Diamane: design, synthesis, properties, and challenges

Guowen Qin, Lailei Wu and Huiyang Gou

ABSTRACT
Diamane, the two-dimensional counterpart of diamond, is achieved from bilayer graphene (BLG) or few-layer graphene (FLG) through surface chemical adsorption or high-pressure technology. Diamane with interlayer sp^3 bonding is found to have excellent heat transfer, ultra-low friction, high natural frequency, and tunable band gap, which shows the potential technological and industrial applications in nano-photonics, ultrasensitive resonator-based sensors, and improved wear resistance. In this review, we summarize the structure characteristics, synthesis strategies, and physical properties of different diamanes, including hydrogenated diamane (HD), fluorinated diamane (FD), and pristine diamane (PD). In addition, we discuss the effect of functional groups, element doping, and stacking order on the physical properties of diamane. Finally, the remaining challenges and future opportunities for the further development of diamane are addressed.

1. Introduction
Graphene is a two-dimensional (2D) layered material having semi-metallic properties with zero band gap. Extensive investigations have been performed to reveal the interesting physical properties. It is found that the physical properties are strongly influenced by the stacking mode or chemisorption functional group. For example, AB stacking BLG shows high carrier mobility [1] and AA stacking BLG makes the split of linear energy bands intersected with each other [2]. The interlayer interaction of bi-layer graphene (BLG) is critical for the presence of superconducting when the twist angle of the BLG changes to be about 1.1°, that is, the “magic” angle [3]. In addition, the chemical adsorption of various functional groups (such as hydrogen [4,5], fluorine [6–8], and oxygen [9]) on the surface of a single-layer graphene (SLG) can modify the chemical bonding and open the band gap. Furthermore, the studies have found that BLG or few-layer graphene (FLG) can generate single C–C bond between layers by the adsorption. It is well known that the free energy difference between graphite and diamond in bulk is 0.03 eV/atom [10], however, the conversion of graphite to diamond usually requires extreme conditions, such as high temperature and high pressure or plasma chemical vapor deposition technology [11–14], due to the high energy barrier of diamond nucleation. The presence of defects or dangling bonds in the precursors [15–17] is found to be able to decrease the energy barrier for diamond nucleation. Intuitively, the 2D graphene functionalized by the heteroatoms (foreign atoms or functional groups) is suggested to be one possible way to decrease the activation energy of the ortho- and para-positions of the hexagonal ring [18] and thus greatly reduce the transition pressure required for carbon atoms from sp^2 to sp^3 bonding state.

The study of functionalized graphene can be traced back to 2007. A structure was proposed by Sofo et al. [5] with hydrogen saturated surfaces of SLG, in which the carbon atoms becomes sp^3 hybridization, and the fully hydrogenated SLG structure was named “graphane.” After that, Elias et al. [4] obtained partially hydrogenated SLG that behaved as an insulator by placing a remarkably conductive graphene sample in hydrogen plasma. Following, the electronic properties of partially hydrogenated SLG were investigated [4,19] and the fully fluorinated SLG [7] were synthesized successfully in experiment. Then in 2009, Chernozatonskii et al. [20] tentatively simulated the C_H structure formed by the adsorption of hydrogen atoms on the BLG of AB (Bernal) stacking and AA (Lonsdaleite) stacking and named them “diamane.” In the past decades, numerous investigations on the properties of diamane were performed and its potential applications were found in the fields of nano-photonics [21,22] and ultrasensitive resonator-based sensors [23]. Recently, it is exciting that the fully fluorinated AB-stacked diamane [24] and pristine diamane with (2110) orientation [25] were synthesized successfully in experiments. It should be noted that in previous literatures, different names, such as diamane [20,24–26], diamondol [27], diamondene [28], or diamene [29], was adopted for diamane, due to the diversity of surface functional groups on the diamond film surface. Here, for the convenience of discussion, we call them collectively as diamane.
In this review, we outline the structural design of diamane, including the stacking sequence of carbon layers, the number of carbon layers, the types of functional groups, and the surface hydrogenation concentration. The electronic structure, mechanical properties, heat transfer and potential superconductivity, and magnetic properties are also summarized. The stability of diamane is analyzed in thermodynamics, including diamane with different types of functional groups and pristine diamane. We also discuss the current challenges and future opportunities in the research of diamane.

2. Structure and property simulation

2.1. Structural design of diamane

The chemical adsorption of functional groups on the carbon rings in graphene, similar to aromatics, usually leads to a disturbance of properties. As shown in Figure 1, different from the flat honeycomb pattern in graphene, the basic unit of graphane (Figure 1(a)) and diamane (Figure 1(b,c)) with the chair-like C₆ rings forms slightly puckered carbon sheets due to the pyramidalization of hydrogenated (fluorinated) carbon atoms. Meanwhile, the presence of heteroatom increases the thickness of the material due to the addition of extra atomic layers. The studies of hydrogenated (fluorinated) diamane [20,26,30,31] indicate that the structure of hydrogenated carbon atoms is similar to diamond, and the presence of hydrogen on the surface makes the crystal lattice distorted slightly. The movement of adjacent carbon atoms in hydrogenated BLG is much smaller than that in hydrogenated SLG, because the coupling between layers drives the graphene flatter.

2.2. Different stacking and electronic structures

Unlike graphane, the stacking sequence of BLG also plays an important role in the structure and properties of diamane. When the rotation angle of the BLG is 60°, AB stacking becomes the most preferred coherent stacking sequence in energy. Without rotations, BLG is simply stacked together with AA stacking. When the different stacked graphenes meet with the surface functional groups, the cubic diamane (c-D) and hexagonal diamane (h-D) are formed, corresponding to the (111) crystal plane of cubic diamond and the (0001) crystal plane of hexagonal diamond [20], respectively. Theoretical calculations showed that the two types of diamanes with the complete hydrogenation were insulated with a narrower band gap, but harder and more brittle than graphane [20]. In addition, three-layer graphene showed the multiple stacking sequence (ABC, AAA, and AAC types) [26] accompanying with different formation energy band gap. The theoretical calculation results are shown in Figure 2. Among all the stacking types, the diamane with Bernal stacking has the lowest formation energy and the widest band gap within the same number of layers. The difference in formation energy of HD with different stacked structures in the same number of layers is less than 0.02 eV/atom. Considering the smaller difference in energy, the existence of every kind of stacked diamane cannot be ruled out. Moreover, it was found that the band gap energy of diamane with a larger number of carbon layers was smaller than that of graphane (3.5 eV), and as the number of carbon layers increases, the band gap decreases gradually. The quantum confinement effect similar to the above situation could appear in even 5-layer HD [32]. This situation is completely different from several members of diamondoid family in that the band gap is close to diamond as the number of layers increases [33].

Figure 1. Atomic structures model of (a) graphene, (b) AB stacking diamane, and (c) AA stacking diamane and (d) The scheme of forming interlayer C-C bonds on the double-layer graphene: hydrogen atoms (light color) settle on both sides of the graphene, causing carbon atoms (dark color) between adjacent layers to form bonds. Reprinted from [20].
2.3. Different conformations and multiple functional groups of diamane

In addition to the stacking sequence, the different conformations of the C₆ skeleton can also lead to varied polymorphs of diamane. In previous studies, graphane with C₆ skeleton was confirmed to have multiple conformations [35–38]. Due to the similarity of skeleton structure, the conformation of diamane could be constructed by following the conformations of cyclohexane and graphane [37, 39, 40]. Generally, the basic units of the C₆ skeleton can be classed into four different conformations, that is, "chair1," "chair2," "boat1," and "boat2" [41] (as shown in Figure 3), corresponding to crystal plane (111), (110) of c-diamond and (1010), (2110) of h-diamond, respectively. The dangling bonds on the surface of the conformations are usually stabilized by different functional groups, such as hydrogen, fluorine, water, ammonia, and oxygen. The results of formation energy and phase transitions show that the energetically favorable conformations of diamane are varied under different temperature and pressure conditions. The theoretical calculations show that diamane with the specific functional groups can be synthesized at relatively lower pressure conditions [21, 24, 41–43].

2.4. Influence of metal substrate and hydrogenation concentration

Substrate materials are vital for the preparation of the atomic-thick diamane films in experiments. Growth, transfer [1, 44], and functionalization [24, 43] of graphene always needs the substrate materials, which makes it necessary to study the interaction between single-sided hydrogenation (fluorination) of graphene and the substrate materials. The adsorption of graphene on metal surfaces can be classified into two categories, a strong interaction by chemical adsorption on the surface of cobalt or nickel and a weak interaction by physical adsorption on the surface of copper or platinum.
The properties of these two different types of substrates were theoretically predicted during graphene hydroge

nation [31]. It was found that, when there was no metal substrate, the one-side hydrogenation/fluorination of BLG was not energetically favorable to form $sp^3$ bonds between neighboring carbon layers. When the AB-stacked BLG was hydrogenated on a metal substrate, the “chair-like” carbon layer could not only be stabilized at the more reactive interface, such as cobalt (0001) and nickel (111), but also could form stable covalent bonds with less reactive interface, such as copper (111). The main driving force for this transformation comes from the hybridization between $sp^3$ orbitals and $dz^2$ orbitals on the metal surface. The induced electronic gap states and spin moment in the carbon layers are confined to the area within 0.5 nm of the metal surface. This metal/$sp^3$ carbon interface was predicted to have superconducting properties [31].

2.5. Thermodynamics of pristine diamane

The transformation to diamane of FLG with clean surface is very attractive. In order to distinguish the functionalized diamane, we refer to diamane with a pristine surface as pristine diamane (PD). Kvashnin et al. [42] studied the thermodynamic phase diagram of the conversion of 2–8 layers of graphene with (111) surface to PD. It is found that when the number of layers was two, the diamond could not be nucleated due to the graphitization effect. This graphitization effect is the conversion of diamond to graphite due to the surface effects in the diamond nanostructure [35,45], which indicates that the diamond film formed by low-layer graphene requires the stability of heteroatom. At greater thicknesses, the nucleation of diamond would not be affected by surface effects. When the number of layers was greater than 5, the pristine diamane become metastable. As the number of layers increases, a semi-metal to semi-conductor transition took place. Paradoxically, molecular dynamics simulation suggested that the conversion of pristine graphene to diamane was reversible [21]. In terms of phase transition pressure, theoretical results support that the formation of PD requires high-pressure conditions and as the number of layers decreases, the phase transition pressure of PD increases accordingly [21,42].

3. Synthesis and characterization of diamane

Experimentally, the studies on diamane are limited to HD, FD, and PD. Due to the unpaired electrons of surface carbon atoms, the synthesis of PD requires extreme higher pressure and the products cannot be maintained.

Figure 3. (a) Top perspective drawing view and (b) side views of graphene functionalized with different layers. Conformational unit is marked in red. Single-layer functionalized graphene is named by conformation, whereas larger-layer films are named by the corresponding orientation of diamond. Reprinted from [41]. Copyright 2015 American Chemical Society.
at ambient pressure. In addition, even though HD and FD have similar structures, the functional group atoms have a significant influence on their properties. So far, it is still difficult to synthesize fully hydrogenated diamane in experiment. The difference in stability also requires the precise control of temperature for HD preparation. Furthermore, the hydrogen and carbon atoms are difficult to characterize their content and valence properties [24]. Here, we have discussed the current experimental investigations of diamane and summarized the available synthesis method of diamane.

3.1. Hydrogenated and hydroxylated diamane

SLG hydrogenation shows that graphene with only one side exposed to hydrogen has a non-stoichiometric composition [4,46] and graphene hydrogenated from one or both sides would also easily lose hydrogen rapidly at moderate temperatures [4]. Furthermore, theoretical results prove that SLG is more difficult to be hydrogenated than SLG [32,46]. Therefore, the preparation of fully hydrogenated diamane remains difficult and requires specific temperature control. In a previous experiment, pressure was applied on the bi-layer and multi-layer graphene samples covered by the water layer through the tip of the scanning probe microscopy (SPM), and it was observed that the electric force microscopy (EFM) response was reduced significantly. However, this phenomenon was not observed in a dry environment [47]. Through simulation, it was believed that the hydroxyl group provided by the water layer on the top promoted the diamondization of graphene under the pressure but the proposed structure could not maintain at the ambient pressure. Hydroxylated diamane was predicted to be a 2D ferromagnetic insulator. Martins et al. [28] performed the high-pressure experiments in a diamond anvil cell (DAC) to functionalize the top of BLG. Water acted as both a pressure transmission medium (PTM) and a provider of hydroxyl or hydrogen atoms in the experiment. The BLG prepared by the chemical vapor deposition is transferred to Teflon substrate. The substrate did not react with the precursor graphene and could prevent the bottom carbon atoms from being functionalized. As a result, chemical adsorption only occurred on top of graphene. Through the measurement of Raman spectroscopy during the pressurization process (Figure 5), it was found that, as the pressure increases, the \( \text{sp}^3 \) hybridization occurred in the carbon layer, forming a mixed \( \text{sp}^2 \) and \( \text{sp}^3 \) and G band broadening. Calculations within density functional theory showed that diamane was formed at 4–5 GPa. Nevertheless, Raman spectroscopy is an indirect method to detect \( \text{sp}^3 \) carbon bonds, and the single-point measurements cannot determine hydrogen position bounded either to the surface of the layer or only to the edge. To prove that graphene forms the interlayer \( \text{sp}^3 \) bonds, more direct evidence is needed in future [48].

Hydrogenation of graphene could be also achieved by the hot filament process at nearly ambient conditions. The hot filament process can effectively generate hydrogen atoms [43,48,49] and avoid ion acceleration damage to the graphene sample. Experimentally, FLG can be grown on Pt(111) by chemical vapor deposition, and then, HD can be prepared by chemical adsorption of carbon atoms on the graphene surface with deuterium atoms produced by the hot wire process [43]. Using synchrotron spectroscopic techniques, it was confirmed that 76% of the carbon atoms in the four-layer graphene formed interlayer \( \text{sp}^3 \) hybridization. Theoretical calculations argued that the surface
adsorption of hydrogen caused the sp^3 hybridization to propagate from the surface to the carbon layers and the bottom carbon atoms interacted with the substrate and were stabilized eventually. The hot filament process can also realize the double-sided hydrogenation of graphene. However, due to the difference in the number of layers and stacking patterns during the preparation of graphene, the hydrogenated products were found to be a variety of mixtures of diamane checked by Raman spectroscopy and Fourier transform infrared (FTIR) microscopy [48].

### 3.2. Fluorinated diamane

When the surface of BLG or FLG is functionalized with fluorine atoms, a diamond-like structure can be obtained, namely fluorinated diamane (FD). Compared with the hydrogenation reaction of graphene, the formation for fluorination of graphene is relatively feasible in experiments. Generally, FD can be obtained at a lower temperature [6,24,36,50] and the thermal stability of FD is significantly better than that of HD [4,51]. FD can be stabilized at 400°C even in air [6,27], and fully fluorinated diamane is more feasible to be prepared experimentally than fully hydrogenated diamane [6,24]. Some reports also described different carbon/fluorine ratios in fluorinated diamane, that is, the new incomplete fluorination of graphene, such as 4:1 [7,52,53], and 2:1 [53]. FD can usually be prepared by “top-down” and “bottom-up” methods: a) Fluorine radical fluorinated graphite to form intercalation compound of graphene [36,54] and other separation techniques [8,27,36,53,55] to obtain FD, as shown in Figure 6. b) To fluoride pre-prepared graphene layer with CF₄ plasma or SF₆ plasma [56] or XeF₂ [6,24,50]. Recently, Bakharev et al. [24] used XeF₂ to fluoride AB stacking graphene on CuNi alloy (111) at ambient pressure and successfully synthesized stable FD over a relatively large area. Through the characterization of samples with different fluorination duration, it is proved that the carbon–carbon interlayer bond is formed by the fluorination of BLG, leading to the formation of FD. The photomicrographs and diffraction patterns of fluorinated and non-fluorinated BLGs match with the corresponding simulation data of FD and AB-stacked BLG, respectively. The K edge and low electron energy loss (EEL) spectra of fluorinated and pristine AB-BLG indicated that AB-BLG fluorination formed a FD that was substantially close to the C₂F stoichiometry. This diamane is a wide band-gap semiconductor, which can be reduced to AB-BLG by electron beam irradiation [24].

### 3.3. Pristine diamane

In a recent experiment, Gao et al. [29] in situ investigated the effect of pressure on the BLG sample (using SiO₂ as the substrate) through the tip of the atomic force microscopy (AFM) probe at room temperature. It is observed that the hardness of obtained sample was almost equivalent to that
of diamond and the electrical conductivity showed a reversible drop upon indentation. It was believed that a diamond-like carbon film was formed in this experiment. However, its ability was hindered as the appearance of unfavorable layered stacking structure (AB stacking), when the thickness of graphene increased (3–5 layers) [29].

Previously, the high-pressure phase transition behavior of the pristine FLG was also studied under hydrostatic and non-hydrostatic conditions in a DAC. The results showed that interlayer $sp^3$ C–C bonds were formed in seven-layered graphene at 16 GPa with partial $sp^2$ bonds [6]. Unfortunately, the graphene structure maintained after the pressure was released. Recently, the phase transition pressure of pristine graphene was estimated by the measurement of resistance [25]. Sheet resistance of samples with different layers as a function of pressure is shown in Figure 7. Combining XRD and theoretical simulation, the hexagonal PD is found to be formed with three-layer or thicker graphene during the compression. In consistent with previous theoretical studies [21,42], the phase transition pressure gradually decreased with the increase of the number of graphene layer. However, the hexagonal PD formed under high pressure could be retained to 1 GPa, contrary to previous theoretical reports [21,42].

The varied stacking order and layers of graphene make diamane can produce the diversified conformations and functional groups with versatile properties of diamane. Here, we summarize several typical preparation methods for producing diamane, as shown in Table 1. As we can see that PD formed under high pressure is

---

**Figure 6.** Schematic representation of the preparation of few-layer fluorinated graphene materials: (a) Intercalated fluorinated graphite compound C$_2$F$_4$·× CF$_3$ can be formed by using fluorinated natural graphite with CF$_3$ at room temperature; (b) thermal decomposition of C$_2$F$_4$·× CF$_3$ to produce several layers of graphene; (c) fluorination of few-layer graphene with chlorine trifluoride at room temperature. Reprinted from [36].

**Figure 7.** Sheet resistance of mechanically exfoliated 12-, hexa-, tetra-, and bi-layer graphene as a function of pressure. (a) Cross-sectional schematic of the designed four-terminal nanodevices. Ti/Au film electrodes were patterned onto the diamond culet and extended with platinum foils. (b) The function of sheet resistance and pressure for 12-, hexa-, tetra-, tri-, and bi-layer graphene measured at room temperature. The inset is pressure dependence of the resistance of graphite. Reprinted from [25]. Copyright 2020 American Chemical Society.
unable to be retained under ambient pressure, HD obtained under pressure is reversibly converted to graphene as the pressure is released, which supports the relatively poor stability of HD. FD is the most stable diamane as observed in experiments.

Table 1. Summary of diamane synthesis methods and its properties.

| Type | Substrate | Precursor | Methods and condition | Product | Retention conditions |
|------|-----------|-----------|-----------------------|---------|---------------------|
| HD   | Teflon    | BLG       | DAC (the sample is pressurized to 15 Gpa and water is used for PTM and the required hydrogen or hydroxyl) [28] | Partially hydrogenated or hydroxylated diamane | High pressure |
| Pt(111) | FLG   | The process of deuterium adsorption using an atomic cracking source by hot filament [43] | Partially hydrogenated diamane | Ambient pressure |
|    | No substrate | BLG and FLG | The hydrogenation process is 200 s by hot filament CVD [48] | Diamond and/or lonsdaleite and/or diamane and/or hybrids of those | Ambient pressure |
| FD   | No substrate | FGIC (fluorinated graphite intercalated compound) | First, FGIC is thermal decomposed into FLG and then, it is fluorinated by FCI, to obtain FD [36] | Partially fluorinated FD | Ambient pressure |
| CuNi(111) surface | AB stacking | BLG | Chemical vapor deposition (BLG is fluorinated by XeF₂ for more than 12 h at 65 °C and 50–60 Torr vapor pressure) [24] | Fully fluorinated FD | Ambient pressure |
| PD   | SiC       | BLG       | Indentation induction by atomic force microscopy probe [29] | Partially sp³ hybrid diamond-like film | High pressure |
|     | No substrate | FLG | High pressure above 19.6 GPa by DAC [25] | Partially PD | Stable above 1 GPa |

Figure 8. Thermal conductivities of different stacked diamane based on the RTA (dashed lines) and the CGP (solid lines) method. Reproduced from [60], with the permission of AIP Publishing.

4. Properties of diamane

Diamane has a narrower band gap than diamond [20], and the band gap is also tunable by the thickness, functional group type, and conformation of diamane [22]. The presence of dopants or defects also manipulates the electronic states to reduce the band gap of diamane [57]. Electron beam irradiation can selectively revert FD to graphene [24,58]. These properties of diamane bring it potential applications in the field of nano-optoelectronics. In addition, due to the low coefficient of friction of hydrogenated surfaces, diamane can also be used to improve the wear resistance of coated mechanical parts [26]. Recent theoretical research on diamane shows that the stacking sequence and functional groups have the significant effect on the thermal conductivity. As shown in Figure 8, compared with FD, HD exhibits superior thermal conductivity. It is worth noting that thermal conductivity of the AA stacking sequence is higher than that of the AB stacking sequence [59,60]. The main contribution of thermal
conductivity comes from out-of-plane acoustic phonon modes in HD to optical modes in FD. Diamane also exhibits great stiffness and it would make diamane very attractive for ultrathin protective coatings, for example, used for aerospace equipment as ultrahigh-strength components in composite materials [48]. In addition, recent studies on the vibrational properties of diamane nanoribbon (DNR) showed that DNR resonator possesses a high natural frequency and a large quality factor (Q-factor) [23]. Different from thermal conductivity, the stacking sequence of diamane has negligible influence on its vibration properties. High frequency in diamane is expected to be used for the ultrasensitive resonator-based sensors.

5. Challenges

Although great progress has been made on diamane both theoretically and experimentally, the complete understanding of diamane remains elusive. First, the synthesis of fully hydrogenated diamane remains difficult due to the varied hydrogenation environment, the hydrogen concentration in HD is not well-controlled and determined, and the hydrogenation mechanism of graphene is uncertain [8,28,43]. Second, the rich structure configurations of diamane may present due to the varied stacking, conformation, layers, and functional groups of graphene [24,28,36,43,47,48,50,51] the available products do not allow a clear understanding of the structure features in the present stage, due to the precursors for the synthesis of diamane with the different stacking sequence of graphene. In addition, the hydrogenation and fluorination methods also make the chemical bonding complicated, not favorable for the characterization of properties. Last but not the end, the diversified physical properties have been predicted for the diamine with different functional groups, many of them needs to be validated in experiments, since only a few of them were synthesized with the functional hydrogen, fluorine, and hydroxyl in experiments.

6. Conclusion

In summary, we overviewed the design, synthesis, and physical properties of diamane together with the current experimental and theoretical results on HD, FD, and PD. We discussed the influence of the concentration and type of functional groups, carbon layer thickness, temperature, and pressure on the preparation of diamane. Further investigations on synthesis and formation mechanism of diamane are highly needed to understand the new type 2D diamond for superlative properties.

Disclosure statement

No potential conflict of interest was reported by the authors.

Notes on Contributors

Guowen Qin is a graduate student in the College of Material Science and Engineering at Yanshan University in China. His research interests are diamond-related superhard materials.

Lailei Wu is a research associate professor at Yanshan University in China. His research interests focus on the design, synthesis, characterization of new functional materials.

Huiyang Gou is a staff scientist at Center for High Pressure Science and Technology Advanced Research in China. His research interests involve the design and synthesis novel functional materials under high pressure.

References

[1] Liu L, Zhou H, Cheng R, et al. High-yield chemical vapor deposition growth of high-quality large-area AB-stacked bilayer graphene. ACS Nano. 2012; 6(9): 8241–8249.

[2] Xu Y, Li X, Dong J. Infrared and Raman spectra of AA-stacking bilayer graphene. Nanotechnology. 2010; 21(6): 065711.

[3] Cao Y, Fatemi V, Fang S, et al. Unconventional superconductivity in magic-angle graphene superlattices. Nature. 2018; 556(7699): 43–50.

[4] Elias DC, Nair RR, Mohiuddin TMG, et al. Control of graphene’s properties by reversible hydrogenation: evidence for graphene. Science. 2009; 323(5914): 610–613.

[5] Sofo JO, Chaudhari AS, Barber GD, et al. Graphane: a two-dimensional hydrocarbon. Phys Rev B. 2007; 75(15): 153401.

[6] Clark SM, Jeon K, Chen J, et al. Few-layer graphene under high pressure: Raman and X-ray diffraction studies. Solid State Commun. 2013; 154: 15–18.

[7] Robinson JT, Burgess JS, Junkermeier CE, et al. Properties of fluorinated graphene films. Nano Lett. 2010; 10(8): 3001–3005.

[8] Zboril R, Karlický F, Bourlinos AB, et al. Graphene fluoride: a stable stoichiometric graphene derivative and its chemical conversion to graphene. Small. 2010; 6(24): 2885–2891.

[9] Mathkar A, Tozier D, Cox P, et al. Controlled, stepwise reduction and band gap manipulation of graphene oxide. J Phys Chem Lett. 2012; 3(8): 986–991.

[10] Angus JC, Hayman CC. Low-pressure, metastable growth of diamond and “diamondlike” phases. Science. 1988;241(4868):913–921.

[11] Bachmann PK, Leers D, Lydtin H. Towards a general concept of diamond chemical vapour deposition. Diamond Relat Mater. 1991; 1(1): 1–12.

[12] Isberg J, Hammersberg J, Johansson E, et al. High carrier mobility in single-crystal plasma-deposited diamond. Science. 2002; 297(5587): 1670–1672.

[13] Butler JE, Sumant AV. The CVD of nanodiamond materials. Chem Vap Deposition. 2008; 14(7–8): 145–160.

[14] Khaliliullin RZ, Eshet H, Kühne TD, et al. Nucleation mechanism for the direct graphite-to-diamond phase transition. Nature Mater. 2011;10(9):693–697.

[15] Boukhvalov DW, Katsnelson MI. Chemical functionalization of graphene with defects. Nano Lett. 2008; 8(12): 4373–4379.

[16] Lambrecht WR, Lee CH, Segall B, et al. Diamond nucleation by hydrogenation of the edges graphitic precursors. Nature (London). 1993; 364(6438): 607–610.

[17] Suarez-Martinez I, Savini G, Haffenden G, et al. Dislocations of Burgers vector c/2 in graphite. Phys Stat Sol (c). 2007; 4(8):2958–2962.
[18] Diankov G, Neumann M, Goldhaber-Gordon D. Extreme monolayer-selectivity of hydrogen-plasma reactions with graphene. *Nano Lett.* 2013; 13(2): 1324–1332.

[19] Balog R, Jørgensen B, Nilsson L, et al. Bandgap opening in graphene induced by patterned hydrogen adsorption. *Nature Mater.* 2010; 9(4): 315–319.

[20] Chernozatonskii LA, Sorokin PB, Kvasnin AG, et al. Diamond-like C, H nanolayer, diamond: simulation of the structure and properties. *JETP Lett.* 2009; 90(2): 134–138.

[21] Paul S, Momeni K. Mechanochemistry of stable diamond and atomically thin diamond films synthesis from bi- and multilayer graphene: a computational study. *J Phys Chem C.* 2019; 123(25): 15751–15760.

[22] Muniz AR, Maroudas D. Opening and tuning of band gap by the formation of diamond superlattices in twisted bilayer graphene. *Phys Rev B.* 2012; 86(7): 75404.

[23] Zheng Z, Zhan H, Nie Y, et al. Single layer diamond - a new ultrathin 2D carbon nanostructure for mechanical resonator. *Carbon.* 2020; 161: 809–815.

[24] Bakharev PV, Huang M, Saxena M, et al. Chemically induced transformation of chemical vapour deposition grown bilayer graphene into fluorinated single-layer diamond. *Nanotechnol.* 2020; 151(1): 59–66.

[25] Ke F, Zhang L, Chen Y, et al. Synthesis of atomically thin hexagonal diamond with compression. *Nano Lett.* 2020; 20(8): 5916–5921.

[26] Chernozatonskii LA, Sorokin PB, Kuzubov AA, et al. Influence of size effect on the electronic and elastic properties of diamond films with nanometer thickness. *J Phys Chem C.* 2011; 115(1): 132–136.

[27] Nair RR, Ren W, Jalil R, et al. Fluorographene: a two-dimensional counterpart of teflon. *Small.* 2010; 6(24): 2877–2884.

[28] Martins LGP, Matos MJS, Paschoal AR, et al. Raman evidence for pressure-induced formation of diamondene. *Nature Commun.* 2017; 88(1): 96.

[29] Gao Y, Cao T, Cellini F, et al. Ultrahard carbon film from epitaxial two-layer graphene. *Nanotechnology.* 2018; 13(2): 133–138.

[30] Boukhvalov DW, Katsnelson MI, Lichtenstein AI. Hydrogen on graphene: electronic structure, total energy, structural distortions and magnetism from first-principles calculations. *Phys Rev B.* 2008; 77(3): 35427.

[31] Odkhud D, Shin D, Ruoff RS, et al. Conversion of multilayer graphene into continuous ultrathin sp3 bonded carbon films on metal surfaces. *Sci Rep.* 2013; 3(1): 3276.

[32] Zhu L, Hu H, Chen Q, et al. Formation and electronic properties of hydrogenated few layer graphene. *Nanotechnology.* 2011; 22(18): 185202.

[33] Landt L, Klunder K, Dahl JE, et al. Optical response of diamond nanocrystals as a function of particle size, shape, and symmetry. *Phys Rev Lett.* 2009; 103(4): 47402.

[34] Dahl JE, Liu SG, Carlsson RKM. Isolation and structure of higherdiamonds, nanometer-sized diamond molecules. *Science.* 2003; 299(5603): 96–99.

[35] Li L, Zhao X. Transformation between different hybridized bonding structures in two-dimensional diamond-based materials. *J Phys Chem C.* 2011; 115(45): 22168–22179.

[36] Grayfer ED, Makotchenko VG, Kibis LS, et al. Synthesis, properties, and dispersion of few-layer graphene fluoride. *Chem Asian J.* 2013; 8(9): 2015–2022.

[37] Artyukhov VL, Chernozatonskii LA. Structure and layer interaction in carbon monofluoride and graphene: a comparative computational study. *J Phys Chem A.* 2010; 114(16): 5389–5396.

[38] Flores MZ, Autreto PA, Legosas SB, et al. Graphene to graphene: a theoretical study. *Nanotechnology.* 2009; 20(46): 465704.

[39] Bhattacharya A, Bhattacharya S, Majumder C, et al. Third conformer of graphene: a first-principles density functional theory study. *Phys Rev B.* 2011; 83(3): 033404.

[40] Leenaerts O, Peelaers H, Hernández-Nieves AD, et al. First-principles investigation of graphene fluoride and graphane. *Phys Rev B.* 2010; 82(19): 195436.

[41] Antipina LY, Sorokin PB. Converting chemically functionalized few-layer graphene to diamond films: a computational study. *J Phys Chem C.* 2015; 119(5): 2828–2836.

[42] Kvasnin AG, Chernozatonskii LA, Yakobson BI, et al. Phase diagram of quasi-two-dimensional carbon, from graphene to diamond. *Nano Lett.* 2014; 14(2): 676–681.

[43] Rajasekaran S, Aibid-Pedersen F, Ogasawara H, et al. Interlayer carbon bond formation induced by hydrogen adsorption in few-layer supported graphene. *Phys Rev Lett.* 2013; 111(8): 85503.

[44] Luo Z, Yu T, Shang J, et al. Large-scale synthesis of bi-layer graphene in strongly coupled stacking order. *Adv Funct Mater.* 2011; 21(5): 911–917.

[45] Shang N, Papakonstantinou P, Wang P, et al. Self-assembled growth, microstructure, and field-emission high-performance of ultrathin diamond nanorods. *ACS Nano.* 2009; 3(4): 1032–1038.

[46] Luo Z, Yu T, Kim K, et al. Thickness-dependent reversible hydrogenation of graphene layers. *ACS Nano.* 2009; 3(7): 1781–1788.

[47] Barboza APM, Guimaraes MHD, Massote DVP, et al. Room-temperature compression-induced diamondization of few-layer graphene. *Adv Mater.* 2011; 23(27): 3014–3017.

[48] Piazza F, Gough K, Monthieux M, et al. Low temperature, pressureless sp2 to sp3 transformation of ultrathin, crystalline carbon films. *Carbon.* 2019; 145: 10–22.

[49] Rajasekaran S, Kaya S, Aibid-Pedersen F, et al. Reversible graphene-metal contact through hydrogenation. *Phys Rev B.* 2012; 86(7): 075417.

[50] Jeon K, Lee Z, Pollak E, et al. Fluorographene: a wide bandgap semiconductor with ultraviolet luminescence. *ACS Nano.* 2011; 5(2): 1042–1046.

[51] Smith D, Howie RT, Crowe IF, et al. Hydrogenation of graphene by reaction at high pressure and high temperature. *ACS Nano.* 2015; 9(8): 8279–8283.

[52] Withers F, Dubois M, Savchenko AK. Electron properties of fluorinated single-layer graphene transistors. *Phys Rev B.* 2010; 82(7): 073403.

[53] Chang H, Cheng J, Liu X, et al. Facile synthesis of wide-band fluorographene semiconductor nanomaterials. *Chem Eur J.* 2011; 17(32): 8896–8903.

[54] Lee WH, Suk JW, Chou H, et al. Selective-area fluorination of graphene with fluoropolymer and laser irradiation. *Nano Lett.* 2012; 12(5): 2374–2378.

[55] Bourlinos AB, Safarova K, Siskova K, et al. The production of chemically converted graphenes from graphite fluoride. *Carbon.* 2012; 50(3): 1425–1428.

[56] Yang H, Chen M, Zhou H, et al. Preferential and reversible fluorination of monolayer graphene. *Phys Rev B.* 2011; 82(19): 195404.

[57] Withers F, Bointon TH, Dubois M, et al. Nitrogen–vacancy centers and dopants in ultrathin diamond films: electronic structure. *J Phys Chem C.* 2013; 117(41): 21376–21381.

[58] Leenaerts O, Peelaers H, Hernández-Nieves AD, et al. First-principles investigation of graphene fluoride and graphane. *Phys Rev B.* 2010; 82(19): 195436.

[59] Zhu LY, Li W, Ding F. Giant thermal conductivity in diamond and the influence of horizontal reflection symmetry on phonon scattering. *Nanoscale.* 2019; 11(10): 4248–4257.

[60] Zuo L, Zhang T. Suppressed thermal conductivity in fluorinated diamond: optical phonon dominant thermal transport. *Appl Phys Lett.* 2019; 115(15): 151904.