, its derivative (*n*, 0), (*n*, *n*) nanotubes (with diameters greater than 8.0 Å) have almost the same gaps of 1.09 eV that are virtually independent of the chirality and diameter (Fig. 3b). The direct band gap makes g-SiC₂ promising as a donor material in solar cells for light absorption, which has been further validated by theoretical simulations. As shown in Fig. 3c, an excitonic solar cell constructed by using g-SiC₂ as a donor material and the GaN monolayer as an acceptor material has a power conversion efficiency (PCE) limit of about 14.2%, confirming potential of use of g-SiC₂ in photovoltaics.²

Besides potential optical applications, the charge transfer processes within g-SiC₂ make it promising in electro-chemical

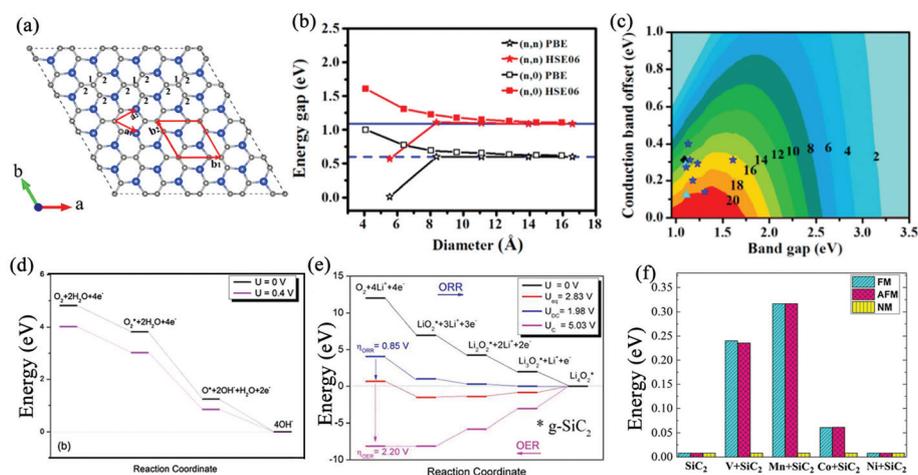


Fig. 3 Crystal structure of the g-SiC₂ with the unit cell marked as red lines. Red vectors **a**₁ and **a**₂ are graphene lattice vectors; **b**₁ and **b**₂ are g-SiC₂ lattice vectors. 1 and 2 denote the two crystallographic independent C atoms. Reproduced with permission from ref. 2. Copyright 2013 American Chemical Society. (b) Band gaps of (*n*, 0) ($3 \leq n \leq 10$) and (*n*, *n*) ($2 \leq n \leq 6$) g-SiC₂ tubes calculated by PBE and HSE06 levels. Reproduced with permission from ref. 2. Copyright 2013 American Chemical Society. Blue horizontal line: band gap of g-SiC₂ siligraphene. (c) The power conversion efficiency limits of the proposed g-SiC₂-based excitonic solar cells (XSC) as a function of the donor band gap and the conduction band offset. Reproduced with permission from ref. 2. Copyright 2013 American Chemical Society. (d) The entire catalytic cycle of g-SiC₂ as an electrocatalyst for the ORR in the alkaline environment. Reproduced with permission from ref. 50. Copyright 2015 Elsevier B.V. (e) The calculated free energy diagrams for the ORR/oxygen evolution reaction (OER) catalyzed by g-SiC₂ at different potentials, $U = 0$ V, U_{eq} , U_{DC} and U_{C} . Reproduced with permission from ref. 46. Copyright 2018 Elsevier B.V. (f) Different magnetic-state energies of pristine g-SiC₂ and X + SiC₂ (X = V, Mn, Co or Ni) when g-SiC₂ is decorated by transition metal atoms in the most stable configurations for spintronic applications. Reproduced with permission from ref. 51. Copyright 2019 Elsevier B.V.

catalysis. Based on charge analysis, the Si atoms are positively charged and can act as the Lewis acid site for adsorption of O₂ molecules.⁵⁰ The DFT simulations showed that O₂ prefers to be adsorbed on the two Si atoms at the *meta*-position with bridge configuration, resulting in strong binding against O₂ (the absolute value of adsorption energy is 1.1 eV) and a low barrier (0.25 eV) for dissociation of adsorbed O₂*. g-SiC₂ exhibits a high rate-determining-step (RDS) activation barrier of 1.18 eV (the step of protonation of first OH*) in the acid environment but a low RDS activation barrier of 0.16 eV (the step of formation of last two OH*) in the alkaline environment. When considering the Eley–Rideal (ER) mechanism, g-SiC₂ shows a high overpotential of 0.96 V in the acid environment but no overpotential in the alkaline environment,⁵⁰ as illustrated in Fig. 3d. Therefore, g-SiC₂ is suitable for metal-free ORR electro-catalysts in alkaline fuel cells.

Moreover, the electro-catalytic performance of g-SiC₂ in non-aqueous lithium–oxygen (Li–O₂) batteries has also been theoretically investigated.⁴⁶ The free energy diagrams for the ORR/OER catalyzed by g-SiC₂ at different potentials as depicted in Fig. 3e elucidate that both the evaluated discharge ($\eta_{\text{ORR}} = 0.85$ V) and charge ($\eta_{\text{OER}} = 2.20$ V) overpotentials are too large for a Li–O₂ battery. Theoretical analysis reveals that the high overpotentials are closely associated with the strong binding of O₂ to g-SiC₂.⁴⁶ Generally speaking, in contrast to its potential in H₂–O₂ fuel cells, g-SiC₂ is not ideal as the cathode catalyst in non-aqueous Li–O₂ batteries.

Unlike its low performance in Li–O₂ batteries, g-SiC₂ is computationally predicted as a promising anchoring material for lithium–sulfur (Li–S) batteries. The binding strength of the S₈ cluster and the soluble lithium polysulfide (Li₂S_{*n*}, including Li₂S₈, Li₂S₆, Li₂S₄, Li₂S₂ and Li₂S) species on g-SiC₂ was systematically investigated *via* DFT calculations.⁵² Compared with

other siligraphenes (g-SiC, g-SiC₃, and g-SiC₅), it is found that g-SiC₂ not only exhibits moderate binding strength with Li₂S_{*n*}, but also stabilizes the almost intact structural motifs and thus avoids its dissolution into the electrolyte. Thus g-SiC₂ shows the capability to immobilize the soluble Li₂S_{*n*} species by suppressing their shuttle effects. Moreover, the conductance of g-SiC₂ only marginally changes after adsorption of Li₂S_{*n*} species, enabling the redox reaction of the Li₂S_{*n*} species anchored on the surface *via* delivering free electrons.

Finally, there are also theoretical studies of g-SiC₂ as the substrate for metal adsorption to design materials with adjustable magnetic properties that are applicable to spintronics. Recently, Golshan *et al.* reported the electronic and magnetic properties of 3D transition metal (TM) decorated g-SiC₂ by spin-polarized DFT calculations.⁵¹ When different TM atoms with various concentrations are adsorbed on SiC₂, various magnetic modes emerge (Fig. 3f). The combination is a ferromagnetic half-metal (FMHM) for V adsorption at both low and high concentrations. As for Mn adsorption, the mixture is FMHM and ferromagnetic metal (FMM) for Mn at low and high concentrations, respectively. When Co is adsorbed on g-SiC₂, the complex behaves as a ferromagnetic bipolar system at low concentration, while for larger concentrations, it becomes an antiferromagnetic semiconductor. In contrast, the Ni-decorated g-SiC₂ always keeps a non-magnetic semiconductor character. This points out a novel path to design materials with tunable magnetic orders from half-metallicity and bipolarity to non-magnetic traits.

3.1.3. g-SiC₃ siligraphene. The atomic structure of g-SiC₃ siligraphene was first proposed by Zhao *et al.*⁵⁵ Within g-SiC₃ siligraphene, a quarter of C atoms at the *para*-position of the graphene honeycomb lattice are uniformly substituted by Si atoms, as shown in Fig. 4a. The unit cell of g-SiC₃ exhibits P6/

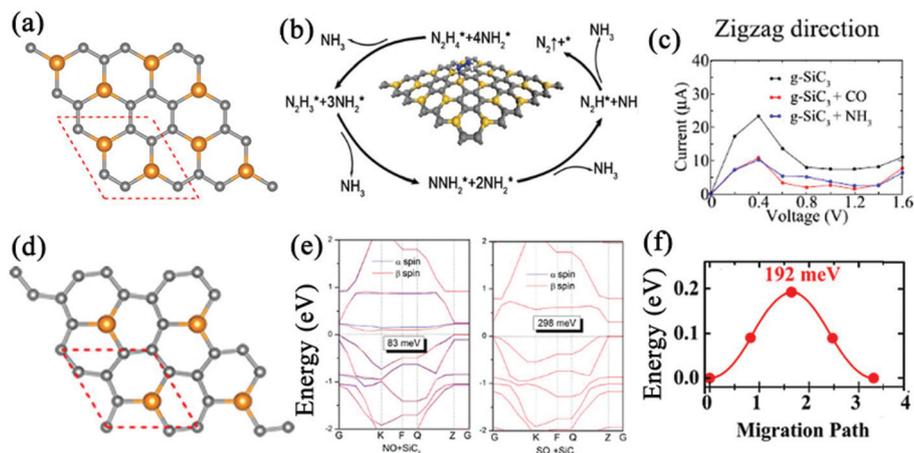


Fig. 4 (a) The crystalline structure of g-SiC₃, with red dash lines marking the unit cell. (b) Schematic depiction of the pathways of catalytic decomposition of hydrazine (N₂H₄) on g-SiC₃. Reproduced with permission from ref. 19. Copyright 2019 Elsevier B.V. (c) Current–voltage characteristics along the armchair and zigzag directions of the g-SiC₃ without and with adsorbed molecules when g-SiC₃ is applied for gas sensing of CO and NH₃. Reproduced with permission from ref. 53. Copyright 2019 American Chemical Society. (d) The crystalline structure of g-SiC₅ with the unit cell marked by red dashed lines. (e) The theoretical band structures of NO and SO₂ adsorbed g-SiC₅ when used as gas sensor. The opened band gap values are marked. Reproduced with permission from ref. 20. Copyright 2017 Elsevier B.V. (f) The optimized Li–vacancy migration pathways on the up side of g-SiC₅ when used in Li-ion batteries (LIBs). Reproduced with permission from ref. 54. Copyright 2018 Elsevier B.V.

mmm symmetry, with the optimized lattice parameter of $a = b \approx 5.6 \text{ \AA}$. All the C atoms in *g*-SiC₃ are equal to each other and, as a result, all the bond angles in *g*-SiC₃ are perfectly 120° without any distortion, making it similar to the expanded graphene.⁵⁵

The electronic analysis elucidates that *g*-SiC₃ is a semi-metal with a DC. Here the couplings among the ring composed of six C atoms (named ring coupling mechanism) account for the formation of the DC feature, as unveiled in two isomorphous phases of *g*-SiC siligraphene.⁵⁶ Moreover, *g*-SiC₃ is illustrated to be a topological insulator (TI) with a non-trivial band gap of 0.43 meV, several orders of magnitude larger than that in graphene.⁵⁵ The electronic and electrical properties of *g*-SiC₃ are essentially unchanged under a compressive external strain of up to -9%,⁵⁷ indicating its high mechanical stability.

There is no evidence showing that *g*-SiC₃ has potential to act as an electro-catalyst. Due to the overbinding of O₂,²⁰ *g*-SiC₃ cannot effectively catalyze the ORR as *g*-SiC₂ does. Another computational study revealed that there exist very high ORR and OER overpotentials when *g*-SiC₃ works as the cathode catalyst in non-aqueous Li-O₂ batteries.⁴⁶ However, *g*-SiC₃ could be used for adsorption and catalytic decomposition of hydrazine (N₂H₄) under mild conditions.^{19,58} The systematic DFT calculations revealed that N₂H₄ prefers to be chemically adsorbed on the *g*-SiC₃ surface with anti configuration, and the N-N bond cleavage (*N₂H₄ → 2*NH₂, * denotes the surface) appears as an initial step. By comparative studies, it is recommended that the pre-adsorbed NH₂ intermediates assisted by intermolecular decomposition should be the optimal pathway for catalytic decomposition of N₂H₄ on *g*-SiC₃, with N₂ and NH₃ being the products (Fig. 4b). The highest activation barrier of 0.83 eV is obtained during the optimal pathway, indicating that *g*-SiC₃ may work as an efficient metal-free catalyst for catalytic decomposition of N₂H₄.¹⁹

Due to the metallic nature of *g*-SiC₃ and its activity against gas molecules, *g*-SiC₃ could be used for gas sensing. This is confirmed by theoretically predicted adsorption behaviors and transport properties for CO and NH₃ molecules adsorbed on *g*-SiC₃ using first-principles calculations and the non-equilibrium Green's function method.⁵³ The physisorption of CO and NH₃ induces a small band gap in *g*-SiC₃. As a result, large resistivity variations are probed when CO and NH₃ molecules are adsorbed. Along the zigzag direction, adsorption of CO and NH₃ causes a more obvious current decrease at a certain voltage (Fig. 4c). The structural flexibility of the sensing medium and the susceptibility of Dirac states to symmetry-breaking distortions are proposed to explain the extraordinary sensitivity of *g*-SiC₃, which is expected to detect CO or NH₃ among diluted gases.

3.1.4. *g*-SiC₅ siligraphene. The *g*-SiC₅ was first predicted in 2015 as a ground state of the Si_{0.17}C_{0.83} material.³⁶ Within *g*-SiC₅, one C atom in the graphene honeycomb lattice is substituted by a Si atom, as shown in Fig. 4d. In the optimized structure of *g*-SiC₅, the unit cell exhibits *P6* symmetry, with a

lattice parameter of $a = b \approx 4.64 \text{ \AA}$.²⁰ There are two different C atoms in the unit cell: the C1 atoms connected directly with one Si atom and two other C atoms, and C2 atoms bonded with three C atoms. All the C1-Si-C1 and C1-C2-C1 angles are 120°. Band structure analysis of *g*-SiC₅ shows that it is semi-metallic with the conduction band minimum (CBM) and VBM in contact with each other at the gamma point to form a DC.

The semimetallic nature of *g*-SiC₅ makes the sensing of gas molecules possible by measuring the change in conductance before and after adsorption. Computational investigations of the adsorption performance of 12 common gas molecules on *g*-SiC₅ reveal that the nucleophilic gas molecules exhibit stable chemisorption on *g*-SiC₅.²⁰ Among them, NO, HCHO and SO₂ show only moderate adsorption energies with *g*-SiC₅ in the range of 0.4–0.6 eV, and considerable band gaps (*e.g.*, 83 meV for HCHO and 265 meV for SO₂) are opened in *g*-SiC₅ due to orbital hybridization, as shown in Fig. 4e. The good selectivity and sensitivity make *g*-SiC₅ promising as the gas sensor for specific air pollutants like NO, HCHO and SO₂.²⁰

In addition, the *g*-SiC₅ material has been proposed as an anode material for lithium-ion batteries (LIBs). The feasibility of *g*-SiC₅ and *g*-SiC₂ as high-capacity anode materials for LIBs was investigated with first-principles calculations.⁵⁴ Taking advantage of the high stability of graphene and the high capacity of silicene, the two siligraphenes show strong adsorption of Li atoms, with the lowest values determined to be -2.536 eV and -2.567 eV for *g*-SiC₅ and *g*-SiC₂, respectively, at the corners of the hexagon far away from the Si atom. The *g*-SiC₅ and *g*-SiC₂ can be fully lithiated into Li₅SiC₅ and Li₅Si₂C₄, respectively, corresponding to the theoretical capacity of 1520 mA h g⁻¹ and 1286 mA h g⁻¹. The dilute Li-vacancy migration pathways on up and down side surfaces of *g*-SiC₅ have diffusion barriers as low as 195 meV and 30 meV, respectively (see Fig. 4f); both are lower than those of *g*-SiC₂. Therefore, *g*-SiC₅ is more favorable as an anode material for LIBs due to its higher theoretical capacity and lower diffusion barriers.

3.1.5. *g*-SiC₇ and β -SiC₇ siligraphenes. The *g*-SiC₇ was confirmed as a low-energy structure in 2015 by using the CE method.³⁶ The unit cell of *g*-SiC₇ belongs to the *P6m2* symmetry group, same as the hexagonal SiC monolayer, with the optimized lattice parameter of $a = b \approx 5.3 \text{ \AA}$.²¹ There are one Si atom and three different types of C atoms per unit cell, where the Si atom trigonally coordinates with the neighboring carbon atoms with a C-Si-C bond angle of 120°, as shown in Fig. 5a. The electronic analysis reveals that *g*-SiC₇ is a semiconductor with a direct band gap (E_g) of 0.76 eV (PBE level) or 1.13 eV (HSE06) (Fig. 5b),²¹ which is larger than that of the above-mentioned *g*-SiC₂ material. The band structure shows that both the VBM and CBM are located at the K point (Fig. 5b), showing potential for light absorption. Based on the high fidelity G_0W_0 with BSE calculations, *g*-SiC₇ is shown to have an exciton binding energy of 0.55 eV. These simulations also placed the optical band gap at 1.0 eV being an ideal value for photovoltaics.²¹ Compared to the *g*-SiC₂ and phosphorene,^{60,61} *g*-SiC₇ possesses an enhanced light absor-

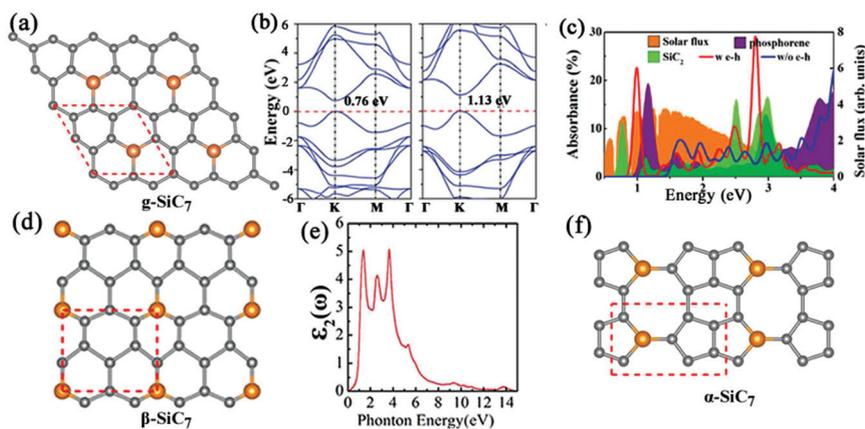


Fig. 5 (a) The crystalline structure of g-SiC₇, with red dashed lines marked the unit cell. (b) Band structure of g-SiC₇ siligraphene obtained from PBE (left) and HSE06 (right) levels, respectively. Reproduced with permission from ref. 21. Copyright 2016 Royal Society of Chemistry. (c) The absorbance spectrum of g-SiC₇ (with and without electron–hole interaction) overlapped to the incident AM1.5 G solar flux for the light donor material photovoltaic application; g-SiC₂ and phosphorene (along the armchair direction) are taken for comparison. Reproduced with permission from ref. 21. Copyright 2016 Royal Society of Chemistry. (d) Low-energy structure of β-SiC₇. (e) The imaginary part of the dielectric function of β-SiC₇ (HSE06 level). Reproduced with permission from ref. 22. Copyright 2019 Wiley-VCH. (f) Low-energy structure of α-SiC₇.

bance for the near infrared and visible region ranging from 0.7–3.0 eV, as depicted in Fig. 5c.²¹ Moreover, the absorbed photon flux (J_{abs}) of g-SiC₇ is 4.64 mA cm⁻², being larger than that in g-SiC₂ (4.06 mA cm⁻²) and phosphorene (3.15 mA cm⁻²),⁶² which makes it usable as a donor material in excitonic solar cells. Moreover, the band gap of g-SiC₇ is tunable, with its value increasing when subjected to biaxial strains from -10% to 10%.^{21,63} Particularly, the band structure of g-SiC₇ changes from direct to indirect under 8% tensile strain and its electrical conductivity reaches the highest value when 6% tensile strain is applied.⁶³

Considering the light weight of g-SiC₇, the hydrogen (H₂) storage characteristics of g-SiC₇ decorated with various light metals were explored.⁵⁹ Through DFT calculations, it is found that g-SiC₇ has strong binding with light metals like Li, Na, K, Mg, Ca, Sc, and Ti and thus exhibits the capability to counteract the competing metal clustering effect. The metal adatoms transfer a fraction of charges to the g-SiC₇ monolayer, leaving a partially charged metal center that could adsorb a maximum of 4 to 5 H₂ molecules. Moreover, the low concentration of metal doping could change the semiconducting g-SiC₇ into a metallic material. 12.5% is confirmed as the favorable doping concentration to reach a high H₂ gravimetric density for the metal decorated g-SiC₇. Particularly, the highest gravimetric density of 6.34 wt% is achieved at the maximum Li concentration (16 H₂ on 4Li-SiC₇) with the ideal H₂ binding energies of 0.2–0.6 eV.⁵⁹

The newly predicted β-SiC₇ siligraphene exhibits *P2mm* symmetry with lattice constants of $a = 5.27 \text{ \AA}$, and $b = 4.57 \text{ \AA}$,²² and is composed of hexagonal rings where the four Si atoms around six carbon ring atoms are arranged as a rectangle (Fig. 5d). The β-SiC₇ siligraphene exhibits a more high stability than g-SiC₇. Calculations of electronic structures demonstrate that β-SiC₇ is a semiconductor with a direct band gap, where

the VBM and CBM are located at the same k point along the path of Γ -X in the BZ. The obtained HSE06 band gap of β-SiC₇ is about 1.01 eV, referring a preferable efficiency of light absorption (Fig. 5e). The calculated hole mobility of β-SiC₇ can reach $\sim 10\,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. The proposed β-SiC₇/g-SiC₇ heterostructure can achieve a maximum PCE of 20.7%, indicating potential of β-SiC₇ as a donor material for photovoltaics.²²

3.2. Si-rich siligraphenes

Compared to the silicon carbides that have a higher ratio of C than Si, the 2D Si_xC with a higher concentration of Si atoms are much less studied due to the preferential sp³ hybridization of Si atoms. Generally, the 2D Si_xC show buckled structures with relatively lower stability. Many of these structures are metallic or semi-metallic. The potential applications of 2D Si_xC are also rarely reported.

Taking the Si-rich counterpart of siligraphenes, the structure and properties of graphitic g-Si_nC ($n = 3, 5, 7$) were theoretically investigated by Peng *et al.*²³ For g-Si₅C and g-Si₇C, the buckled structures were found to be slightly more stable than the corresponding planar structures. They share the same symmetry group as g-SiC₅ and g-SiC₇C but have a larger lattice. As seen from the electronic bands of the buckled g-Si₅C (Fig. 6a), it is semimetallic with a DC feature appearing around the Γ point. Meanwhile, the buckled g-Si₇C is a semiconductor with an energy gap of 0.433 eV at the K point.

Particularly, the g-Si₃C is a much more studied case than g-Si₅C and g-Si₇C materials due to its unique band structures as its C-rich counterpart g-SiC₃,^{55,56} as shown in Fig. 6b. Here the overlapping of p^z orbitals of C and Si atoms results in conjugated π orbitals extended throughout the framework, and thus produces the asymmetric distribution of wave functions around the C and Si atoms.⁵⁵ As a result, the g-Si₃C is semi-metallic with a DC featured band structure due to the ring

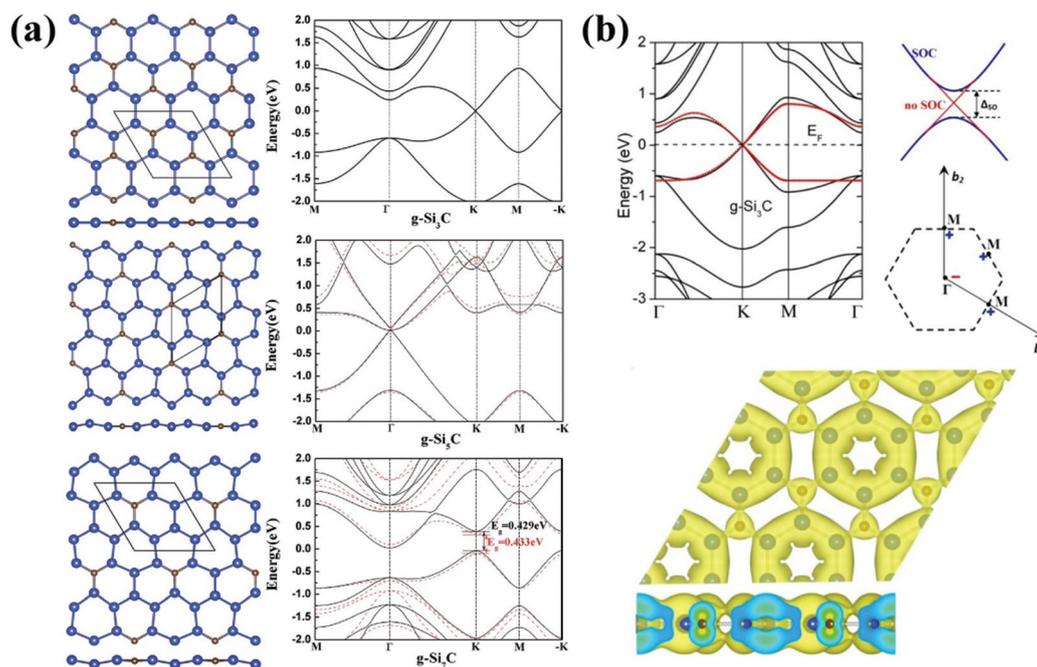


Fig. 6 (a) The atomistic structure (left) and band structure (right) of $g\text{-Si}_n\text{C}$ for $n = 3, 5$ and 7 . In the right panel, the black solid and red dashed curves denote the band structure of the flat and buckled structures, respectively. Reproduced with permission from ref. 23. Copyright 2019 Royal Society of Chemistry. (b) Band structures of $g\text{-Si}_3\text{C}$ along high-symmetry points (upper panel). Black and red lines represent the data obtained from DFT calculations and tight-binding model, respectively. Schematic representation of the enlarged view of the electronic bands with (blue) and without (red) spin-orbit coupling in the proximity of a Dirac point and a Brillouin zone (BZ) path are also shown. Lower panel: The spatial distribution of the electron wave functions of the two Dirac bands in BZ. Both top and side views are displayed. Reproduced with permission from ref. 55. Copyright 2014 American Physical Society.

coupling mechanism referring to the couplings of six Si ring atoms.⁵⁶

The semi-metallic nature of $g\text{-Si}_3\text{C}$ ensures its good electrical conductivity, based on which Dai *et al.* theoretically proposed and evaluated its potential as an anode material for LIBs.⁶⁴ It is reported that the adsorption energy for lithium atoms on $g\text{-Si}_3\text{C}$ (-2.58 eV) is large enough to ensure a good stability during the lithiation and de-lithiation processes. The fully lithiated $g\text{-Si}_3\text{C}$ possesses a composition of $(\text{Li}_6\text{Si}_3\text{C})_2$, corresponding to a high theoretical capacity of 1675 mA h g^{-1} and a low open-circuit voltage of 0.20 eV. However, the diffusion barrier of Li atoms on $g\text{-Si}_3\text{C}$ is 0.46 eV, which is relatively high and may hinder the practical applications of $g\text{-Si}_3\text{C}$ in LIBs.

3.3. Non-siligraphene 2D Si-C structures

Though these siligraphenes were extensively studied with many reports, there are many more 2D SiC_x materials exhibiting structures that are quite different from the reference graphene honeycomb. Unlike the 3-coordinated Si atoms in siligraphenes that show $sp^2\text{-}sp^3$ hybridization characteristics, in many non-siligraphene cases, the Si atoms prefer sp^3 hybridization with a 4-coordination feature. It should be pointed out that all the 2D SiC_x structures discussed below have local

minima in energy, with computationally validated structural, dynamic and thermodynamic stabilities.

3.3.1. $t\text{-SiC}$, $t\text{-Si}_2\text{C}$ siligraphenes and $\gamma\text{-siligraphyne}$. In 2017 Fan *et al.* predicted two types of novel structural motifs with distinctive bonding patterns.²⁸ The first type of 2D Si-C sheet, containing $t\text{-SiC}$ (Fig. 7a) and $t\text{-Si}_2\text{C}$ (Fig. 7b) siligraphenes, can be characterized by tetragonal lattices. Among them, the $t\text{-SiC}$ monolayer is defined by each C atom bonding with four neighboring Si atoms in a puckered plane with a thickness of about 1 Å, constituting a quasi-planar four-coordinated rectangular moiety.²⁸ This moiety resembles our previously reported monolayers of ZrC⁶⁵ and TiN,⁶⁶ representing a lattice prototype in the family of 2D materials. Interestingly, this structure exhibits an insulator-semimetal transition when subject to the external strain,²⁸ indicating the promising applications for strain-dependent optoelectronic sensors. The $t\text{-Si}_2\text{C}$ siligraphene forms an exactly flat rectangular structure, also adopting the four-coordinating way in the chemical bonding process. The optimized lattice constants are $a = 2.8$ Å and $b = 9.1$ Å. Band structure calculations indicate that $t\text{-Si}_2\text{C}$ is metallic. The $3p^z$ electrons of Si atoms and the $2p^z$ orbitals on the C atoms occupy the bands near the Fermi level, which accounts for the metallic property in the $t\text{-Si}_2\text{C}$.²⁸ The second type of 2D Si-C sheet is named $\gamma\text{-siligraphyne}$ with acetylenic linkages ($\text{-C}\equiv\text{C-}$) and possesses high pore sizes and Poisson's ratio.

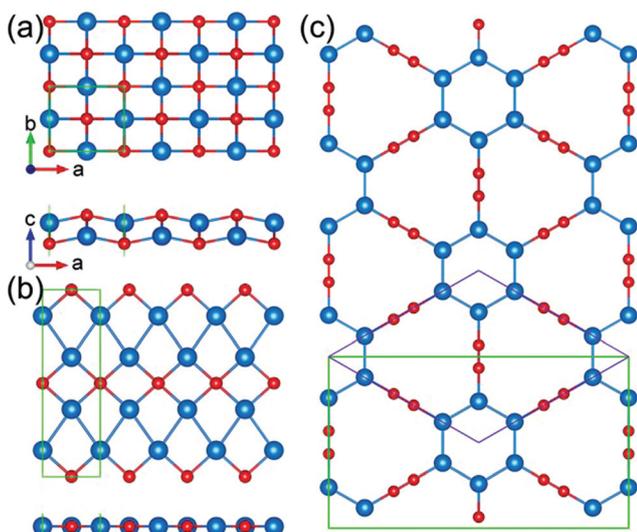


Fig. 7 Top (upper) and side (lower) views of the structure of (a) *t*-SiC, (b) *t*-Si₂C and (c) γ -silagraphyne monolayer. Blue balls: Si atoms; red balls: C atoms. The rhombohedra (violet) and rectangular (green) unit cells are also indicated. Reproduced with permission from ref. 28. Copyright 2017, Royal Society of Chemistry.

These features make it a potential material for applications in separation membranes and catalysis. Moreover, γ -silagraphyne (Fig. 7c) demonstrates a direct band gap of 0.89 eV, enabling a strong optical absorption in the visible-light region.²⁸

3.3.2. pt-SiC₂ and penta-SiC₂ silagraphenes. As the earliest sample of the 2D SiC_x structure, the planar tetra-coordinated SiC₂ (pt-SiC₂) silagraphene was predicted in 2011.²⁴ As shown in Fig. 8a, the pt-SiC₂ silagraphene is purely planar with each Si atom bonding with four carbon atoms to form a ptSi moiety, which is composed of the SiC₄ molecule as a building block. It is proposed that the planarity-preferred ethylene-like skeletons account for the planar SiC₂ network. The pt-SiC₂ is metallic with several energy levels crossing around the Fermi level. The metallic nature of SiC₂ mainly originates from the π -type C≡C bonds, which is significantly different from the semimetallic graphene or semiconducting *g*-SiC. To this end, there are no proposed applications or following studies on pt-SiC₂; however, more 2D materials with SiC₂ stoichiometry (including the *g*-SiC₂) are then inspired by the design of pt-SiC₂.

The penta-SiC₂ is another 2D Si-C material that shares the composition of SiC₂, which was theoretically designed by Lopez-Bezanilla and Littlewood in 2015.²⁵ The penta-SiC₂ is an isostructure of the penta-graphene,⁶⁸ where the two sp³ hybridized C atoms are substituted by two Si atoms. All the pentagons in penta-SiC₂ are equal with four equivalent Si-C and one C-C edges, as shown in Fig. 8b. Different from the *g*-SiC₂ or pt-SiC₂, penta-SiC₂ exhibits a significant buckled structure, with a thickness of 1.3 Å. The penta-SiC₂ is a semiconductor with an indirect band gap of 2.40 eV (HSE06 results).⁶⁷ A detailed analysis of the contribution of atomic orbitals revealed that the C p_z orbital dominates the CBM, while the VBM is mainly composed of the p orbitals of C and Si atoms.²⁵ Compared with

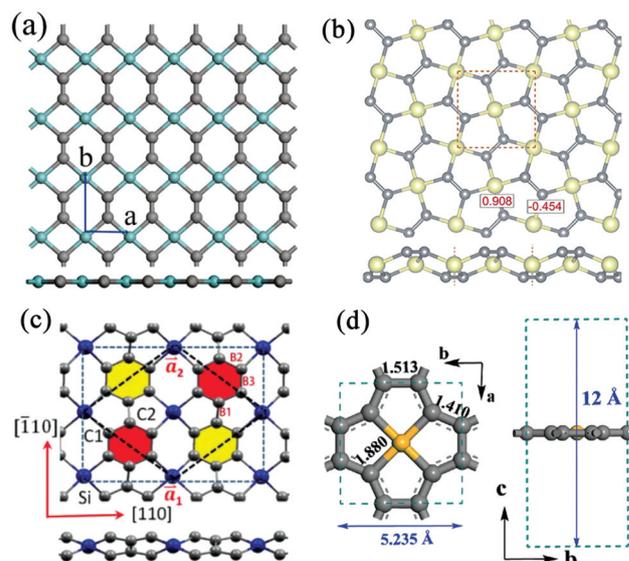


Fig. 8 The optimized geometric structures of (a) pt-SiC₂ (both the top view and side view). Reproduced with permission from ref. 24. Copyright 2011 American Chemical Society. (b) Penta-SiC₂ (both the top view and side view). Reproduced with permission from ref. 67. Copyright 2016 Royal Society of Chemistry. (c) 2D SiC₆ (both the top view and side view). Reproduced with permission from ref. 26. Copyright 2018, Royal Society of Chemistry. (d) 2D SiC₈ with indicated lattice parameters (both the top view and side view). Reproduced with permission from ref. 27. Copyright 2018 Royal Society of Chemistry.

penta-graphene, a greater light absorption for both the visible and the ultraviolet spectral ranges is found for penta-SiC₂, making it suitable for photovoltaic applications. Moreover, penta-SiC₂ exhibits an enhanced electronic transport that originates from the delocalization of electronic states and smaller variations of the electrostatic potential within the system.⁶⁷ By applying in-plane tensile or compressible strain, the electronic transport properties could be effectively tuned by strain-engineering. In particular, under the uniaxial compressive strain of -8% along the *a*-direction, the hole mobility of penta-SiC₂ along the *b*-direction could be enhanced by almost three orders of magnitude up to $1.14 \times 10^6 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$. Therefore, p-SiC₂ may be also suitable for applications in electronic and optoelectronic devices.⁶⁹

3.3.3. SiC₆ silagraphene. The 2D SiC₆ is composed of sp²-hybridized C and sp³-hybridized Si atoms with a *Cmma* symmetry.²⁶ As shown in Fig. 8c, two lattice basis vectors (**a**₁) and (**a**₂) are equal in length (6.5 Å) with an angle of 73.7°, forming a rhombic unit cell. The phenylsilane composed of a benzene ring and sp³-hybridized Si atoms are presumably the synthetic components of 2D SiC₆. The 2D SiC₆ has an indirect band gap of 0.225 eV (PBE) or 0.727 eV (HSE06). Under a compressive strain, SiC₆ could convert to a direct band gap semiconductor. However with the increase of tensile strain, the band gap firstly decreases to a minimum value and then increases. Subsequently, the hole and electron carrier mobilities in SiC₆ can be significantly improved by applying external strain.

Moreover, SiC₆ is reported as an auxetic material with negative Poisson's ratios, rendering its ability to bear a biaxial tensile strain up to 18%. Thus the 2D SiC₆ shows potential for application in mechano-electronic devices.²⁶

3.3.4. α -SiC₇ monolayer. The α -SiC₇ structure proposed in 2019 is one novel 2D structure with a composition of 1 : 7.²² As shown in Fig. 5f, the α -SiC₇ is composed of pentagons, hexagons, and heptagons in a flat basal plane, belonging to *P2mm* symmetry with optimized $a = 0.40$ nm and $b = 0.65$ nm. The α -SiC₇ material has better structural stability compared to that of the γ -SiC₇. Calculations of electronic structures demonstrate that α -SiC₇ possesses a semimetallic feature with small electronic and hole pockets due to the existing bands crossing the Fermi energy.²²

3.3.5. 2D SiC₈ silagraphene. The planar SiC₈ silagraphene is initially constructed with the optimized stable C₁₂H₈Si molecule as a building block. As shown in Fig. 8d, the optimized 2D SiC₈ silagraphene exhibits *P4/mmm* symmetry and lattice parameters of $a = b \approx 5.2$ Å.²⁷ In SiC₈, the Si atom adopts tetra-coordination with the surrounding C atoms, while the 8 C atoms form a conjugated eight-membered ring. The SiC₈ silagraphene is metallic, characterized by several energy bands near the Fermi level in the band structure. Its nature as a conductor and as an electron acceptor makes it possible to work as an anode material in LIBs. The calculated theoretical capacity of the SiC₈ sheet is 1297 mA h g⁻¹, much larger than that of graphene. Nonetheless, the diffusion of Li and Li⁺ in SiC₈ silagraphene is acceptable due to low migration barriers, and the average cell voltages are close to the voltage value of the commercial anode materials.²⁷

4. Experimental advances in the synthesis of 2D silicon carbides

Reliable production of 2D atomically thin Si-C sheets with a uniform size and properties is essential to translating superior properties into high-performance devices. Top-down (such as mechanical exfoliation)⁷⁰ and bottom-up (such as chemical vapor deposition)^{71,72} methods are the main routes for the fabrication of 2D materials. Over about the last decade, despite the numerous theoretical guidelines including structure predictions and simulations of electronic properties for 2D Si-C crystals, experimental fabrication techniques are still underdeveloped. In the Si-C system, a stronger Si-C covalent bond length inhibits the overlaps of p-p orbital and thus leads to the preference of sp³ hybridization of Si atoms across the Si-C network,⁷³ which significantly differs from the pure sp² hybridization in graphene. This trend makes the interlayer coupling far stronger than the van der Waals force in the 2D Si-C monolayer and potentially disables its bare cleavage that requires an extra post-etching process⁷⁴ thus entitling high fabrication cost. In particular, the fabricated Si-C system is a form of 3D bulk phase with a thickness in the scale of μm .⁷⁴ So that, synthetic routes toward the high-quality 2D Si-C crystals have to resort to other approaches.

In theory, Bijoy *et al.* reported that 2D layers of SiC can be exfoliated by lithiation with an average lithium intercalation potential of 0.2 V.⁷⁵ In experiment, to the best of our knowledge, only a few phases of 2D Si-C crystals have been prepared to be within the nanoscale in experiment, that is, 2D SiC and SiC₂ siligraphenes. Lin *et al.* demonstrated that 2D SiC nanoflakes with thicknesses down to 0.5–1.5 nm could be possibly obtained *via* solution exfoliation by sonication of wurtzite SiC.¹⁰ However, the *a*- and *c*-axis lattice constants of fabricated 2D SiC are reported to be 0.266 and 0.694 nm, respectively, which are inconsistent with other experimental observations⁷⁶ and are very close to those of a typical graphite (0.246 and 0.67 nm). The use of the exfoliation technique in producing 2D SiC from 3D SiC was also doubted after analyzing the lattice constant and X-ray powder diffraction peaks.⁴⁹ Yaghoubi and coworkers have thus speculated that what has been observed is a form of graphene.⁴⁹ Conversely, they also found different several-layer thick sheets of SiC siligraphene with different stacking orders as characterized by field-emission scanning electron micrographs and further analyzed by DFT calculations.⁴⁹ These experimental explorations constitute the synthetic progress toward high quality 2D Si-C sheets.

Following the top-down methods, the bottom-up approach was also reported for the quasi-2D SiC: the siligraphene with the thickness below 10 nm and lateral length of 0.3–5 μm was experimentally produced by reaction between graphene and a Si source.⁷⁷ Interestingly, the quasi-2D SiC₂ siligraphene was also found during this process as a byproduct with a thickness smaller than 2 nm, which can be stable for over 3 months under ambient conditions. This technique resembles the formation of SiC nanotubes and nanowires *via* the reaction of Si with C nanotubes.⁷⁶ Zou *et al.* reported a one-step solothermal route that can be utilized to prepare the 2H-SiC nanoflakes with the diameters of 200–500 nm and a thickness of ~ 15 nm.⁷⁸ Besides, β -SiC nanoplatelets were synthesized using waste plastic as the economical C source.⁷⁹ The final samples of nanoplatelets possess a hexagonal shape with the thicknesses of ~ 50 nm, the lengths of 300–500 nm and the interplanar spacing of 0.25 nm. Next, the nanocrystalline, microcrystalline and epitaxial cubic SiC films were reported to be fabricated through the chemical vapor deposition method.⁸⁰ Chabi and co-workers synthesized the 2D SiC nanosheets with an average thickness of 2–3 nm and an average size of 2 μm by merging the ultra-light 3D graphene foam and SiO at high temperature.⁷³

In spite of these efforts, a truly 2D siligraphene monolayer is yet to be realized due to mixed orbital hybridization modes (sp² and sp³) present in 2D Si-C materials. Notably, the single-atom-thick SiC siligraphene nanograins assembling within the graphene oxide pores were observed by atomic resolution scanning transmission electron microscopy.⁸¹ Although the successful synthesis of the Si-C monolayer is not claimed, the observation of small area nanograins may help to further refine experimental efforts towards realization of high quality 2D Si-C systems. Besides SiC and SiC₂ siligraphenes, Si-doped graphene could be considered as another siligraphene with a

small ratio of Si/C. Zhang *et al.* reported that Si-doped graphene with a large surface area was synthesized using a chemical vapor deposition method at the doping levels of 2.7–4.5%.⁸² However, the larger doping concentrations of Si atoms into graphene leading to larger band gaps are still challenging. We expect more reports on the experimental fabrication of single-atom-thick high quality monolayer or few-layer Si–C crystals will be emerging in the near future boosting the fundamental research and highlighting their practical applications.

5. Prospects and summary

The fascinating physical and chemical properties make 2D Si–C crystals promising materials for a variety of future technological uses. While great progress has been made in simulating the properties and structure of 2D Si–C materials, so far, many theoretically predicted 2D Si–C systems are yet to be synthesized. The limited experimental observations of 2D Si–C still contain some contradicting signatures of known SiC nanosheets that need to be clarified. The lack of experimental synthetic routes is currently the largest bottleneck in the field, which hinders further exploration of these systems. We expect more 2D Si–C materials with high quality to be soon fabricated and measured towards realizing theoretically predicted functionalities that can be attained by the modern state-of-art preparation methods. Despite this setback, the modeling development of 2D Si–C materials is in a full swing due to their high potential in the modern electronic industry. Besides, reducing dimensionality in the structure, *i.e.*, the exploration of 1D and 0D Si–C nanosystems also became a promising research direction somewhat making up for the deficiency of the synthesis of pure 2D Si–C crystals. Here, numerous cases have been investigated in theory and/or in experiment, including systems such as SiC nanoribbons,^{83,84} nanowires,⁷⁶ nanotubes,^{2,76,85–87} SiC-nanograins,⁸¹ 0D quantum dots,⁸⁸ and related heterostructures.⁷⁶ Besides 2D Si–C materials, theoretical design of 2D pure C-based materials is another feasible way to advance the knowledge of carbon chemistry in modern device applications. Notably, multiple studies of 2D transition-metal carbides (such as TiC,⁶⁵ TaC,⁸⁹ FeC₂,⁹⁰ *etc.*), III–C,⁹¹ and IV–C⁹² families are reported in experiment and/or theory. These studies could be further enriching the research direction for 2D C-based materials.

In summary, we have provided an overview of the recent progress in theoretical modeling of 2D Si–C materials in terms of materials design, morphology, physicochemical properties, and indicated their potential applications. 2D Si–C crystals have an intriguing versatility of structures and properties. This makes 2D Si–C sheets to stand up in the burgeoning family of 2D layered materials with great promise for their applications in sensors, catalysts, electronics, spintronics, photovoltaics, *etc.* However, at the moment, experimental research seems to lag behind modeling advances. Subsequently, with the development of experimental fabrication routes, more fundamental

and technological breakthroughs of high-quality 2D Si–C crystals can be expected in the near future.

Conflicts of interest

There are no conflicts to declare.

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References

- 1 X. Xu, C. Liu, Z. Sun, T. Cao, Z. Zhang, E. Wang, Z. Liu and K. Liu, *Chem. Soc. Rev.*, 2018, **47**, 3059–3099.
- 2 L.-J. Zhou, Y.-F. Zhang and L.-M. Wu, *Nano Lett.*, 2013, **13**, 5431–5436.
- 3 S. Y. Zhou, G.-H. Gweon, A. V. Fedorov, P. N. First, W. A. D. Heer, D.-H. Lee, F. Guinea, A. H. C. Neto and A. Lanzara, *Nat. Mater.*, 2007, **6**, 770–775.
- 4 S. Y. Zhou, D. A. Siegel, A. V. Fedorov, F. E. Gabaly, A. K. Schmid, A. H. C. Neto, D.-H. Lee and A. Lanzara, *Nat. Mater.*, 2008, **7**, 259–260.
- 5 H. Sahin, M. Topsakal and S. Ciraci, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **83**, 115432.
- 6 J. O. Sofo, A. S. Chaudhari and G. D. Barber, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **75**, 153401.
- 7 H. Min, B. Sahu, S. K. Banerjee and A. H. MacDonald, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2007, **75**, 155115.
- 8 L. Yang, C.-H. Park, Y.-W. Son, M. L. Cohen and S. G. Louie, *Phys. Rev. Lett.*, 2007, **99**, 186801.
- 9 H. J. Xiang, B. Huang, Z. Y. Li, S.-H. Wei, J. L. Yang and X. G. Gong, *Phys. Rev. X*, 2012, **2**, 011003.
- 10 S. S. Lin, *J. Phys. Chem. C*, 2012, **116**, 3951–3955.
- 11 J. P. Perdew and A. Zunger, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1981, **23**, 5048–5079.
- 12 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2003, **118**, 8207–8215.
- 13 J. Heyd, G. E. Scuseria and M. Ernzerhof, *J. Chem. Phys.*, 2006, **124**, 219906.
- 14 S. Q. Wu, M. Ji, C. Z. Wang, M. C. Nguyen, X. Zhao, K. Umemoto, R. M. Wentzcovitch and K. M. Ho, *J. Phys.: Condens. Matter*, 2013, **26**, 035402.
- 15 C. W. Glass, A. R. Oganov and N. Hansen, *Comput. Phys. Commun.*, 2006, **175**, 713–720.

- 16 Y.-Y. Zhang, W. Gao, S. Chen, H. Xiang and X.-G. Gong, *Comput. Mater. Sci.*, 2015, **98**, 51–55.
- 17 Y. Wang, J. Lv, L. Zhu and Y. Ma, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **82**, 094116.
- 18 J. M. Sanchez, F. Ducastelle and D. Gratias, *Physica A*, 1984, **128**, 334–350.
- 19 F. Zheng, H. Dong, Y. Ji and Y. Li, *Appl. Surf. Sci.*, 2019, **469**, 316–324.
- 20 H. Dong, L. Wang, L. Zhou, T. Hou and Y. Li, *Carbon*, 2017, **113**, 114–121.
- 21 H. Dong, L. Zhou, T. Frauenheim, T. Hou, S.-T. Lee and Y. Li, *Nanoscale*, 2016, **8**, 6994–6999.
- 22 J. Guan, L. Zhang, K. Deng, Y. Du and E. Kan, *Adv. Theory Simul.*, 2019, **2**, 1900058.
- 23 X. Tang, W. Liu, C. Luo, X. Peng and J. Zhong, *RSC Adv.*, 2019, **9**, 12276–12281.
- 24 Y. Li, F. Li, Z. Zhou and Z. Chen, *J. Am. Chem. Soc.*, 2011, **133**, 900–908.
- 25 A. Lopez-Bezanilla and P. B. Littlewood, *J. Phys. Chem. C*, 2015, **119**, 19469–19474.
- 26 X. Liu, X. Shao, B. Yang and M. Zhao, *Nanoscale*, 2018, **10**, 2108–2114.
- 27 M.-J. Sun, X. Cao and Z. Cao, *Nanoscale*, 2018, **10**, 10450–10458.
- 28 D. Fan, S. Lu, Y. Guo and X. Hu, *J. Mater. Chem. C*, 2017, **5**, 3561–3567.
- 29 R. Xu, X. Zou, B. Liu and H.-M. Cheng, *Mater. Today*, 2018, **21**, 391–418.
- 30 I. Shtepliuk, V. Khranovskyy and R. Yakimova, *Semicond. Sci. Technol.*, 2016, **31**, 113004.
- 31 X. Xiao, H. Wang, P. Urbankowski and Y. Gogotsi, *Chem. Soc. Rev.*, 2018, **47**, 8744–8765.
- 32 Q. Tang, Z. Zhou and Z. Chen, *Wiley Interdiscip. Rev.: Comput. Mol. Sci.*, 2015, **5**, 360–379.
- 33 X. Luo, J. Yang, H. Liu, X. Wu, Y. Wang, Y. Ma, S.-H. Wei, X. Gong and H. Xiang, *J. Am. Chem. Soc.*, 2011, **133**, 16285–16290.
- 34 Y. Wang, J. Lv, L. Zhu and Y. Ma, *Comput. Phys. Commun.*, 2012, **183**, 2063–2070.
- 35 J. Zhang, J. Ren, H. Fu, Z. Ding, H. Li and S. Meng, *Sci. China: Phys., Mech. Astron.*, 2015, **58**, 106801.
- 36 Z. Shi, Z. Zhang, A. Kutana and B. I. Yakobson, *ACS Nano*, 2015, **9**, 9802–9809.
- 37 R. Saito, M. Fujita, G. Dresselhaus and M. S. Dresselhaus, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 1992, **46**, 1804–1811.
- 38 N. Shima and H. Aoki, *Phys. Rev. Lett.*, 1993, **71**, 4389–4392.
- 39 D.-T. Nguyen and M.-Q. Le, *Superlattices Microstruct.*, 2016, **98**, 102–115.
- 40 X. Qin, Y. Liu, X. Li, J. Xu, B. Chi, D. Zhai and X. Zhao, *J. Phys. Chem. Lett.*, 2015, **6**, 1333–1339.
- 41 L. Wang and H. Sun, *J. Mol. Model.*, 2012, **18**, 4811–4818.
- 42 X. K. Lu, T. Y. Xin, Q. Zhang, Q. Xu, T. H. Wei and Y. X. Wang, *Nanotechnology*, 2018, **29**, 315701.
- 43 L. Pan, H. J. Liu, Y. W. Wen, X. J. Tan, H. Y. Lv, J. Shi and X. F. Tang, *Phys. Lett. A*, 2011, **375**, 614–619.
- 44 H. C. Hsueh, G. Y. Guo and S. G. Louie, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**, 085404.
- 45 P. Zhang, B. B. Xiao, X. L. Hou, Y. F. Zhu and Q. Jiang, *Sci. Rep.*, 2014, **4**, 1–8.
- 46 H. Dong, Y. Ji, T. Hou and Y. Li, *Carbon*, 2018, **126**, 580–587.
- 47 E. Bekaroglu, M. Topsakal, S. Cahangirov and S. Ciraci, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2010, **81**, 075433.
- 48 X. Lin, S. Lin, Y. Xu, A. A. Hakro, T. Hasan, B. Zhang, B. Yu, J. Luo, E. Li and H. Chen, *J. Mater. Chem. C*, 2013, **1**, 2131–2135.
- 49 A. Yaghoubi, K. Masenelli-Varlot, O. Boisson, S. Ramesh and P. Melinon, *Chem. Mater.*, 2018, **30**, 7234–7244.
- 50 H. Dong, B. Lin, K. Gilmore, T. Hou, S.-T. Lee and Y. Li, *J. Power Sources*, 2015, **299**, 371–379.
- 51 M. F. Saadi, R. Safaiee and M. M. Golshan, *Appl. Surf. Sci.*, 2019, **481**, 484–497.
- 52 Y. Zhao, J. Zhao and Q. Cai, *Appl. Surf. Sci.*, 2018, **440**, 889–896.
- 53 V. Babar, S. Sharma and U. Schwingenschlögl, *J. Phys. Chem. C*, 2019, **123**, 13104–13109.
- 54 H. Wang, M. Wu, X. Lei, Z. Tian, B. Xu, K. Huang and C. Ouyang, *Nano Energy*, 2018, **49**, 67–76.
- 55 M. Zhao and R. Zhang, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2014, **89**, 195427.
- 56 X. Qin, Y. Wu, Y. Liu, B. Chi, X. Li, Y. Wang and X. Zhao, *Sci. Rep.*, 2017, **7**, 10546.
- 57 M. Houmad, M. H. Mohammed, R. Masrouf, A. El Kenz and A. Benyoussef, *J. Phys. Chem. Solids*, 2019, **127**, 231–237.
- 58 F. Zheng, H. Dong, Y. Ji and Y. Li, *Int. J. Hydrogen Energy*, 2019, **44**, 6055–6064.
- 59 S. R. Naqvi, T. Hussain, W. Luo and R. Ahuja, *Nano Res.*, 2018, **11**, 3802–3813.
- 60 L. Kou, C. Chen and S. C. Smith, *J. Phys. Chem. Lett.*, 2015, **6**, 2794–2805.
- 61 H. Liu, A. T. Neal, Z. Zhu, Z. Luo, X. Xu, D. Tománek and P. D. Ye, *ACS Nano*, 2014, **8**, 4033–4041.
- 62 L. Zhou, J. Zhang, Z. Zhuo, L. Kou, W. Ma, B. Shao, A. Du, S. Meng and T. Frauenheim, *J. Phys. Chem. Lett.*, 2016, **7**, 1880–1887.
- 63 M. Houmad, I. Essaoudi, A. Ainane, A. El Kenz, A. Benyoussef and R. Ahuja, *Optik*, 2019, **177**, 118–122.
- 64 Y. Dong, W. Wei, X. Lv, B. Huang and Y. Dai, *Appl. Surf. Sci.*, 2019, **479**, 519–524.
- 65 L. Zhou, B. Shao, W. Shi, Y. Sun, C. Felser, B. Yan and T. Frauenheim, *2D Mater.*, 2016, **3**, 035022.
- 66 L. Zhou, Z. Zhuo, L. Kou, A. Du and S. Tretiak, *Nano Lett.*, 2017, **17**, 4466–4472.
- 67 G. R. Berdiyrov and M. El-Amine Madjet, *RSC Adv.*, 2016, **6**, 50867–50873.
- 68 S. Zhang, J. Zhou, Q. Wang, X. Chen, Y. Kawazoe and P. Jena, *Proc. Natl. Acad. Sci. U. S. A.*, 2015, **112**, 2372–2377.
- 69 Y. Xu, Z. Ning, H. Zhang, G. Ni, H. Shao, B. Peng, X. Zhang, X. He, Y. Zhu and H. Zhu, *RSC Adv.*, 2017, **7**, 45705–45713.
- 70 K. Lee, H.-Y. Kim, M. Lotya, J. N. Coleman, G.-T. Kim and G. S. Duesberg, *Adv. Mater.*, 2011, **23**, 4178–4182.

- 71 X. Li, W. Cai, J. An, S. Kim, J. Nah, D. Yang, R. Piner, A. Velamakanni, I. Jung, E. Tutuc, S. K. Banerjee, L. Colombo and R. S. Ruoff, *Science*, 2009, **324**, 1312–1314.
- 72 Y.-H. Lee, X.-Q. Zhang, W. Zhang, M.-T. Chang, C.-T. Lin, K.-D. Chang, Y.-C. Yu, J. T.-W. Wang, C.-S. Chang, L.-J. Li and T.-W. Lin, *Adv. Mater.*, 2012, **24**, 2320–2325.
- 73 S. Chabi, H. Chang, Y. Xia and Y. Zhu, *Nanotechnology*, 2016, **27**, 075602.
- 74 M. Syväjärvi, R. Yakimova and E. Janzén, *J. Cryst. Growth*, 2000, **208**, 409–415.
- 75 T. K. Bijoy, J. Karthikeyan and P. Murugan, *J. Phys. Chem. C*, 2017, **121**, 15106–15113.
- 76 X.-H. Sun, C.-P. Li, W.-K. Wong, N.-B. Wong, C.-S. Lee, S.-T. Lee and B.-K. Teo, *J. Am. Chem. Soc.*, 2002, **124**, 14464–14471.
- 77 S. Lin, S. Zhang, X. Li, W. Xu, X. Pi, X. Liu, F. Wang, H. Wu and H. Chen, *J. Phys. Chem. C*, 2015, **119**, 19772–19779.
- 78 G. Zou, C. Dong, K. Xiong, H. Li, C. Jiang and Y. Qian, *Appl. Phys. Lett.*, 2006, **88**, 071913.
- 79 Z. Ju, L. Xu, Q. Pang, Z. Xing, X. Ma and Y. Qian, *Nanotechnology*, 2009, **20**, 355604.
- 80 H. Zhuang, N. Yang, L. Zhang, R. Fuchs and X. Jiang, *ACS Appl. Mater. Interfaces*, 2015, **7**, 10886–10895.
- 81 T. Susi, V. Skákalová, A. Mittelberger, P. Kotrusz, M. Hulman, T. J. Pennycook, C. Mangler, J. Kotakoski and J. C. Meyer, *Sci. Rep.*, 2017, **7**, 4399.
- 82 S. J. Zhang, S. S. Lin, X. Q. Li, X. Y. Liu, H. A. Wu, W. L. Xu, P. Wang, Z. Q. Wu, H. K. Zhong and Z. J. Xu, *Nanoscale*, 2016, **8**, 226–232.
- 83 J. Cui, Z. Zhang, D. Liu, D. Zhang, W. Hu, L. Zou, Y. Lu, C. Zhang, H. Lu, C. Tang, N. Jiang, I. P. Parkin and D. Guo, *Nano Lett.*, 2019, **19**, 6569–6576.
- 84 X. Zheng, X. Chen, L. Zhang, L. Xiao, S. Jia, Z. Zeng and H. Guo, *2D Mater.*, 2017, **4**, 025013.
- 85 G. Mpourmpakis, G. E. Froudakis, G. P. Lithoxos and J. Samios, *Nano Lett.*, 2006, **6**, 1581–1583.
- 86 W. Shi, S. Wu and Z. Wang, *Physica E*, 2016, **81**, 192–195.
- 87 M. Menon, E. Richter, A. Mavrandonakis, G. Froudakis and A. N. Andriotis, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2004, **69**, 115322.
- 88 D. Dai, X. Guo and J. Fan, *Appl. Phys. Lett.*, 2015, **106**, 053115.
- 89 L. Zhou, W. Shi, Y. Sun, B. Shao, C. Felser, B. Yan and T. Frauenheim, *2D Mater.*, 2016, **3**, 035018.
- 90 T. Zhao, J. Zhou, Q. Wang, Y. Kawazoe and P. Jena, *ACS Appl. Mater. Interfaces*, 2016, **8**, 26207–26212.
- 91 Y. Xu, J. Dai and X. C. Zeng, *J. Phys. Chem. Lett.*, 2016, **7**, 302–307.
- 92 T.-Y. Lü, X.-X. Liao, H.-Q. Wang and J.-C. Zheng, *J. Mater. Chem.*, 2012, **22**, 10062–10068.