

Defect engineering in multilayer-graphene and graphite films: Generation, control, and applications

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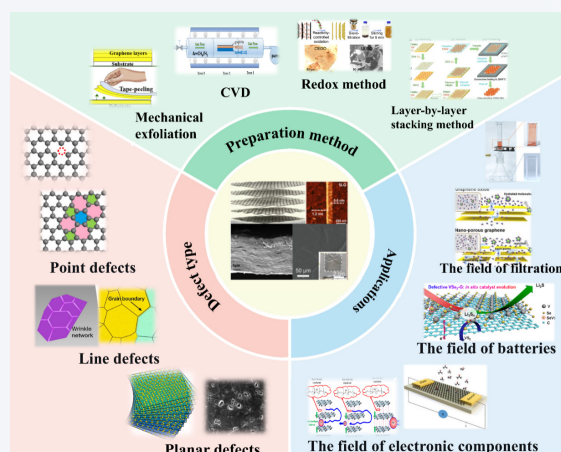
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ABSTRACT: Compared to single-layer graphene (SLG), multilayer graphene (MLG) and graphite films (GF) offer superior mechanical stability, tunable electrical conductivity, and lower manufacturing costs. However, during their preparation and transfer processes, defects such as vacancies, grain boundaries, wrinkles, and stacking disorder are inevitably introduced, and these defects have a critical impact on material performance. The defects such as vacancies, dopant atoms, and edges can enhance gas adsorption, catalytic activity, and ion storage capacity, while the defects such as grain boundaries and dislocations reduce electrical conductivity, strength, and thermal transport properties. Therefore, defect engineering mainly focuses on precisely controlling the type, density, and distribution of defects through methods such as ion implantation, plasma treatment, laser irradiation, and strain engineering, and on repairing them via high-temperature annealing or chemical methods. For applications requiring extremely high carrier mobility or thermal conductivity, nearly defect-free single-crystal MLG/GF can also be prepared, and applications of defect-engineered MLG or GF in corrosion protection, thermal management, energy storage, sensors, electronics, and quantum physics are discussed.

KEYWORDS: multilayer graphene, graphite films, defect engineering



1 Introduction

Since the successful isolation of single-layer graphene (SLG) in 2004 [1], this material has demonstrated exceptional properties, including ultrahigh carrier mobility (exceeding $200,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) [2], extraordinary thermal conductivity ($\sim 5000 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$) [3], remarkable mechanical strength (theoretical tensile strength up to 130 GPa, albeit highly sensitive to defects), and high optical transparency ($\sim 97.7\%$ transmittance), opening new avenues for fundamental research and advanced technologies. As the number of layers increases, these properties evolve systematically. Multilayer graphene (MLG) (2–10 layers) [4–6] exhibits reduced carrier

mobility ($10,000\text{--}50,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$) and thermal conductivity ($2000\text{--}3000 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$), but offers enhanced mechanical stability and tunable electrical conductivity via layer number and doping. Graphite films (GF) (> 10 layers) [7] show properties approaching those of bulk graphite, with carrier mobility further decreasing to $1000\text{--}5000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and thermal conductivity to $500\text{--}1500 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, while mechanical strength and electrical conductivity become more robust, and manufacturing cost is substantially reduced. This layer-dependent performance evolution provides a basis for material selection in different applications. In contrast to SLG, MLG and GF retain many outstanding characteristics while offering distinct advantages, such as enhanced mechanical stability [8], tunable electrical properties, good thermal conductivity [9, 10], lower fabrication costs, and greater scalability. These unique attributes give MLG and GF broad application prospects in fields such as energy storage, flexible electronics, and composite materials [11–13].

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Defects are almost inevitably introduced during the preparation and transfer of MLG and GF. The type, density, distribution, and interlayer interactions of these defects critically determine the final material performance. Different fabrication routes, including mechanical exfoliation [14, 15], chemical vapor deposition (CVD) [16, 17], redox methods, electrochemical exfoliation [18], and layer-by-layer assembly [19], as well as transfer techniques [20, 21] (e.g., wet and dry transfer), generate distinct defect characteristics [22, 23]. For instance, CVD tends to produce grain boundaries, wrinkles, and dopant impurities, while wet transfer often leaves polymer residues, cracks, or wrinkles.

It is worth noting that the effects of defects on the properties of MLG and GF can be both beneficial and detrimental. On the one hand, vacancies [24, 25], dopant atoms, and edge defects [26, 27] can serve as active sites, enhancing gas adsorption, catalytic activity, and ion storage capacity, thus boosting performance in catalysis, energy storage, and sensing. On the other hand, grain boundaries [28], dislocations, wrinkles [29], and stacking disorders significantly scatter charge carriers, reducing electrical conductivity and mechanical strength, and may even accelerate corrosion or degrade thermal conductivity. Therefore, precisely controlling the type, density, and spatial distribution of defects during fabrication and transfer has become a central challenge in defect engineering of MLG and GF.

The core concept of defect engineering is rooted in understanding the relationship between defect formation mechanisms and material properties: intentionally introducing beneficial defects while suppressing or repairing detrimental ones,

thereby achieving targeted performance optimization. Specifically, precise defect introduction can be realized via ion implantation [30, 31], plasma treatment [32], laser irradiation, and strain engineering [33], whereas selective repair of undesirable defects can be accomplished through high-temperature annealing [34], chemical repair, and directed carbon-source deposition. As a result, defect engineering has found widespread applications in anti-corrosion coatings [35], thermal interface materials, battery electrodes [36], gas separation membranes [37], electromagnetic shielding [38], flexible sensors, and quantum devices.

2 Methods for preparing MLG and GF

2.1 Mechanical peeling method

The core principle of the mechanical exfoliation method is to use external physical forces, such as shear and friction, to overcome the weak van der Waals forces between graphite layers, thereby peeling MLG or GF from large graphite crystals. Taking the most classic tape exfoliation method as an example, a small piece of adhesive tape is pressed onto the surface of a high-quality graphite crystal to ensure full contact between the two. The tape is then quickly peeled off, leaving multiple layers of graphite sheets adhered to it. By repeatedly folding and peeling the tape, the thickness of the graphite sheets can be gradually reduced until multilayer or even SLG is obtained (Fig. 1(a)) [39]. For instance, Shi et al. used traditional mechanical exfoliation to peel rhombic graphite with 7–50 layers from bulk crystals [4].

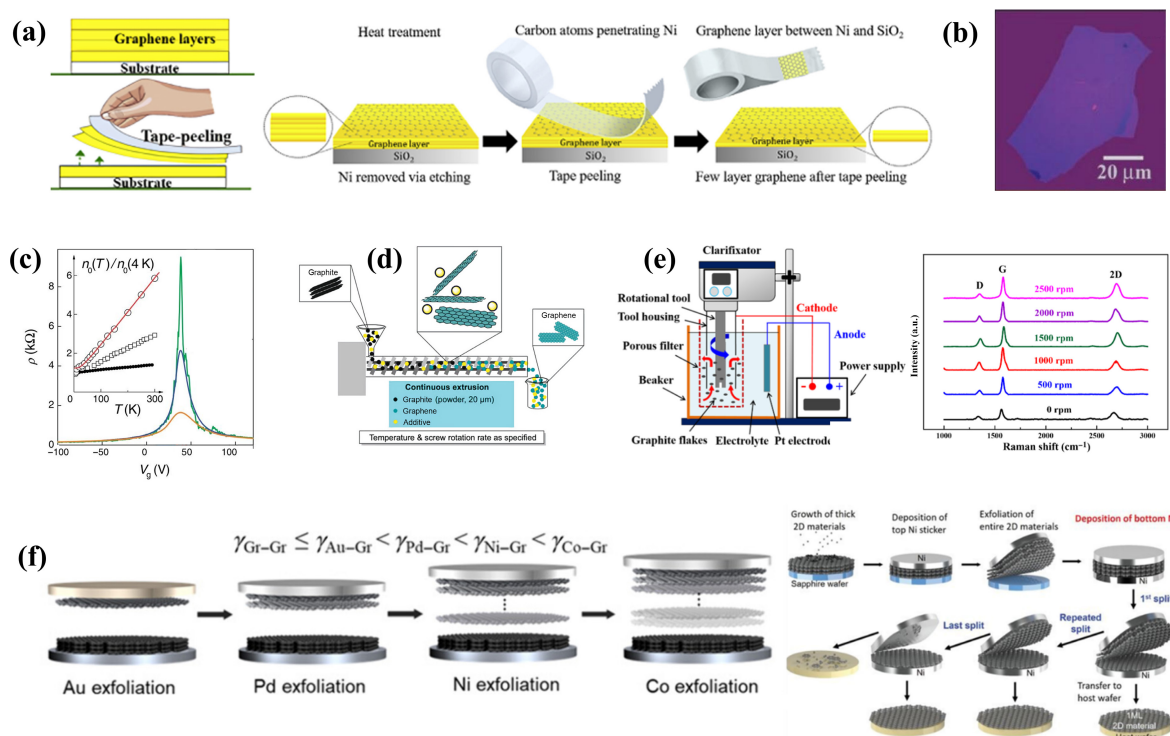


Figure 1 Different mechanical exfoliation methods. (a) Schematic illustration of the tape exfoliation process. Reproduced with permission from Ref. [39], © Elsevier Ltd. 2019. (b) MLG is prepared by mechanical exfoliation. (c) Resistivity–gate voltage (ρ – V_g) curve of the sample in (b), from which a carrier mobility of $\sim 10,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ can be calculated. Reproduced with permission from Ref. [1], © American Association for the Advancement of Science 2004. (d) Schematic of MLG preparation via continuous graphite exfoliation. Reproduced with permission from Ref. [41], © Chen, H. L. et al. 2024. (e) Schematic of a hybrid electrochemical/mechanical exfoliation device, along with Raman spectra of exfoliated samples at different rotational speeds. Reproduced with permission from Ref. [43], © Springer-Verlag London Ltd., part of Springer Nature 2019. (f) Schematic of atomically precise exfoliation of van der Waals nanomaterials (NMs) achieved by adjusting the binding energy. Reproduced with permission from Ref. [44], © Moon, J. Y. et al. 2024.

Traditional mechanical exfoliation methods can produce high-quality MLG and GF samples. The resulting samples exhibit few defects, high carrier mobility, good structural integrity, and clean edges, thereby preserving the intrinsic physicochemical properties of MLG and GF (Figs. 1(b) and 1(c)) [1, 6, 40]. This method is relatively simple to operate and does not require sophisticated equipment. To address these limitations, various strategies have been developed. Equipment innovation enables continuous production, and automated control of exfoliation parameters allows precise regulation of MLG size and thickness (Fig. 1(d)) [41]. The unique properties of supercritical fluids can be leveraged to enhance interlayer penetration [42]. Ultrasonic-assisted mechanical exfoliation can be used to prepare MLG from expandable graphite (Fig. 1(e)). Alternatively, chemical media can be introduced to reduce interlayer forces via electrochemical assistance, thereby improving exfoliation efficiency while minimizing flake damage [43].

Layer engineering exfoliation (LEE), a current research hotspot in mechanical exfoliation, overcomes the limitations of traditional techniques that can only exfoliate single layers or random numbers of layers. By adjusting the binding energy between the stress source and graphene, LEE achieves atomic-level precision. Using metal stress sources with different binding energies, such as Au, Pd, Ni, and Co, graphene with varying numbers of layers can be selectively exfoliated (Fig. 1(f)), enabling the preparation of high-quality MLG [44]. LEE achieves this by regulating the interfacial binding energy between metal films and graphene or GF. This method yields millimeter-scale MLG that is defect-free and free of polymethyl methacrylate (PMMA) or metal residues, with a mobility exceeding $20,000 \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$ at 300 K, approaching the performance of perfect graphene. By enabling tunable-layer-number, large-area, highly reproducible, and high-quality MLG exfoliation [45], LEE effectively addresses the limitations of traditional mechanical exfoliation methods, such as small size, low yield, and difficulty in controlling the number of layers.

2.2 Chemical vapor deposition

The principle of CVD synthesis of MLG and GF is based on the decomposition of gaseous carbon sources at high temperatures in the presence of a catalyst, during which carbon atoms are generated, adsorb, diffuse, react, and deposit on the substrate surface (Fig. 2(a)) [46]. Depending on the carbon solubility of the substrate, two primary growth mechanisms exist. For metal substrates with high carbon solubility, such as Ni, carbon atoms released from the decomposition of the carbon source dissolve into the substrate at high temperatures. As the temperature decreases, the solubility of carbon decreases, causing supersaturated carbon atoms to precipitate from the substrate and rearrange on the surface to form MLG or GF. This is known as the dissolution-precipitation mechanism (Fig. 2(b)) [47]. In contrast, Cu is a metal substrate with low carbon solubility; carbon atoms primarily adsorb and diffuse on the surface. When the concentration reaches a level sufficient to satisfy nucleation conditions, they grow directly on the surface to form a film, a process referred to as the surface-catalyzed growth mechanism [48]. Various types of CVD methods are available. Among them, low-pressure CVD (LPCVD), atmospheric-pressure CVD (APCVD), and plasma-enhanced CVD (PECVD) are the most commonly used for preparing MLG. Additionally, microwave plasma CVD (MPCVD) and metal-organic CVD (MOCVD) have also been employed in recent years.

LPCVD relies on gaseous precursors diffusing and reacting

under low-pressure conditions. The low pressure accelerates gas diffusion, significantly improving film uniformity and step coverage while maintaining low defect density, avoiding the uneven thickness issues of atmospheric pressure CVD [48]. However, LPCVD has drawbacks, including high temperature requirements, slow deposition rates, high equipment maintenance, and reliance on vacuum systems [49].

In MLG growth on copper foil below 10 mbar, trace oxygen inhibits nucleation, slows growth, or etches the graphene. Under oxygen-free conditions, growth rates become quantitatively predictable, reproducibility greatly improves, and surface contamination is absent [50]. Conversely, introducing trace CO_2 creates defects by slightly etching the first graphene layer, providing pathways for carbon source diffusion. This enables continuous bilayer graphene with more than 94% coverage within 20 min, over three times conventional efficiency, with no edge curling or grain boundary defects [51].

APCVD is a process conducted under atmospheric pressure. During deposition, the substrate is placed in a reaction chamber, and gaseous carbon sources and carrier gases are introduced; the carbon sources decompose at high temperatures to form the deposited film [52]. The advantages include relatively simple equipment, no need for vacuum systems, lower costs, and the ability to achieve large-area deposition. The disadvantages are that film uniformity may be poor, nucleation density is high and uneven, and misaligned grain boundaries form when adjacent graphene islands join. Due to the fast growth rate, the interlayer stacking lacks a distinct structure. Additionally, surface morphology issues such as wrinkles and cracks are common (Fig. 2(c)) [53].

Traditional thermal CVD relies on the high-temperature decomposition of reaction gases, which presents challenges such as strict thermal resistance requirements for substrates, slow film deposition rates, and difficulties in preparing high-quality MLG and GF. In contrast, PECVD uses radio frequency (RF) or direct current (DC) plasma to activate carbon sources, thereby accelerating chemical reaction rates. The process is carried out under controlled vacuum conditions and typically involves two steps: First, a SLG film is grown, followed by the growth of MLG or GF on top of it (Fig. 2(d)) [54]. This method reduces the reaction temperature (to as low as around 200°C) [49], which not only minimizes thermal damage to the substrate but also enables compatibility with various substrates such as sapphire, silicon dioxide, and cobalt foil. The growth principles on cobalt foil and silver substrates are illustrated in Figs. 2(e) and 2(f) [55, 56]. Furthermore, the plasma promotes uniform gas decomposition, which helps improve film uniformity and quality, and enables large-scale production.

However, this technique suffers from plasma-induced defects; high-energy particle bombardment can lead to defects such as vacancies and sp^3 hybridization in the graphene layers (Fig. 2(g)) [55]. These defects must be minimized by optimizing plasma parameters, designing gas flow control structures, and performing substrate pretreatment [54]. RF PECVD, in particular, is widely used in the semiconductor industry. To address the issue of high-energy ion bombardment of the substrate in PECVD, microwave plasma-enhanced chemical vapor deposition (MPECVD) uses microwaves as an energy source and couples this energy into the reaction gas via a microwave resonant cavity. The resulting plasma features a low electron temperature ($0.5\text{--}2 \text{ eV}$) and high ionization efficiency, enabling efficient decomposition of carbon sources such as methane while simultaneously reducing damage to graphene

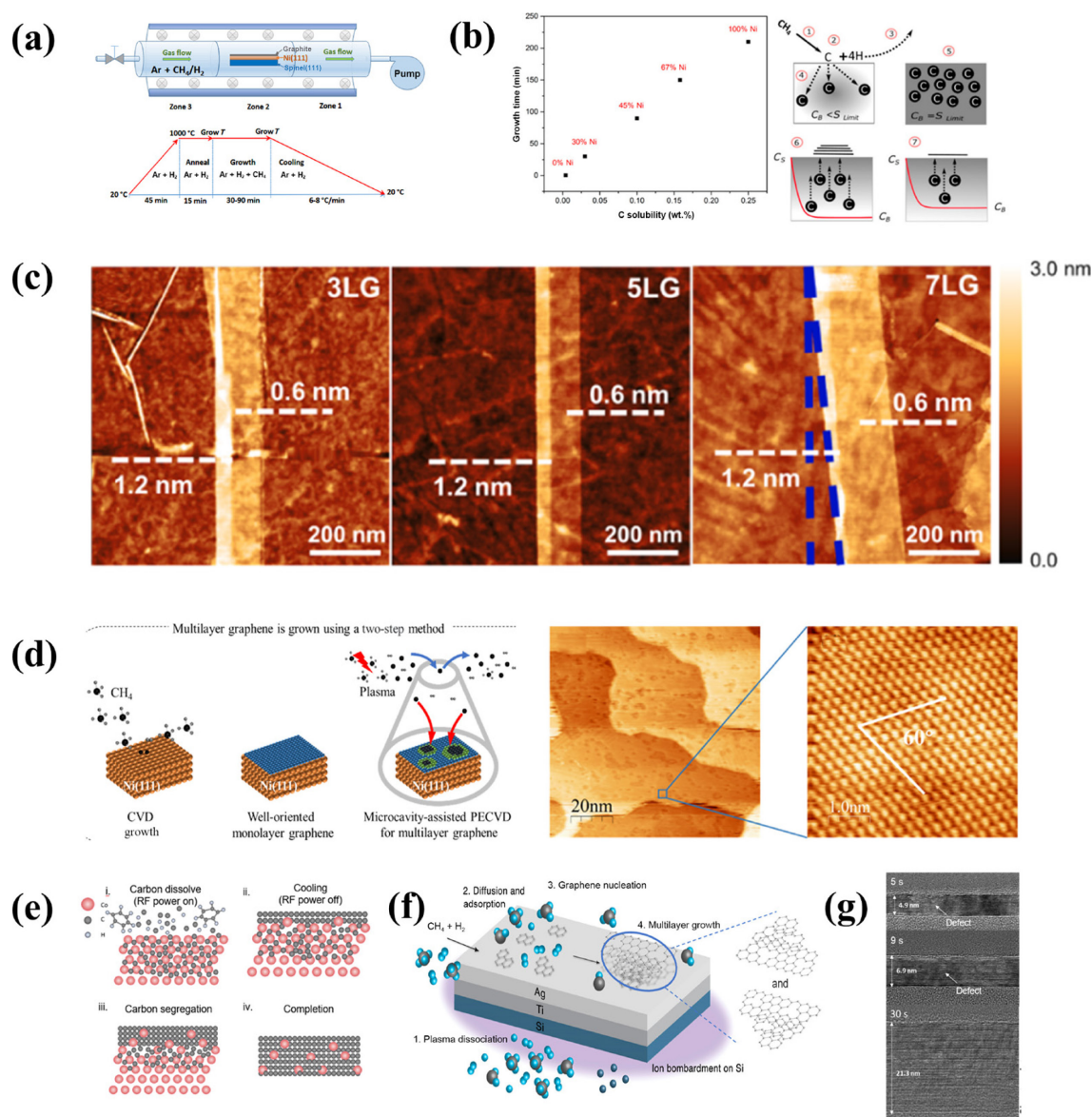


Figure 2 Schematic diagram of CVD growth of MLG and GF. (a) Schematic diagram of the preparation principle and parameters of CVD. Reproduced with permission from Ref. [46], © Lu, Z. H. et al. 2020. (b) Schematic diagram of growth on copper-nickel alloy substrate. Reproduced with permission from Ref. [47], © Al-Hilfi, S. H. et al. 2021. (c) Defects such as wrinkles are generated when preparing MLG using the chemical vapor deposition method. Reproduced with permission from Ref. [58], © Elsevier B.V. 2022. (d) Schematic diagram of the two-step growth process of MLG. Reproduced with permission from Ref. [54], © American Chemical Society 2024. (e) Growth mechanism of MLG on cobalt foil. Reproduced with permission from Ref. [55], © American Chemical Society 2023. (f) PECVD graphene growth mechanism on silver. Reproduced with permission from Ref. [49], © Lu, C. H. et al. 2023. (g) The thickness of GF corresponding to different CVD process durations and the occurrence of defects in the layer. Reproduced with permission from Ref. [55], © American Chemical Society 2023.

layers caused by high-energy particle bombardment, thereby achieving low-damage and high-uniformity growth. Photothermal chemical vapor deposition (PT-CVD), a variant of CVD, is used to prepare MLG by converting light energy into thermal energy to drive chemical reactions [57]. It does not rely on metal catalysts, and its rapid heating and cooling processes shorten growth time. With low sensitivity to cooling rates, it enables growth at relatively low temperatures, reducing thermal damage to the substrate; however, this technique demands high standards for equipment and process control.

2.3 Redox method

The core principle of the redox method is to introduce oxygen-

containing functional groups into the graphite interlayers through chemical oxidation, thereby exfoliating them into graphene oxide (GO) (Fig. 3(a)) [59]. Following reduction treatment to remove some of the functional groups, the conjugated structure of graphite is restored, forming MLG or GF (Fig. 3(b)) [60].

For example, GO can be obtained by oxidizing natural graphite using the modified Hummers' method. After dispersion in an aqueous solution, deposition onto a copper mesh, and drying, a multilayer GO film is formed, which is then reduced to MLG through vacuum annealing at 100–500 °C [61]. Alternatively, using waste graphite from spent lithium-ion batteries as a raw material, along with a sulfuric acid-potassium permanganate-peracetic acid ternary system, a “one-pot” oxidation–reduction process can

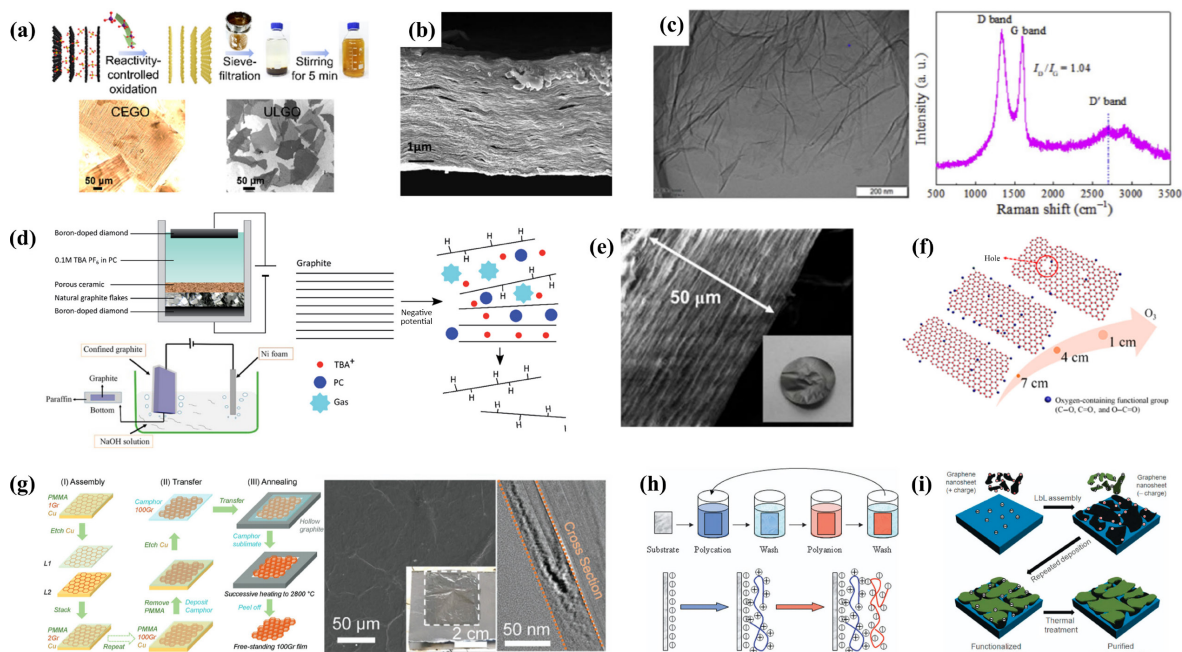


Figure 3 Different preparation methods and characterization. (a) Schematic diagram of the preparation of graphene oxide. Reproduced with permission from Ref. [59], © American Chemical Society 2016. (b) Image of thick GF prepared by redox method. Reproduced with permission from Ref. [60], © Elsevier B.V. 2019. (c) Images and Raman maps of multi-defect GF prepared by the redox method. Reproduced with permission from Ref. [60], © Elsevier B.V. 2019. (d) Schematic diagram of electrochemical exfoliation. Reproduced with permission from Ref. [67], © American Chemical Society 2017. (e) GF prepared by electrochemical exfoliation method. Reproduced with permission from Ref. [69], © Chen, D. H. et al. 2019. (f) The process of preparing graphene layers in electrochemical exfoliation by forming pores through the action of ozone. Reproduced with permission from Ref. [67], © American Chemical Society 2017. (g) Schematic diagram of the preparation process of multilayer stacked graphene film samples, including assembly, transfer and annealing steps, as well as the sample images. Reproduced with permission from Ref. [70], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2019. (h) Schematic diagram of layer-by-layer stacking due to electrostatic interaction and covalent bond principle. Reproduced with permission from Ref. [74], © Xiang, Y. et al. 2012. (i) Schematic diagram of the principle of electrostatic + π - π interaction layered stacking. Reproduced with permission from Ref. [73], © American Chemical Society 2011.

directly prepare multilayer reduced graphene oxide (rGO) (Fig. 3(c)) [60].

The oxidation–reduction method enables large-scale production of large-area MLG [59], offers process flexibility, and supports diverse reduction approaches, including chemical and thermal reduction. Furthermore, the electrical and optical properties of the films can be optimized by adjusting the reduction conditions [62]. However, the oxidation process introduces structural defects that are difficult to completely eliminate after reduction, limiting the film's conductivity. The performance of GO varies significantly depending on the oxidation method: GO prepared by the Hummers' method tends to form pores due to its high content of carbonyl and carboxyl groups, which affects the film's mechanical strength; whereas GO prepared by the Brodie method features a more uniform hydroxyl distribution and superior mechanical properties [63]. Additionally, the stacking of layers and residual impurities in multilayer structures may reduce carrier mobility. Although thermal reduction can improve the crystal structure, high temperatures may exacerbate defects [64].

2.4 Electrochemical stripping method

The principle of the electrochemical exfoliation method involves applying a voltage to a graphite electrode in an electrolyte, causing ions in the electrolyte to intercalate between graphite layers [65]. Combined with the exfoliation effect of gases generated during electrolysis, this process separates the graphite layers to form MLG (Fig. 3(d)) [66, 67]. Additionally, by adjusting the electrolysis parameters, the number of layers, defects, and properties of the

product can be controlled [68]. This method offers high production efficiency and is scalable, with a yield up to 85%. The product quality is excellent; for example, graphene prepared in a confined space using NaOH as the electrolyte exhibits low defect density [69], and transparent conductive films treated with NH_4NO_3 achieve a sheet resistance as low as $1.21 \text{ k}\Omega\cdot\text{sq}^{-1}$ [67]. Furthermore, the process is environmentally friendly and flexible, requiring no strong oxidizing agents or toxic reducing agents; the electrolyte can be either an aqueous system or a low-toxicity organic solvent. By adjusting the voltage, electrolyte type, and potential mode, the number of layers, dimensions, and electrical properties can be tuned. The GF prepared by the electrochemical exfoliation method is shown in Fig. 3(e) [69]. However, limitations exist: Since oxidation occurs at edges and grain boundaries, significant edge oxidation takes place during the exfoliation process, and the method requires a relatively complex post-treatment procedure. The processing diagram is shown in Fig. 3(f) [67].

2.5 Layer-by-layer stacking method

Layer-by-layer stacking for MLG/GF falls into two types: physical transfer stacking and electrostatic self-assembly. Physical transfer stacking uses CVD-grown SLG as the basic unit, with repeated wet transfer (PMMA as temporary support, copper foil etched) to build stacks with controllable layer numbers, followed by high-temperature post-processing to optimize structure and performance [70–72]. This fabrication route is often accompanied by significant defects in the initial stage. The transfer process readily introduces residual metal nanoparticles, amorphous carbon contaminants, and

microscopic voids, leading to a prominent D peak in the Raman spectrum. After high-temperature annealing at 2000 °C or higher, interlayer contaminants are removed, defects are repaired, the interlayer spacing decreases from 3.44 to 3.36 Å, and AB stacking is formed in some regions, yielding a highly crystalline film. The preparation process of this method is shown in Fig. 3(g) [70]. The optimized material exhibits a micrometer-scale tensile modulus of 290 GPa, a fracture strength of 5.8 GPa, an in-plane thermal conductivity of 2292 W·m⁻¹·K⁻¹, and an electrical conductivity of 2.2×10^5 S·m⁻¹. As the number of layers increases, the upper graphene layers effectively shield the substrate's doping effects, and the Raman characteristics gradually approach those of intrinsic graphene [71]. When MLG is used as a core layer and composited with silicon nitride and molybdenum, the Young's modulus of the composite film increases by 29% compared to pure SiN films, the fracture load increases by more than 8 times, and the transmittance at a wavelength of 13.5 nm in the extreme ultraviolet (UV) reaches 52.67% [72].

The electrostatic self-assembly approach relies on electrostatic interactions to construct multilayer films. SLG sheets are functionalized to carry opposite charges, allowing them to be alternately deposited to form bilayers, which can be repeated to build up a well-ordered multilayer structure. Various strategies have been explored, including pure electrostatic interactions [73] or combinations of electrostatic forces with other interactions such as covalent bonding (Fig. 3(h)) [74] and π - π interactions (Fig. 3(i)) [73], among others [75]. The basic principle involves treating one batch of SLG sheets to make them positively charged, while another batch is made negatively charged; the positive and negative sheets are then assembled layer by layer through electrostatic attraction, forming a sandwich-like structure. However, this layer-by-layer self-assembly method may introduce structural imperfections such as folding, wrinkles, and other textural defects, which can lead to non-uniform coverage [73].

2.6 Other methods

The arc discharge method synthesizes MLG/GF by applying a voltage to a graphite electrode in a controlled atmosphere,

generating arc plasma that evaporates the electrode into carbon atoms/clusters, which then nucleate and deposit. The arc discharge plasma device is shown in Fig. 4(a) [60, 76–78]. Advantages: no vacuum needed [79], no toxic reagents or flammable gases, no toxic emissions [80], and no complex substrates or transfer steps; products obtained by adjusting current and gas pressure using graphite feedstock [80]. Drawbacks: Disordered nucleation during plasma cooling causes defects (vacancies and edge defects) [81]; uneven temperature/carbon concentration leads to layer number fluctuations and poor uniformity [78]; and trace impurities from electrodes or atmosphere introduce contaminants.

Pyrolysis heats precursors to remove impurities, repair defects, and form multilayer carbon materials. For example, a propane flame heats a graphite ribbon, overcoming van der Waals forces to exfoliate and deposit MLG onto glass [82]. In another example, when a mixture of indium (In) particles and graphite is annealed at 900 °C, In first catalyzes the oxidation of graphite to produce carbon oxide gas, which then undergoes further catalytic graphitization to form MLG. The experimental setup is shown in Fig. 4(b) [83].

Flash Joule heating passes a high current through carbon feedstock, reaching more than 3000 K within milliseconds to seconds, rearranging atoms into sp² graphene; rapid cooling (up to 10⁴ K·s⁻¹) yields a disordered layered structure. Advantages: works with non-graphite feedstocks (e.g., coal), no solvents or chemical reagents, low energy consumption (~7.2 kJ·g⁻¹), and controllable cost (Fig. 4(c)) [84, 85]. Drawbacks: Impurities cause vacancy defects or heteroatom doping; raw material affects flake size uniformity [86]; and disordered structure hinders interlayer electron transport.

Liquid-phase exfoliation uses ultrasound to generate cavitation, microjets, and shock waves that overcome interlayer van der Waals forces in graphite, enabling layer-by-layer exfoliation. The principle is shown in Fig. 4(d) [87]. Shear forces minimize flake fracture [88]. Advantages: no corrosive reagents, environmentally friendly, minimal damage to sp² structure [89], and size and layer number controllable via ultrasonic parameters and solvents [90].

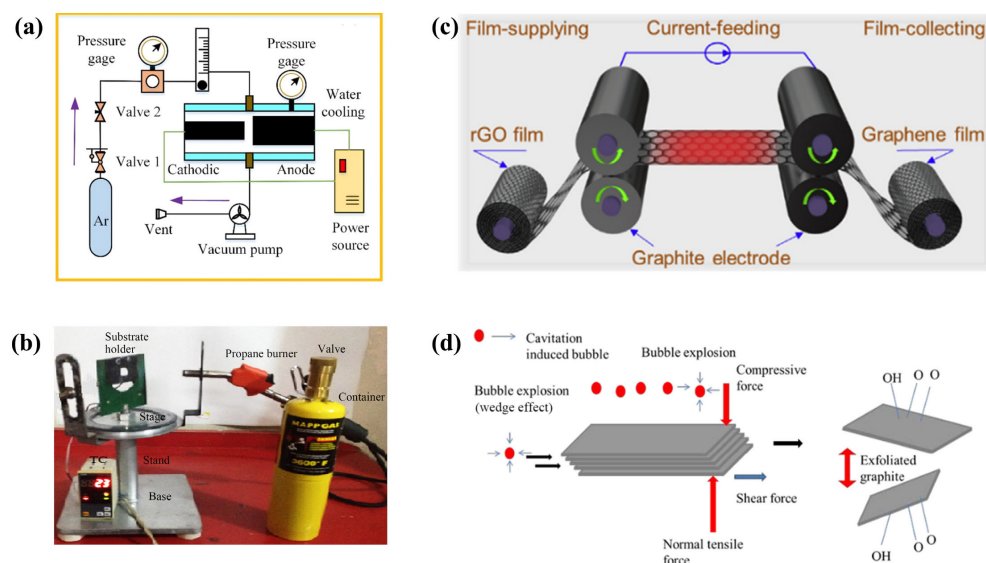


Figure 4 Schematic diagram of other preparation methods. (a) Arc-discharge plasma experimental set-up. Reproduced with permission from Ref. [79], © Tan, H. et al. 2019. (b) The photo of flames synthesis technique. Reproduced with permission from Ref. [82], © Ha, J. M. et al. 2016. (c) Schematic of the pressurized roll-based production of GFs by Joule heating. Reproduced with permission from Ref. [85], © Elsevier Ltd. 2019. (d) Illustration of the possible mechanism of graphite exfoliation. Reproduced with permission from Ref. [87], © Lin, Z. et al. 2017.

Disadvantages: high energy consumption, cost optimization needed for scale-up, some solvents are toxic, and surfactants/intercalants are difficult to completely remove.

This section introduces the preparation methods for MLG/GF: mechanical exfoliation (high quality and low yield), chemical vapor deposition (large area and defective), redox method (low cost and high residue), electrochemical exfoliation (green and moderate quality), layer-by-layer stacking (controllable and time-consuming), arc discharge (simple process and uneven), pyrolysis (high crystallinity and high energy consumption), flash Joule heating (ultrafast and turbostratic structure), and liquid-phase exfoliation (easy operation and poor layer-number controllability). For comparison, Fig. 5 presents a radar chart of these nine methods, visually illustrating the relative strengths and weaknesses of each method. In addition, Table 1 summarizes the advantages, disadvantages, defect types, and performance characteristics of each preparation method. Each method has its own bias in terms of defect formation and control. The rational selection of a preparation method is beneficial for subsequent defect control and defect engineering applications.

3 Defects in MLG and GF

As already indicated in Section 2, various defects are inevitably generated during the preparation process. However, defects in MLG and GF are not merely superficial imperfections; they play a decisive role in determining the electrical, thermal, mechanical, and chemical properties of the material. Therefore, understanding the nature, density, and distribution of defects is essential for both fundamental research and practical applications. For example, point defects can create active sites for gas sensing and energy storage, line defects generally reduce mechanical strength, and nanopores, as a type of planar defect, can be applied in filtration devices. This section systematically summarizes the types, characterization

methods, and property impacts of defects in MLG and GF, thereby laying the foundation for the subsequent discussion of defect engineering strategies.

3.1 Types of defects and characterization methods

3.1.1 Point defects

Point defects primarily include vacancy defects [31], substitution defects, and interstitial defects. Vacancy defects are classified into single vacancies (Fig. 6(a)), double vacancies (Fig. 6(b)), and multiple vacancies [102], which involve the absence of one or more carbon atoms in the graphene lattice, resulting in local lattice structural incompleteness. Substitution defects occur when carbon atoms in the lattice are replaced by other atoms, forming heteroatom doping. Interstitial defects involve the insertion of extra atoms into the interstitial sites of the graphene lattice, causing local lattice distortion.

The STW defect occurs when two carbon atoms rotate 90° about the midpoint of their bond, reconfiguring four adjacent hexagons into two pentagons and two heptagons, thereby forming a 5-7-7-5 symmetric structure (Fig. 6(c)) [102], which is the distinguishing topological feature of the STW defect. Essentially, it is a symmetric combination containing two pairs of 5-7 rings and represents a topological point defect with no net gain or loss of atoms. Pentagonal defects involve the presence of isolated pentagonal rings in the lattice, with no atomic loss or gain; they result solely from lattice ring structural distortion, leading to positive curvature in the local lattice [103, 104].

Point defects can be observed via transmission electron microscopy to identify intrinsic carbon point defects, such as carbon atom vacancies and pentagonal ring/heptagonal ring topological defects [105]. Scanning transmission electron microscopy (STEM) is a derivative technique of transmission electron microscopy that achieves atomic-level resolution and can

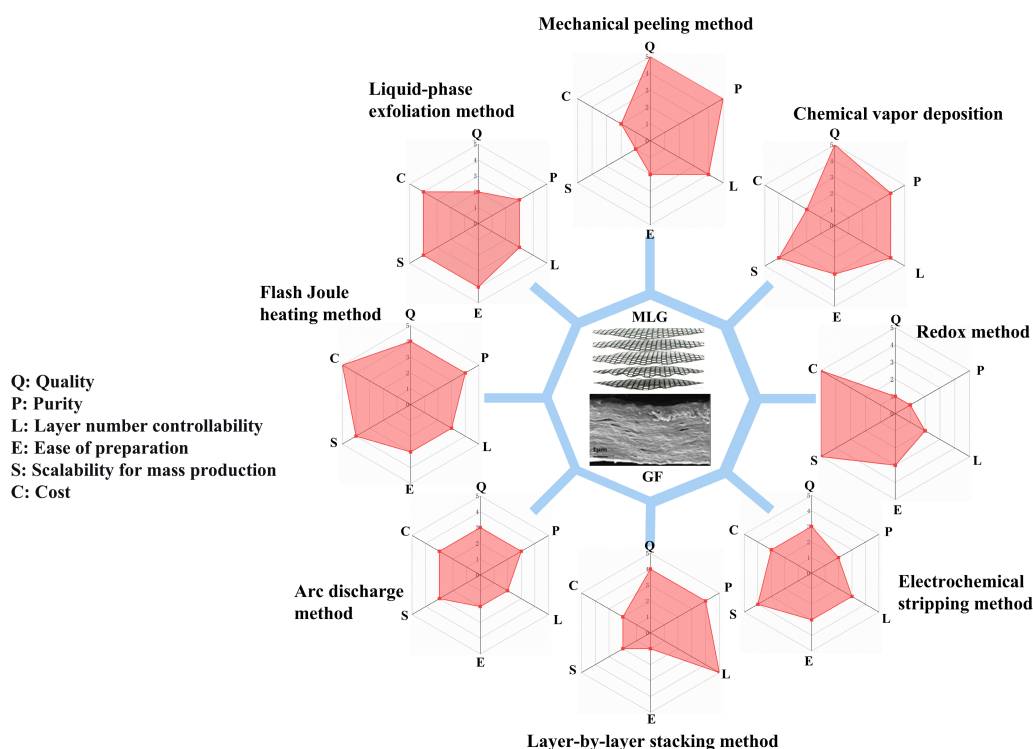


Figure 5 The radar chart of common methods for preparing MLG and GF, where higher values are more favorable.

Table 1 Advantages, disadvantages, defect types, and performance characteristics of different preparation methods

Preparation method	Advantages	Disadvantages	Main defect types	Representative performance	Ref.
Mechanical exfoliation	High quality, intact sp^2 structure, and atomic-level thickness control	Extremely low yield and not scalable	Nearly no intrinsic defects	Mobility of $110,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ and electrical conductivity of $5.26 \times 10^5 \text{ S} \cdot \text{m}^{-1}$	[91, 92]
Chemical vapor deposition	Wafer-scale production, precise layer control, and high-quality single-crystal graphene films	Requires high temperature and vacuum, high equipment cost, complex process, and defects introduced during transfer	Vacancies, grain boundaries, wrinkles, holes, and stacking disorder	Thermal conductivity of $4914 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, electrical conductivity of $6.18 \times 10^7 \text{ S} \cdot \text{m}^{-1}$, and mobility from more than 40,000 to more than $100,000 \text{ cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$ at room temperature	[93–95]
Redox method	Scalable, low cost, flexible process, and compatible with various substrates	Strong oxidants cause structural defects and degraded performance, difficult waste treatment, and environmental pollution	Structural defects, residual oxygen-containing groups, and disordered stacking	Electrical conductivity of $1.49 \times 10^6 \text{ S} \cdot \text{m}^{-1}$ and EMI shielding effectiveness of 70.3 dB	[96]
Electrochemical exfoliation	Environmentally friendly and no strong oxidants	Inevitable edge oxidation and relatively low yield	Edge defects, sheet fracture, and non-uniform size distribution	Electrical conductivity of $7.28 \times 10^4 \text{ S} \cdot \text{m}^{-1}$	[97]
Layer-by-layer stacking method	Precisely controllable layer number, designable heterostructures, and compatible with transfer processes	Tedious and time-consuming, interface contamination, and defect accumulation after multiple transfers	Interface contamination, defect accumulation, and weak interlayer bonding	Tensile strength of 5.8 GPa, thermal conductivity of $2292 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, and electrical conductivity of $2.2 \times 10^5 \text{ S} \cdot \text{m}^{-1}$	[70]
Arc discharge method	No toxic reagents, environmentally friendly, high crystallinity, and few intrinsic defects	Expensive equipment, low yield, and high energy consumption	Interlayer wrinkles and edge defects	Thermal conductivity of $1644 \pm 11 \text{ W} \cdot \text{m} \cdot \text{K}^{-1}$	[98]
Flash Joule heating	Ultra-fast (milliseconds), low energy consumption ($\sim 7.2 \text{ kJ} \cdot \text{g}^{-1}$), and can use non-graphite precursors	Difficult to produce continuous films and poor thickness control	Vacancies, structural disorder, and non-uniform flake size	Electrical conductivity of $2.25 \times 10^4 \text{ S} \cdot \text{cm}^{-1}$, thermal conductivity of $2034.4 \pm 68 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$, and Young's modulus of 969 GPa	[99]
Liquid-phase exfoliation	Simple equipment, low cost, scalable, high purity, flexible process, and tunable size and layer number	Low yield and residual solvent affects intrinsic properties	Edge defects, wrinkles, and pores	Electrical conductivity $> 1.0 \times 10^5 \text{ S} \cdot \text{m}^{-1}$ and EMI SE of $\sim 72 \text{ dB}$	[100, 101]

directly identify and distinguish vacancy defects [106]. In addition to direct observation, characterization can also be performed using Raman spectroscopy via the I_D/I_G ratio; for example, when $I_D/I_G \approx 3$, literature standards indicate that the corresponding defect is a vacancy or a nanopore defect [104].

3.1.2 Linear defects

Linear defects primarily include grain boundary defects, edge defects, wrinkle defects, and cracks. Grain boundary defects are the boundaries between different grains in polycrystalline graphene (Fig. 6(d)) [107]. Edge defects are a common form of slip-induced damage, primarily manifesting as edge fractures (Figs. 6(e) and 6(f)) [22, 28], fragmentation, and the evolution of a jagged morphology in graphene flakes, often accompanied by bending of the graphene stack. Ideally, edges are classified as zigzag or armchair; however, in actual preparation, they are invariably accompanied by defects, primarily comprising three types: edge atomic vacancy defects, edge reconstruction defects, and edge functional group defects [108]. Wrinkle defects are characterized by localized folding or bending on the surface of MLG or GF (Fig. 6(g)) [109], forming three-dimensional undulating structures, with the amplitude of undulation inversely proportional to the number of layers [29]. They are classified into “upright collapsed wrinkles” and “folded wrinkles” (Fig. 6(h)) [109], preferentially oriented along the armchair or zigzag directions of the graphene lattice [110]. The

interlayer spacing in the wrinkled regions increases from 3.34 to 3.83 Å, and interlayer coupling weakens [29]. Cracks are defined in molecular dynamics simulations as through-going or locally propagating gaps formed by the rupture of carbon–carbon covalent bonds in functionally graded MLG origami under nanoindentation loading [111].

Raman spectroscopy is the most critical characterization method for line defects, the appearance of the D peak directly confirms their presence. An I_D/I_G ratio of 0.92 indicates that the defects are predominantly edge-line defects [27]. Characterization can also be performed via the I_D/I_G ratio; for example, $I_D/I_G \approx 3.5$ is a typical feature of graphene grain boundaries or other edge defects [28]. In addition to indirect methods, scanning tunneling microscopy or high-resolution transmission electron microscopy can directly observe line defects; for example, high-resolution transmission electron microscopy can reveal graphene stacking discontinuities and bending, while scanning electron microscopy (SEM) can directly assess the severity of line defects [22]. Atomic force microscopy (AFM) is the primary characterization method for wrinkle defects; AFM can be used to determine the height and width of MLG wrinkles and calculate the aspect ratio [29].

3.1.3 Planar defects

Planar defects mainly include stacking defects and pore defects. Stacking defects mainly manifest as deviations in the stacking order of graphene layers from the ideal AB stacking and can be broadly

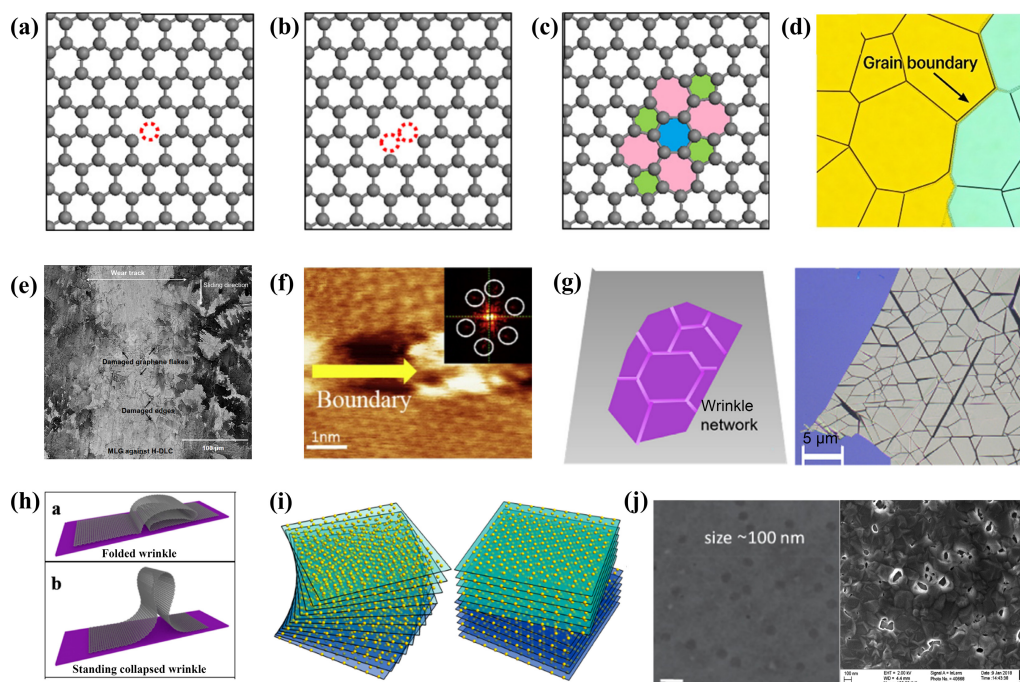


Figure 6 Types of defects. (a) Single vacancy defect. (b) Double vacancy defect. (c) Defect of 5-7-7-5. Reproduced with permission from Ref. [102], © Elsevier Ltd. 2018. (d) Grain boundary defect. (e) Edge defects. Reproduced with permission from Ref. [22], © Elsevier Ltd. 2016. (f) Boundary defect. Reproduced with permission from Ref. [28], © Elsevier Ltd. 2016. (g) Folded wrinkle. (h) Vertical collapse fold and folded fold. Reproduced with permission from Ref. [109], © American Chemical Society 2016. (i) Stacking defect. Reproduced with permission from Ref. [23], © American Chemical Society 2019. (j) Pore defect. Reproduced with permission from Ref. [119], © Mund, B. K. et al. 2020.

categorized into two types. The first is rotational stacking defects, which refer to structural deviations characterized by non-zero rotational angles between layers without a fixed periodicity; they are commonly found in twisted MLG and are classified as “completely disordered stacking” (Fig. 6(i)) [23, 112]. The second is disordered stacking defects, such as the insertion of heterostructures into the ideal stack or stacking domain walls formed by interlayer slippage [113]. Pore defects are nanoscale pore structures formed on the surfaces of MLG and GF, typically resulting from fabrication defects or intentional etching (Fig. 6(j)). Based on size, they can be classified into sub-nanometer pores (< 1 nm), nanometer pores, and micrometer pores; pores of different sizes correspond to different functional applications [114–117].

Raman spectroscopy, as the most commonly used non-destructive characterization tool, primarily distinguishes stacking structures based on the peak shape of the G' band: The G' band of an ideal AB stack exhibits asymmetry, whereas disordered stacks exhibit symmetric peaks. Furthermore, the presence of nanopores can be confirmed by defect-related peak intensity ratios (e.g., $I_D/I_G = 0.431$, and $I_D/I_D' = 3.26$) [104]. Transmission electron microscopy (TEM) provides direct visual evidence of stacking and pore defects. Cross-sectional TEM allows for direct observation of interlayer spacing and the gradient distribution of stacking defects [11, 31, 118]. Atomic-resolution STEM imaging clearly resolves stacking faults, such as the distinct boundary formed between ABA fault regions and ideal ABC regions on a rhombic graphite surface due to differences in atomic packing density [118].

3.2 Impact of defects

3.2.1 Impact on electrical properties

Vacancies, dislocations, and edge defects disrupt lattice periodicity

and act as scattering centers, reducing carrier mobility and conductivity. For example, LBSA self-assembled MLG films have an initial sheet resistance of $\sim 82 \text{ k}\Omega\text{-sq}^{-1}$ due to edge defects; UV/ozone (UVO) treatment repairs these defects, lowering sheet resistance to $\sim 30 \text{ k}\Omega\text{-sq}^{-1}$ after 5 min (Fig. 7(a)) [120]. Point defects have a dual effect on electrical conductivity: Donor doping introduces free electrons, while acceptor doping introduces holes, both of which increase carrier concentration. At low doping levels, this may partially offset the decrease in mobility and slightly increase electrical conductivity [90]; high doping leads to enhanced scattering, which conversely causes a decrease in electrical conductivity. Interlayer stacking defects weaken interlayer electron coupling and increase interlayer resistance, leading to a decrease in overall conductivity.

3.2.2 Effects on optical properties

Defects (vacancies, Stone–Wales, and N/B doping) disrupt lattice periodicity and π -conjugation, enhance electron localization, and reduce the highest occupied molecular orbital–lowest unoccupied molecular orbital (HOMO–LUMO) gap from 2.10 (defect-free) to 0.62–2.04 eV. This alters the absorption spectrum: Single defects cause a blue shift (554–591 nm), while double defects cause a red shift (598–668 nm). Higher defect concentrations significantly lower absorption intensity (Figs. 7(b) and 7(c)) [103]. Vacancy defects introduced by ion implantation form a depth-dependent distribution in MLG; the evolution of such defects induced by laser annealing alters lattice stress and electron scattering probabilities, further affecting optical properties [25].

3.2.3 Effects on mechanical properties

Vacancies create dangling bonds, while pentagonal/heptagonal defects at grain boundaries cause stress concentrations, both

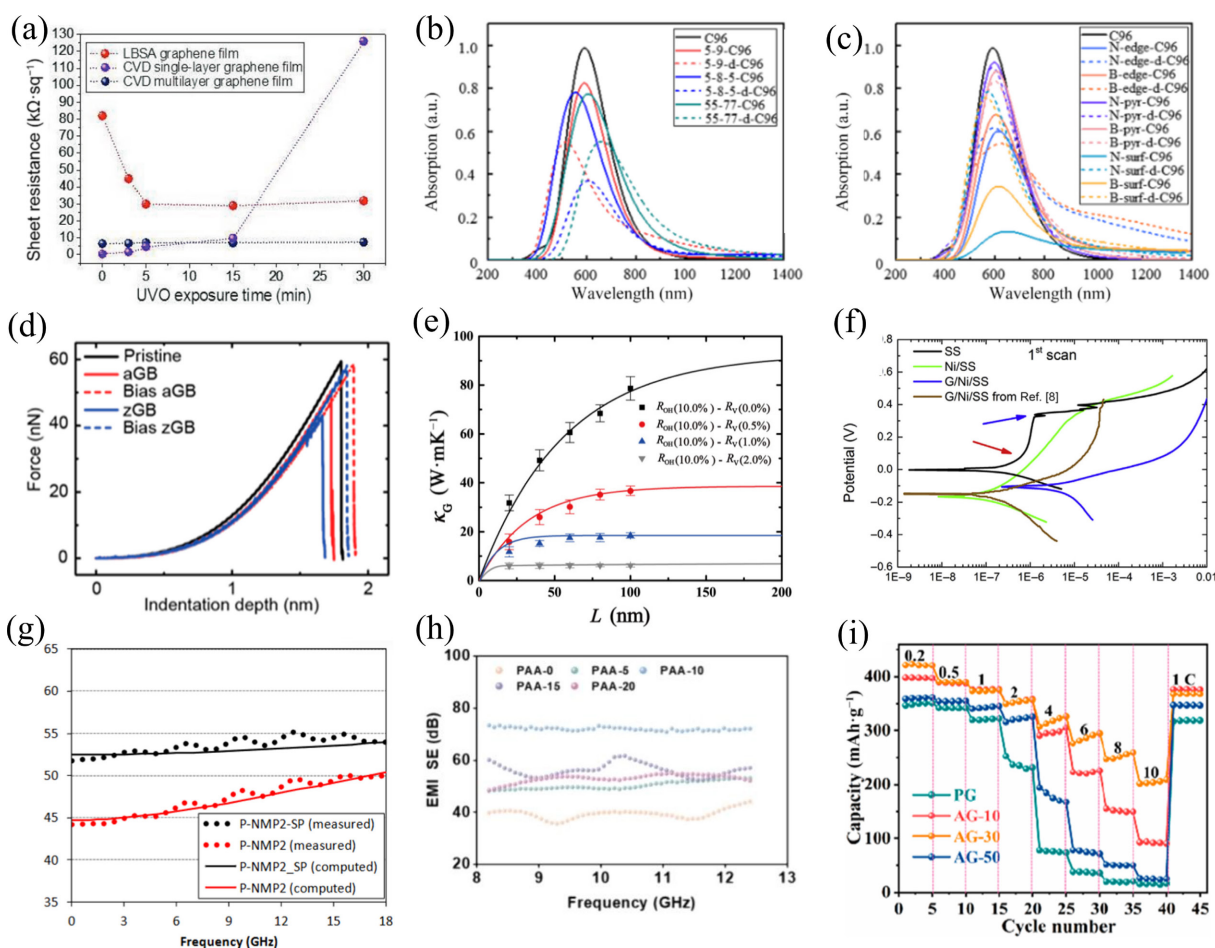


Figure 7 The impact of defects on performance. (a) After UVO treatment, LBSA exhibits reduced edge defects and a rapid decrease in surface resistance. Reproduced with permission from Ref. [120], © Elsevier B.V. 2018. (b) and (c) The effects of different defects on the blue shift and red shift of light. Reproduced with permission from Ref. [103], © Liu, W. et al. 2023. (d) Grain boundary defects reduce mechanical fracture strength. Reproduced with permission from Ref. [8], © American Chemical Society 2014. (e) Vacancy defects reduce thermal conductivity. Reproduced with permission from Ref. [123], © Yang, Y. et al. 2019. (f) The lower the defect density, the better the corrosion resistance. Reproduced with permission from Ref. [124], © Elsevier B.V. 2015. (g) Reduced pore size and interlayer spacing result in improved electromagnetic shielding performance. Reproduced with permission from Ref. [90], © Elsevier Ltd. 2015. (h) A moderate defect density improves electromagnetic shielding performance. Reproduced with permission from Ref. [9], © American Chemical Society 2025. (i) The AG-30, with its superior properties, far outperforms other modified graphites in terms of magnification performance. Reproduced with permission from Ref. [105], © American Chemical Society 2022.

reducing tensile strength and fracture toughness. Higher defect density lowers stress tolerance, and grain boundaries alone can reduce global strength by 14%–28% (Fig. 7(d)) [8]. Stacking increases the fracture strain of defective MLG as upper layers cover lower-layer defects and provide stress pathways; however, overlapping defect layers create weak zones that reduce overall stiffness and shear modulus. At a fixed graphene volume fraction of 6.44%, defect density is negatively correlated with mechanical properties: Defect-free graphene has the highest tensile strength and fracture strain, while increasing defect fraction from 2% to 6% progressively lowers peak stress, elastic modulus, and fracture strain [121].

3.2.4 Effects on thermal properties

Thermal conductivity depends on the degree of phonon scattering. Defects directly reduce thermal conductivity by scattering phonons and altering phonon dispersion. Non-equilibrium molecular dynamics simulations have revealed that the misorientation angle of grain boundaries strongly influences thermal conductivity. The fundamental reason is that grain boundaries at different angles

scatter phonons with varying intensities [122]. Low-defect and well-oriented MLG achieves high thermal conductivity (500 W·m⁻¹·K⁻¹). In graphene oxide, thermal conductivity drops with vacancy defects; above 2% vacancies, it converges to 6.01 W·m⁻¹·K⁻¹ (20 nm sample). Without vacancies, 10% oxidation causes a reduction of ~90% (Fig. 7(e)) [123].

3.2.5 Effects on chemical properties

Defect reactivity order (highest to lowest): single vacancies > hydrogenated zigzag edges/555–777 divacancies > Stone–Wales > hydrogenated armchair edges > perfect graphene. Vacancies and pinholes expose metal substrates, causing galvanic corrosion; defect density is negatively correlated with corrosion resistance (Fig. 7(f)) [124]. In the field of electrocatalysis, graphene clusters containing specific point or line defects exhibit excellent electrocatalytic performance for the oxygen reduction reaction, with the defect sites serving as catalytically active sites [125].

3.2.6 Other effects

In tribology, fewer defects in MLG (as a hydraulic oil additive) form

a stable transfer film (solid lubricant), reducing the friction coefficient to 0.04; more defects cause unstable lubrication due to agglomeration [126]. Defect density directly affects lubricating film quality. For EMI shielding, MLG paper with defect networks achieves 73.2 dB; defect repair improves shielding by 10–15 dB in the RF range (Figs. 7(g) and 7(h)) [9, 90]. In thick GF, shielding increases linearly as defect density decreases [9]. In lithium-ion storage, defect engineering introduces a pseudocapacitive mechanism. Defect content shows a nonlinear effect on performance, confirming that “moderate defects” are key to optimal electrochemical performance (Fig. 7(i)) [105].

This section classifies defects into three types: point defects (vacancies, substitutional atoms, interstitial atoms, and Stone–Wales defects), line defects (grain boundaries, edges, wrinkles, and cracks), and planar defects (stacking faults and nanopores). These defects are primarily characterized by Raman spectroscopy, transmission electron microscopy, scanning electron microscopy, and atomic force microscopy.

The effects of defects can be both beneficial and detrimental. For example, vacancies and heteroatom dopants can enhance catalytic activity, ion storage capacity, and gas adsorption performance, benefiting energy storage and sensor applications. In contrast, grain boundaries and wrinkles can severely degrade electrical conductivity, thermal transport properties, and mechanical strength, posing challenges for high-performance electronic devices and thermal management.

Stacking faults and nanopores can enable unique functionalities such as tunable interlayer coupling and molecular sieving. Moreover, in lithium-ion battery anodes, “moderate defects” yield optimal electrochemical performance. This section lays the foundation for the subsequent defect engineering to precisely control the type, size, and density of defects, which is crucial for tailoring the properties of MLG/GF and is the key to translating them into practical applications.

4 Defect engineering in MLG and GF

As established in Section 3, defects can have both detrimental and beneficial effects. Therefore, it is necessary to precisely control beneficial defects through defect engineering while suppressing or even eliminating harmful ones. This section focuses on defect engineering strategies, mainly including methods for the controlled introduction of defects, techniques for defect repair, and the preparation of nearly defect-free single-crystal MLG and GF. Finally, representative applications of defect engineering in various fields are also presented.

4.1 Methods for introducing and controlling defects in MLG and GF

4.1.1 Ion-related methods

Ion implantation involves bombarding the lattice of MLG with high-energy ions to break carbon–carbon covalent bonds, thereby introducing atomic- or nanoscale defects such as vacancies and nanopores. This process modulates the material’s surface chemistry, electronic structure, and mechanical properties.

In particular, oxygen ion implantation utilizes chemical reactions to simultaneously introduce structural defects and oxygen-containing functional groups, primarily generating point defects and edge defects (Fig. 8(a)). As the treatment time increases, both

defect density [28, 31] and surface roughness [30] increase. Nitrogen ion implantation forms doping defects by substituting carbon sites with nitrogen atoms, leading to lattice disorder and the formation of new chemical bonds (Fig. 8(b)), which can enhance carrier concentration and lithium adsorption capacity [32].

Argon ion implantation, primarily involving physical bombardment, introduces structural defects and reduces mechanical properties. The molecular dynamics simulation process of argon ion introduction is shown in Fig. 8(c) [25, 127], making it suitable for applications such as nanomechanical resonators and filtration membranes that require the preservation of intrinsic chemical properties [104, 128]. Hydrogen ion implantation, on the other hand, utilizes ion energies of 5–25 eV [129] to achieve precise control over three types of defects, surface distortion, vacancies/nanopores, and interlayer exfoliation, and due to the buffering effect between layers, exhibits superior damage resistance compared to monolayers [127].

Meanwhile, high-energy He⁺ helium ion irradiation precisely introduces atomic-scale point defects, primarily of the vacancy type, through collision effects (Fig. 8(d)), with both defect density and distribution being quantitatively controllable via irradiation dose [130].

4.1.2 Physical treatment methods

Physical treatment methods offer advantages such as being environmentally friendly with no chemical residues, controllable defect types, and ease of scaling. For example, irradiation with a 532 nm laser can introduce vacancies and grain boundary defects in the graphene contact region, with defect density increasing as laser power increases. After treatment, the metal–graphene contact resistance is significantly reduced to 250 $\Omega\cdot\mu\text{m}$, a decrease of 70% compared to untreated devices, thereby enhancing device performance (Figs. 8(e) and 8(f)) [130]. UV irradiation can similarly generate vacancy defects (Fig. 8(g)); combined with subsequent heat treatment, this allows oxygen to diffuse through the vacancies to the Cu surface. At the same time, UV irradiation can simultaneously remove PMMA residues from the MLG surface, achieving an integrated “defect introduction–surface cleaning” process and simplifying the fabrication workflow [24].

Furthermore, defect introduction via sliding between MLG and different materials can significantly improve tribological properties. For example, when rubbing against H-DLC, the coefficient of friction drops to as low as 0.08, representing a reduction of over 80% compared to the original state. This is attributed to the dissociation of H₂O at the defect sites, leading to the adsorption of H/OH and the formation of a passivation layer [22].

4.1.3 Other methods

MLG was composited with polypropylene via melt blending. The high-temperature processing introduced lattice defects, and the defect distribution was controlled by adjusting the MLG concentration (0.1 wt.%–3 wt.%). The most uniform dispersion was observed at a loading of 0.5 wt.%; at 1 wt.%, the dielectric constant of the composite decreased by 18%, while mechanical strength and thermal stability were enhanced [33].

By utilizing the electron avalanche effect triggered by the contact between two-dimensional electronegative materials and MLG, interlayer interactions were regulated via charge transfer, introducing interlayer twisting and disordered structures. This weakened the interlayer van der Waals interactions, reducing the

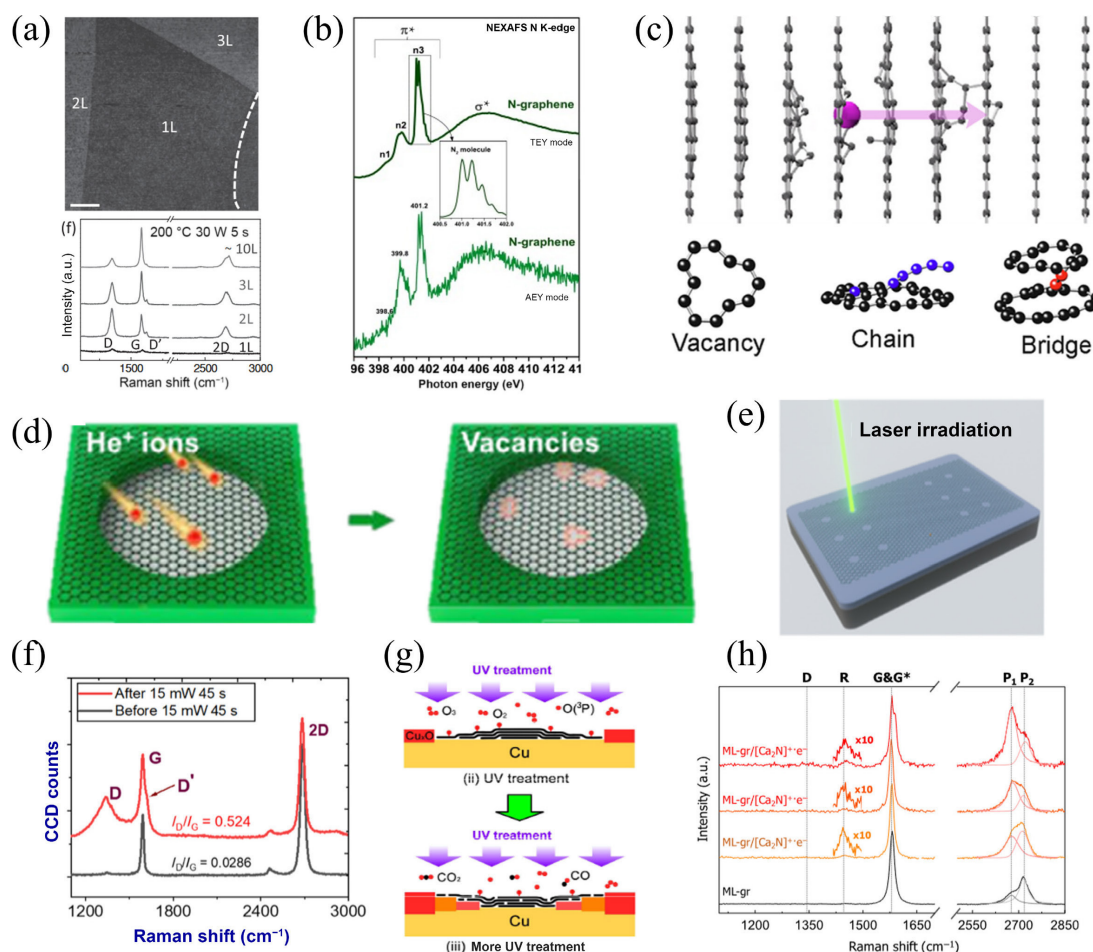


Figure 8 Methods for introducing defects. (a) Oxygen plasma irradiation of MLG produces point defects and edge defects. Reproduced with permission from Ref. [31], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2014. (b) Lattice disorder and the formation of new chemical bonds resulting from the introduction of nitrogen ions. Reproduced with permission from Ref. [32], © Elsevier B.V. 2025. (c) Cross-section screenshot taken from an MD simulation run of Ar⁺ implantation in MLG. Reproduced with permission from Ref. [25], © American Chemical Society 2017. (d) Schematic of the decoupled defect nucleation and pore expansion process. Reproduced with permission from Ref. [130], © American Chemical Society 2021. (e) Schematic diagram of laser irradiation. Reproduced with permission from Ref. [130], © American Chemical Society 2021. (g) Schematic diagram of ultraviolet irradiation. Reproduced with permission from Ref. [24], © American Chemical Society 2016. (h) The injection of a high concentration of electrons caused twisting between the layers. Reproduced with permission from Ref. [131], © American Chemical Society 2019.

contact resistance to 500 Ω-μm and significantly improving metal contact performance (Fig. 8(h)) [131].

During the CVD process, MLG was grown using a PVP solution as the precursor and spherical Ag nanoparticles as the substrate. Curved-surface growth disrupted the hexagonal symmetry, introducing structural defects; the more defects present, the lower the thermal conductivity and the higher the resistivity. An optimal balance for TIM applications was achieved at a PVP loading of 60 wt.%, with a thermal conductivity of 71 W·m⁻¹·K⁻¹ and a resistivity of 6.0 × 10⁻⁸ Ω·m, combining high thermal conductivity with appropriate electrical insulation properties [27].

To provide readers with a concise overview, Table 2 summarizes these defect-introduction methods, the resulting defect types, key control parameters, associated performance changes, and typical applications.

4.2 Defect removal and optimization

4.2.1 Repair of defects

Defect repair in graphene is a key method for enhancing its

electrical, mechanical, and thermal properties. High-temperature annealing promotes the recombination of vacancies with adsorbed atoms by providing energy for atomic diffusion and lowering the migration energy barrier of carbon atoms [132], thereby repairing vacancies, stacking defects, and oxygen-containing functional groups. In an argon plasma environment, the repair effect increases with rising temperature: repair begins at 300 °C, electrical properties recover significantly at 500 °C, defect density decreases substantially at 750 °C, and the optimal repair effect is achieved at 900 °C (Fig. 9(a)). Under these conditions, the two-dimensional (2D) sp² carbon network is largely reconstructed, and the graphene domain size increases from 10 to approximately 80 nm [133]. To address the issues of “uneven carbon source distribution and random repair sites” in conventional annealing, carbonized dehydroascorbic acid (CDA) was used as a repair agent. At 800 °C, CDA precisely adsorbed via hydrogen bonding onto defect sites such as ketone and carboxyl groups on graphene oxide, enabling targeted defect localization and directed repair, while bridging small-sized graphene flakes (Fig. 9(b)) [134]. A “SLG-rGO composite structure” was constructed using SLG as a scaffold. Vacancy filling began at

Table 2 Methods of defect introduction, defect Types, control methods, performance changes, and applications

Methods	Defect type	Control defects	Performance changes	Applications	Ref.
UV exposure	Voids	UV exposure time, heating time, and temperature	Accelerating the oxidation reaction	Determination of the number of graphene layers. Optical differentiation of graphene layers based on copper oxide thickness variation	[24]
300 eV argon ion bombardment	Voids	Adjusting parameters such as ion dose and processing time	The introduction of vacancies induces lattice distortion, generating in-plane tensile stress, thereby altering the resonant frequency	Applied to nanomechanical switches or timers, because defects act as a stress source to control the resonant frequency	[25]
Argon plasma irradiation	Voids and oxygen-containing functional group	Controlling the plasma power and duration, as well as the annealing temperature and pressure	The water contact angle was reduced from its inherent value of 45° to 9°, and then changed to 55° after high-temperature treatment	Applied to microfluidics and self-cleaning due to hydrophilic and hydrophobic properties	[128]
Oxygen plasma irradiation	Structural defects	Adjusting the oxygen flow rate	Increase in active adsorption sites and an increase in resistance	Defects create more active adsorption sites, enhancing charge transfer between gas molecules and graphene, with applications in gas sensors	[30]
Argon plasma irradiation	Voids and pore defects	Adjusting the plasma exposure time, argon flow rate, and pressure	Pristine MLG shows metallic behavior ($dR/dT > 0$), while plasma-treated p-MLG shows semiconducting behavior ($dR/dT < 0$)	Nonlinear devices (e.g., rectifiers and switches)	[104]
Oxygen plasma irradiation	Point defects and nanopores	Adjusting the RF power, time, and temperature of the plasma	The introduction of defects leads to an increase in defect density, which can be further enlarged into nanopores with controllable sizes	Applied to gas separation and water treatment due to the pore size	[31]
Hydrogen ion bombardment	Voids and porosity defects	Regulation of H ⁺ ion energy and flux	10 eV H ⁺ bombardment enables layer-by-layer removal of graphene, while under 25 eV H ⁺ bombardment, H ₂ molecules are stably trapped in the interlayer space of graphene	Applied to patterning/etching and high-density hydrogen storage	[129]
Exposure to He ²⁺ ions	Point defects and Stone–Wales defects	Controlling defect density by adjusting the irradiation dose	MLG exhibits defect self-passivation, where interlayer linking partially compensates the modulus degradation	Applied to space radiation shielding materials, as irradiation generates interlayer crosslinking that compensates for in-plane defects	[127]
<i>In-situ</i> defect induction on the MLG surface via mechanical sliding	Edge cracking and increased interlayer spacing	Adjusting the type of abrasive material	Sliding-induced defects provide active sites for water dissociation, forming H/OH passivation layers and thereby reducing friction	Solid lubricant in atmospheric environments due to its low coefficient of friction	[22]
Irradiate with a 532 nm laser	Grain boundaries and vacancies	Adjusting laser power	The contact resistance was reduced by approximately 70% to 72%	It is applied in high-performance and low-power electronic devices, such as radio-frequency transistors and sensors	[26]
Nitrogen ion bombardment	Vacancy and nitrogen substitution defect	Controlling defect concentration by adjusting nitrogen ion energy and bombardment time	Vacancy defects and pyridinic nitrogen provide the ability to adsorb a large amount of lithium on the surface of MLG	Applied to high-performance lithium-ion battery anode materials or lithium-nitrogen batteries	[32]
Pre-oxidation + high-temperature KOH chemical activation	Nanopore	Regulating pore size and density by adjusting the degree of pre-oxidation and KOH activation parameters	The retention rate for 1 nm dyes in water is 99%, and the retention rate for NaCl is 20%	Applied to water purification/nanofiltration membranes due to the pore size of 3 nm and pore density of 10 ¹⁵ m ⁻²	[114]
Thermal shock (rapid cooling in liquid nitrogen)	Fold defects	Controlling the number of immersion cycles and the cooling rate	Weakened interlayer coupling and strain localization	Applied to straintronics because local strain can modify the band structure, generate pseudo-magnetic fields, and modulate electronic transport	[29]
Thermal shock (rapid cooling in liquid nitrogen)	Wrinkle	Controlling the number of immersion cycles and the cooling rate	Weakened interlayer coupling and significantly enhanced chemical reactivity	Applied to selective chemical etching/patterning because chemical reactivity can be selectively enhanced	[110]

1000–1500 °C; at 1800–2000 °C, SLG guided carbon atoms to reconstruct sp² structures, causing vacancies to virtually disappear; and at 2200–2400 °C, rGO domains grew laterally, with I_D/I_G decreasing to less than 0.01 and domain size increasing from 100 nm to 1.4 μm, achieving the crystallinity of high-quality

MLG (Fig. 9(c)) [135]. Furthermore, introducing nitrogen into GO via the hydrothermal method delays the lattice recovery of defective graphene, preserving a large number of vacancies and grain boundaries even at 2000 °C. These retained high-temperature defects significantly lower the energy barrier for carbon atom

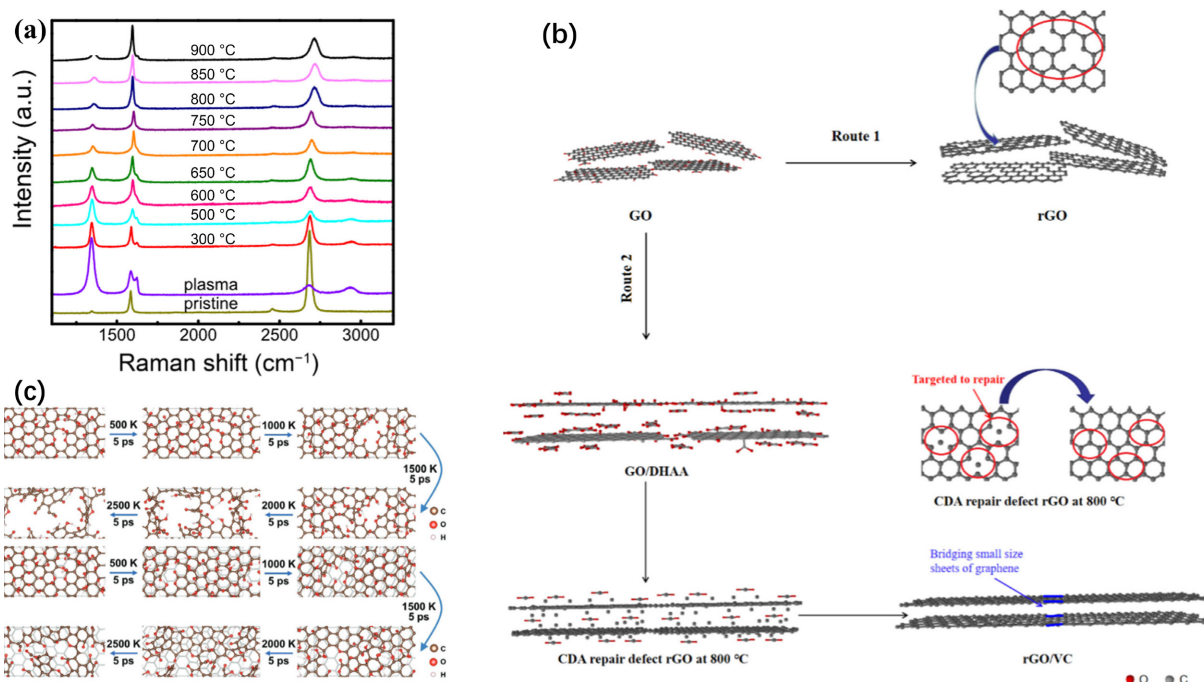


Figure 9 Methods for repair of defects (a) Raman spectra of defect-repaired samples at different temperatures. Reproduced with permission from Ref. [132], © Elsevier B.V. 2019. (b) Schematic illustration of CDA-mediated targeted repair of graphene defects and bridging of small-sized flakes. Reproduced with permission from Ref. [134], © Li, J. et al. 2020. (c) Structural evolution of bare graphene and graphene on a graphitized layer (SLG) during a five-step annealing process. Reproduced with permission from Ref. [135], © Guo, M. H. et al. 2024.

migration in the graphitization range of 2000–3000 °C, driving rapid grain growth and ordering. After repair, the electrical conductivity reaches $2.0 \times 10^4 \text{ S} \cdot \text{cm}^{-1}$, and the thermal conductivity reaches $1.7 \times 10^3 \text{ W} \cdot \text{m}^{-1} \cdot \text{K}^{-1}$ [34].

4.2.2 Transfer methods for MLG and GF

Defects can arise during both preparation and transfer, so transfer methods must be improved to minimize new defects. Common methods include wet and dry transfer. Wet transfer is mature and widely used: It uses a liquid to separate graphene from the growth substrate. Advantages: simple, low-cost, and large-area. Drawbacks: liquid residues, wrinkles, and damage; the traditional PMMA support layer leaves significant chemical residues.

To address the residue issue, researchers have explored various alternative support layers. Paraffin wax, due to its high chemical inertness and weak interaction with graphene, undergoes no complex chemical reactions during thermal evaporation removal, enabling the intact transfer of centimeter-scale graphene sheets (Fig. 10(a)) [136]. Camphor has an adsorption energy of only 0.09 eV with graphene; its weak interaction and low sublimation temperature ensure no residue and no damage to sensitive substrates, while its “oil boundary” effectively reduces mechanical damage during transfer (Fig. 10(b)) [137]. Rosin also interacts weakly with graphene, allowing the support layer to be removed at room temperature to avoid high-temperature damage; combined with the solubility of benzyl ether, this enables low-residue transfer of MLG (Fig. 10(c)) [138]. Further developments in methods that eliminate the need for a polymer support layer have completely resolved the residue issue. For example, using copper foil directly as the support layer achieves a polymer-free and clean graphene surface (Fig. 10(d)) [139]. Additionally, the double-sided simultaneous wet transfer technique significantly improves transfer efficiency and reduces chemical residues. Using nickel foil as the

growth substrate, one side is transferred to an EVA/PET polymer substrate via hot-press lamination, while the other side utilizes the “floating separation” principle in FeCl_3 etching solution. The oxide layer formed during etching prevents graphene aggregation on both sides, and the exposed graphene floats on the surface of the etching solution due to differences in surface tension, thereby enabling the simultaneous recovery of MLG from both sides of the nickel foil (Fig. 10(e)) [140].

The dry transfer method avoids liquid etchants/solvents, using mechanical forces, physical adsorption, or inorganic support layers to protect MLG and separate it from the growth substrate (Fig. 10(f)) [141]. It introduces minimal contamination, prevents wrinkling/rupture from liquid surface tension, preserves high quality, and allows substrate reuse. However, it requires high precision and technical expertise, and is costly.

4.2.3 single-crystal MLG and GF

The above discussion focuses on polycrystalline MLG and GF, which contain various defects. In contrast, single-crystal versions are nearly defect-free, making their preparation particularly important. Early on, single-crystal MLG and GF suffered from small growth dimensions and poor layer/quality control. With advancing techniques, growth dimensions have gradually increased from small scales to wafer-scale or larger, ranging from millimeter to centimeter scales.

The main preparation methods include the isothermal carbon diffusion continuous epitaxy method (Fig. 11(a)) [7] and mechanical exfoliation. Single-crystal nickel is a typical substrate due to its high carbon solubility and large carbon diffusion rate, providing an abundant carbon source. The stepped edges on nickel promote rapid nucleation and epitaxial growth, yielding high-quality MLG and GF [142]. For example, a single-crystal Ni foil is pressed onto the surface of a solid carbon source, placed on an

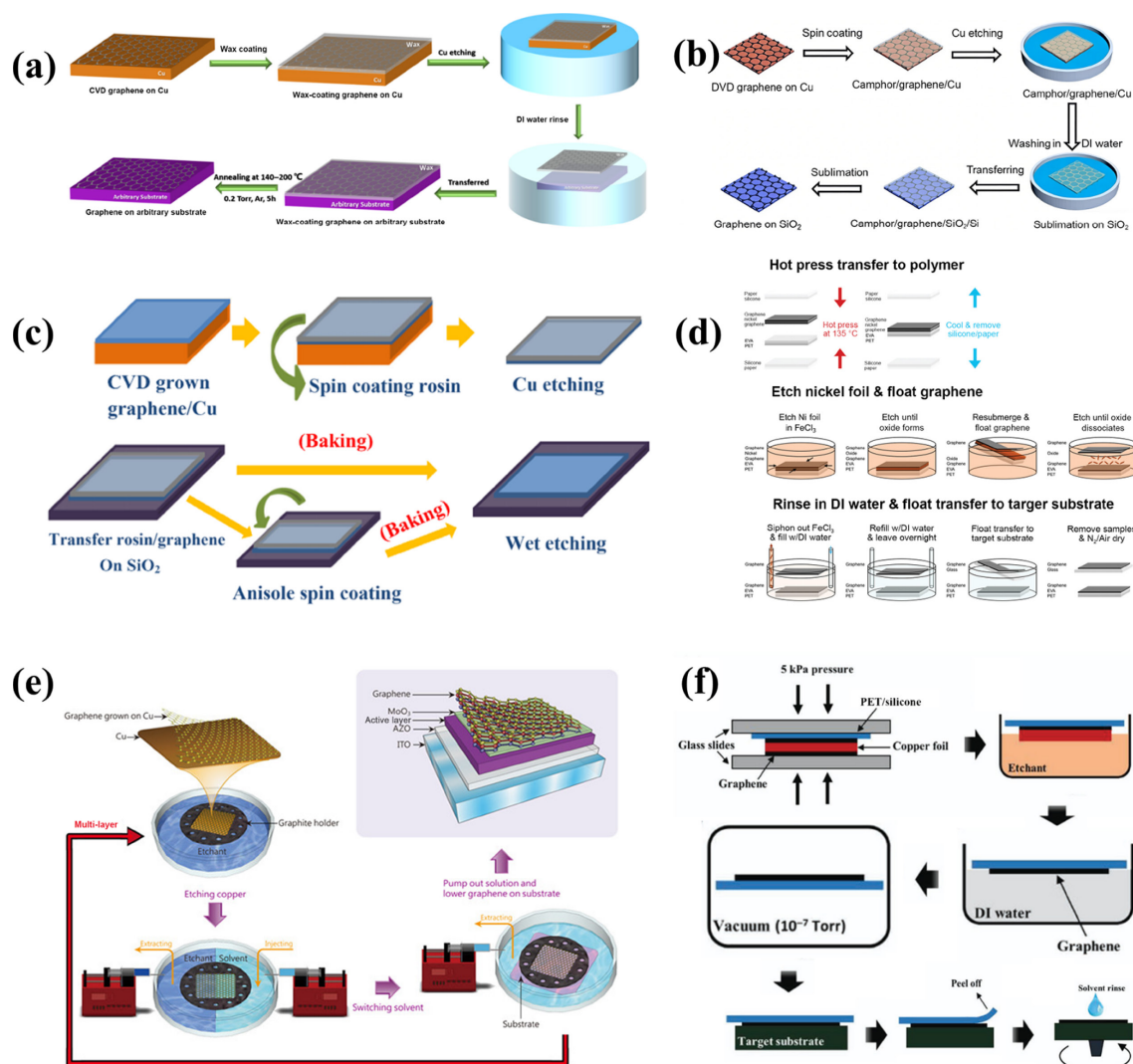


Figure 10 Methods for transferring MLG and GF. (a) Chemically illustrated graphene transfer assisted by wax (reproduced with permission from Ref. [136], © American Chemical Society 2019), (b) by camphor (reproduced with permission from Ref. [137], © Elsevier Inc. 2019), and (c) by rosin (reproduced with permission from Ref. [138], © Shahzad, K. et al. 2020). (d) Schematic illustration of the polymer-free transfer process. Reproduced with permission from Ref. [140], © Wiley-VCH GmbH 2020. (e) Schematic diagram of the bifacial float transfer technique to polymer and target substrates, including. Reproduced with permission from Ref. [139], © Chen, Y. et al. 2016. (f) Schematic diagram of the dry transfer process. Reproduced with permission from Ref. [141], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2018.

alumina substrate, and loaded into a CVD furnace. The system is fed with 800 sccm of Ar and 50 sccm of H_2 and heated to 1300 °C within 2 h, and the temperature is maintained for 1–120 h. This results in a single-crystal graphene film with a thermal conductivity of $\sim 2880 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, an intrinsic Young's modulus of 1.0 TPa, dimensions of $2 \text{ cm} \times 3 \text{ cm}$, and a thickness of up to 35 μm , comprising over 100,000 layers (Figs. 11(b) and 11(c)) [7].

Single-crystal copper substrates have weak carbon solubility, so carbon atoms nucleate and grow directly on the surface during CVD. Their highly ordered atomic arrangement enables self-limiting growth of uniform monolayer graphene, and high lattice matching reduces defects. For example, using CVD at 1060 °C, H_2/CH_4 ratio of 100:1–1000:1, pressure of 2.0–30.0 Torr, and growth time of 30–60 min, three-layer single-crystal graphene was grown on Cu(111) foil with a mobility of $\sim 5000 \text{ cm}^2\cdot\text{V}^{-1}\cdot\text{s}^{-1}$ [143]. Another substrate option is a CuNi alloy thin film, which offers the advantage of more precise control over the number of graphene layers. For example, a single-crystal CuNi substrate is placed into the CVD chamber, heated to 1050 °C, and a mixture of 1000 sccm

Ar, 200 sccm H_2 , and 10 sccm CH_4 is introduced during the carbon dissolution stage. After maintaining the temperature for 40 min, the H_2 flow rate is reduced to initiate the growth and segregation phase, followed by slow cooling to 850 °C. This process yields a 2-inch wafer with a coverage rate exceeding 95% of three-layer graphene [15, 144].

Using a Joule heating method with a Ni-Mo alloy melt on a graphite substrate (stacked Ni/Mo foils), a flat alloy melt enables high-speed carbon dissolution/precipitation at 6.2 layers $\cdot\text{s}^{-1}$. Intentional evaporation of Ni creates a porous substrate, reducing interfacial interaction and eliminating internal stress, yielding a mirror-like GF with 100% AB stacking and millimeter-sized grains. The film exhibits an electrical conductivity of $2.25 \times 10^4 \text{ S}\cdot\text{cm}^{-1}$, an in-plane thermal conductivity of $2034.4 \pm 68 \text{ W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$, a Young's modulus of $969 \pm 69 \text{ GPa}$, a tensile strength of $1.29 \pm 0.203 \text{ GPa}$, and a density of $2.25 \text{ g}\cdot\text{cm}^{-3}$ (close to natural graphite) (Figs. 11(d)–11(j)) [99].

There are two approaches for preparing single-crystal MLG and GF via mechanical exfoliation: One involves directly exfoliating

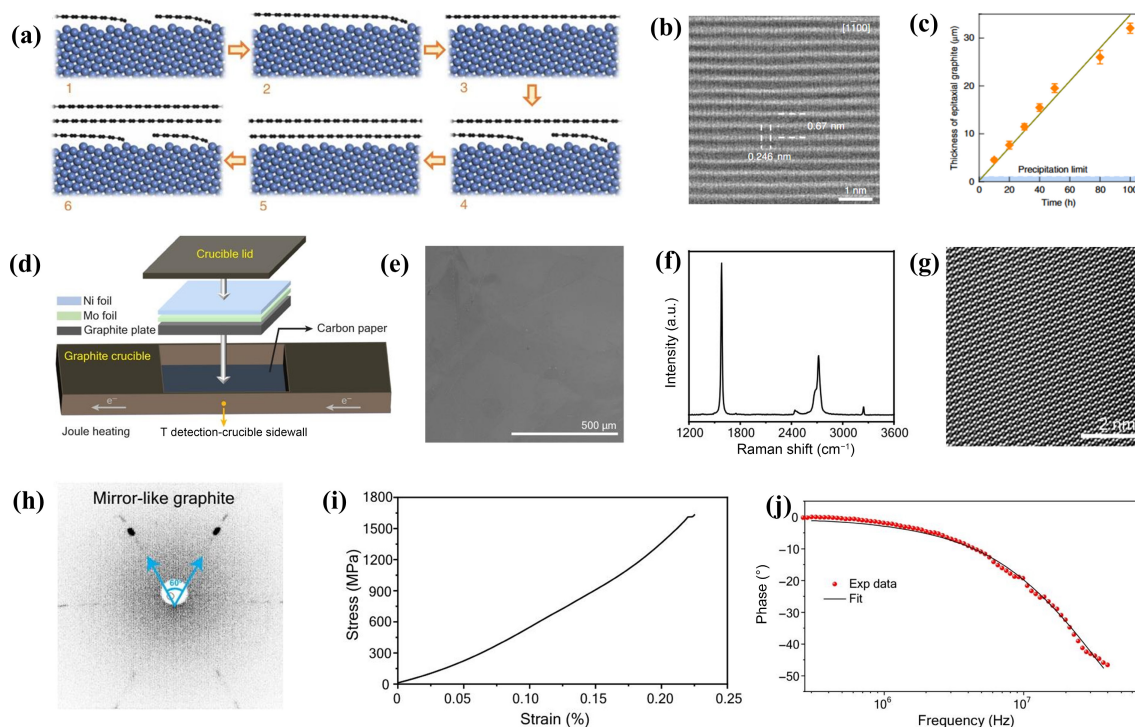


Figure 11 Methods for the preparation of single-crystal GF and characterization of their properties. (a) Schematic diagram of the epitaxial process of graphite growth on the Ni surface. (b) The interlayer spacing of single-crystal GF. (c) The thickness of a ten-thousand-layer single-crystal GF. Reproduced with permission from Ref. [7], © Zhang, Z. B. et al. 2022. (d) Schematic illustration of the dissolution-precipitation method using a nickel-molybdenum alloy melt. (e) Large-area single-crystal GF. (f) Defect-free Raman spectrum. (g) TEM image demonstrating well-ordered lattice arrangement at the atomic scale, with no defects such as vacancies or dislocations. (h) Laue diffraction pattern confirming single-crystal characteristics and AB stacking. (i) Schematic illustration of exceptional mechanical properties. (j) Experimental measurements and model fitting of extremely high thermal conductivity. Reproduced with permission from Ref. [99], © Zhang, L. Y. et al. 2025.

MLG and GF from a graphite block [15, 144–146], while the other involves exfoliating SLG and then artificially stacking the SLG sheets into MLG, followed by methods such as heating to strengthen the interlayer van der Waals forces [145].

In summary, the preparation of nearly defect-free single-crystal MLG and GF has been achieved by various methods. Table 3 summarizes the key parameters, substrate choices, achieved properties, dimensions, and thicknesses of these representative single-crystal samples.

This section reviews defect types, characterization, and their effects on the electrical, thermal, and mechanical properties of MLG and GF. Optimized transfer methods reduce secondary defects. Single-crystal versions, being nearly defect-free, largely avoid these issues; their preparation has evolved from small-scale to wafer-scale controlled growth. Future research should focus on precise layer-number control in large-scale single crystals, non-destructive transfer technologies, and a deeper understanding of defect-property relationships to enable applications in high-end electronic devices.

4.3 Applications of defect engineering

4.3.1 Protection and thermal management

MLG, despite manufacturing/transfer defects, outperforms amorphous carbon films of the same thickness as a hydrogen diffusion barrier. Defects like voids self-seal via carbon redeposition from etching, delaying hydrogenation of the underlying material, and achieving significantly longer hydrogenation times [35]. CVD-grown MLG on Monel 400 uses interlayer defect complementarity

(upper layers mask lower defects) to achieve full coverage, reducing corrosion current density by ~ 2 orders of magnitude. It remains intact after 1008 h of immersion, as corrosion products at defect sites further seal pores [154]. In a nickel layer/MLG coating (G/Ni/SS) constructed on a stainless steel surface, defects such as grain boundaries in the MLG extend the diffusion path of the corrosive medium through a “maze effect”, synergistically inhibiting Cl^- penetration with the nickel layer; no significant corrosion was observed after 504 h of immersion in boiling seawater [124]. Highly oriented coatings composed of low-defect and multilayer modified graphene and epoxy resin, prepared via microfluidic processes, reduce corrosion medium penetration pathways due to their low-defect nature, demonstrating excellent long-term corrosion resistance (Fig. 12(a)) [155]. A biomimetic coating prepared by using polydopamine as a “suture” to repair structural defects in MLG exhibits corrosion resistance far superior to that of traditional epoxy coatings, while also possessing anisotropic thermal and electrical conductivity properties. The anti-corrosion barrier mechanism is shown in the figure (Fig. 12(b)) [156]. In copper corrosion protection, bilayer graphene tightly bonds with copper through heavy doping of the bottom layer, covering steps and defect sites on the copper surface. This effectively creates a “second barrier” beneath the defects, preventing chain corrosion. It can protect copper materials for over 5 years at room temperature and for up to 1000 h at 200 °C [157].

In the field of filtration and separation, composite membranes constructed from graphene oxide and polypyrrole nanoplates form hierarchical channels through defect engineering. They exhibit a retention rate exceeding 96% for dyes such as Congo red, a retention rate below 15% for inorganic salts such as NaCl, and a

Table 3 Methods for preparing single-crystal MLG and GF, their properties, dimensions, and thickness

Preparation method	Key growth parameters	Substrate	Performance	Dimensions	Thickness	Ref.
CVD	1300 °C, 800 sccm argon, and 50 sccm hydrogen	Single-crystal Ni	2880 W·m ⁻¹ ·K ⁻¹ , 1.0 TPa	2 cm × 3 cm	Over 100,000 layers	[7]
CVD	1077 °C, H ₂ 65 sccm + CH ₄ 0.1 sccm	Copper foil	5000 cm ² ·V ⁻¹ ·s ⁻¹	N/A	2–4 layers	[143]
CVD	900 °C, 3 °C·min ⁻¹	Sapphire	N/A	N/A	3–6 layers	[146]
CVD	1050 °C, 1000 sccm Ar + 200 sccm H ₂ + 10 sccm CH ₄	Cu ₈₀ Ni ₂₀ alloy film	Sheet resistance as low as 475 Ω·sq ⁻¹	Wafer-level	3 layers	[147]
CVD	850 °C, 0.5 °C·min ⁻¹	Ni(111)	N/A	Wafer-level	Layers ≥ 3	[142]
CVD	1000–1100 °C, < 10 °C·min ⁻¹	N/A	N/A	N/A	50 layers	[15]
Mechanical peeling	N/A	N/A	N/A	Millimeters	6–40 layers	[148]
Mechanical peeling	N/A	N/A	The Hall resistance can reach 78% in a zero magnetic field.	N/A	4 layers	[15]
Mechanical peeling	N/A	SiO ₂ /Si	N/A	> 5000 μm ²	3 layers	[149]
Mechanical peeling	Annealing temperature: 350 °C	N/A	≥ 100,000 cm ² ·V ⁻¹ ·s ⁻¹	N/A	3 layers	[150]
Cut-and-stack method	Applying different AC voltages and probe loading forces	N/A	The maximum critical magnetic field can reach 400 mT.	N/A	3 layers	[145]
Joule heating	2250 °C, cooling rate: 3 °C·min ⁻¹	Ni-Mo alloy melt	2034.4 ± 68 W·m ⁻¹ ·K ⁻¹ , 2.25 × 10 ⁴ S·cm ⁻¹ , 1020 GPa	12 mm × 13 mm	145 μm	[99]
VASP Software Simulation	N/A	N/A	Polarization modulation, and band structure modulation	N/A	4–6 layers	[151]
VASP Software Simulation	N/A	N/A	N/A	Millimeters	3 layers	[152]
Simulation based on first-principles calculations	N/A	N/A	High conductivity, wide concentration sensitivity,	N/A	4 layers	[153]

water flux of 310 L·m⁻²·h⁻¹·bar⁻¹, which is more than five times that of traditional two-dimensional membranes (Fig. 12(c)) [37]. Multilayer AGO membranes with abundant nanopores achieve 80%–99% retention of organic dyes (~ 1 nm hydrated diameter). Interlayer channel defects (8.99 Å) block hydrated ions and macromolecular dyes, while nanopores allow water passage, yielding synergistic high flux and selectivity. Water flux is six times that of conventional GO membranes and far exceeds commercial nanofiltration membranes; higher pore density further increases flux (Fig. 12(d)).

Using PVP as a carbon source, defect-containing MLG (3–4 nm thick) was grown on Ag nanoparticles via CVD. With 60 wt.% PVP, high-temperature agglomeration of Ag is prevented. The defect-containing graphene layers maintain thermal conduction pathways while enhancing electrical conductivity to 6.0 × 10⁻⁸ Ω·m, meeting the requirements for thermal interface materials (high thermal conductivity, low electrical leakage) [27]. Interlayer cross-linking defects in MLG induced by high-energy He²⁺ ion irradiation can enhance its resistance to radiation damage, demonstrating application potential in thermal protection coatings for space detection equipment [127]. By introducing approximately 0.1% biaxial tensile strain, which disrupts the crystal symmetry of graphene, the thermal conductivity of MLG is reduced by about 70%. Both pressure-driven and electrostatic strain mechanisms can achieve dynamic regulation of thermal conductivity, making this approach applicable to thermal management devices such as high-efficiency thermal switches and thermal diodes [158]. Increased surface roughness enhances phonon-boundary scattering and reduces phonon drift velocity, thereby lowering thermal conductivity; this property can be utilized to tailor the thermal

performance of heat dissipation materials for electronic devices [157]. By optimizing structural defects such as grain size and orientation, the thermal conductivity of GF can be increased to 3200 W·m⁻¹·K⁻¹, which is 60% higher than that of commercial pyrolytic graphite sheets, significantly enhancing the heat dissipation capacity of electronic products and high-power systems [159]. MLG prepared via hydrogen iodide chemical reduction and graphitization thermal reduction, with structural and defect regulation introduced through HI treatment, exhibits high orientation, abundant defects, and a three-dimensional porous structure. It achieves a conductivity of 1.2 × 10⁵ S·m⁻¹, an electromagnetic interference (EMI) shielding efficiency of 70 dB at a thickness of 35 μm, and a thermal conductivity of 864 W·m⁻¹·K⁻¹. This provides a solution for integrated flexible shielding and thermal management coatings (Fig. 12(e)) [38].

4.3.2 Energy and electronic device applications

In batteries, MLG defects serve as ion storage sites. In sodium-ion batteries, defects in hard carbon store Na⁺ under gradient voltage, forming semimetallic/metallic Na with co-intercalation [160]. In lithium-ion batteries, nanosecond-laser-prepared porous MLG on polyimide offers a large surface area and ion channels, maintaining 580 mAh·g⁻¹ after 300 cycles [36, 161]; edge defects and interlayer disorder increase storage sites, giving 573 mAh·g⁻¹ after 50 cycles, with 10–50 nm interlayer spacing promoting Li⁺ diffusion [162]. In lithium-sulfur batteries, a defect-doped VSe₂-vertical graphene heterostructure uses Se vacancies to generate VS₂, enhancing polysulfide adsorption/conversion, suppressing the shuttle effect, and improving conductivity and kinetics. The principle of the discharge process is shown in the figure. (Fig. 12(f)) [163].

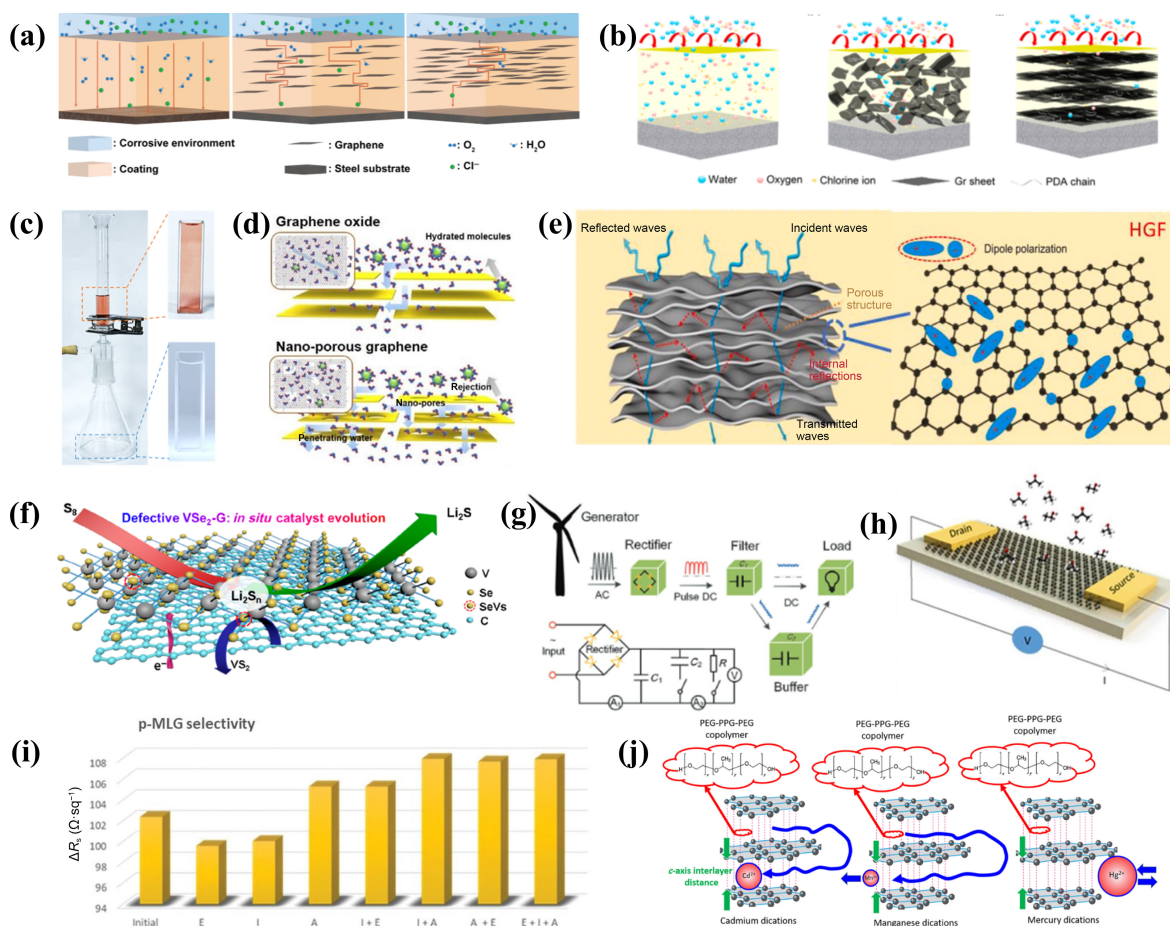


Figure 12 The application of defect engineering in multiple fields. (a) Schematic diagram of anti-corrosion mechanism of coating (left: EP coating, center: CAG0.5%/EP coating, right: CAG1%/EP coating). Reproduced with permission from Ref. [155], © Published by Elsevier B.V. 2023. (b) Schematic diagrams of barrier mechanism for (left: epoxy, center: PDA-G-EP, right: I-PDA-G-EP coating systems. Reproduced with permission from Ref. [156], © American Chemical Society 2022. (c) Photograph of a dead-end filtration device for separating CR dye. Reproduced with permission from Ref. [37], © Zhang, T. M. et al. 2025. (d) Schematic illustration of transport of water molecules through normal GO and nano-porous graphene membrane. Reproduced with permission from Ref. [114], © Kim, D. W. et al. 2016. (e) Proposed EMI shielding mechanism of HGF. Reproduced with permission from Ref. [38], © Elsevier Ltd. 2023. (f) Scheme showing the discharge process at the SeVs-VSe₂-VG/CC/S cathode. Reproduced with permission from Ref. [163], © American Chemical Society 2020. (g) The application of MLG with micro-cracks in supercapacitors. Reproduced with permission from Ref. [165], © Wiley-VCH GmbH 2023. (h) A schematic design of the flat or patterned MLG-based sensors for E/I/A-containing cancer marker detection. (i) MLG with crease defects performs better in detection. Reproduced with permission from Ref. [168], © The Royal Society of Chemistry 2019. (j) Suggested mechanism for capture and sensing of Cd²⁺ ions from water by MLG. Reproduced with permission from Ref. [169], © Elsevier B.V. 2019.

In the field of hydrogen energy, edge defects and interlayer pores in graphene nanosheets provide adsorption sites for hydrogen molecules, achieving a hydrogen storage capacity of 2.47 wt.% under conditions of 99 K and 2 bar. The interlayer network structure formed by defect regulation generates a “nanopump” effect, increasing the compressed storage density of hydrogen molecules [164]. In the field of hydrogen separation, the introduction of vacancies and pores into bilayer graphene via helium ion irradiation and hydrogen plasma results in selectivities of 495 and 877 for H₂/N₂ and H₂/CH₄, respectively, along with a high H₂ permeation flux, making them suitable for hydrogen purification and recovery [130].

In the field of electronic devices, by leveraging the proximity effect of the 2D electronegative material Ca₂N⁺e⁻, high-density electron doping, interlayer decoupling, and torsional defects are achieved in MLG, reducing the graphene-metal contact resistance to 500 Ω·μm. This makes the approach suitable for applications with high requirements for interfacial electrical performance, such as RF transistors and flexible electronics [131]. In the field of

supercapacitors, roll-to-roll imprinting technology was used to introduce microcrack arrays into dense MLG as vertical ion transport channels, increasing the ion diffusion coefficient by a factor of 6 while maintaining high packing density. This enabled supercapacitors to achieve a capacity retention rate of 76% under high loading (Fig. 12(g)) [165]. In the field of optoelectronic detection, low-defect-density MLG integrated with epitaxial silicon to form a heterojunction exhibits high responsivity and detection sensitivity in the near-infrared spectrum [166].

In the field of sensors, by controlling the defect type and density of MLG, the adsorption and recognition capabilities for specific substances can be enhanced. In gas sensors, after introducing controllable defects via oxygen plasma, the sensitivity to NO₂ increased from 11% to 32%; the change in sample resistance due to defects was significant, enabling efficient detection [30]. By adjusting the CVD growth temperature to alter the intrinsic defect density, the response and recovery times of sensors can be optimized to meet the requirements of different scenarios [167]. In the field of biosensing, both MLG with abundant surface defects

and crumpled structures can achieve selective detection by interacting with lung cancer-related biomarkers at defect sites (Figs. 12(h) and 12(i)) [168]. In the detection of heavy metal ions in aqueous solutions, MLG derived from natural graphite utilizes defect sites to specifically bind with cadmium ions. The defect-regulated interlayer spacing matches the hydration radius of Cd^{2+} , enabling selective capture with a minimum detection limit of 5 ppb (Fig. 12(j)) [169].

4.3.3 Research in the field of electronic fundamentals and frontier physics

By tuning the twist angle in bilayer graphene, a flat band (bandwidth of 31 ± 5 meV) near the Fermi level promotes correlated electron phenomena; the bandgap is back-gate-tunable, enabling studies of superconductivity and correlated insulators [170]. In a trilayer graphene/h-BN moiré superlattice, defect-rich superstructures from periodic interlayer modulation allow gate- and electric-field-controlled insulating states, realizing a gate-tunable Mott insulator [171]. Interlayer twist defects induce flat bands and quantum states for exploring superconductivity and topological insulation [113].

For electronic transport, an Al_2O_3 diffusion layer reduces grain boundaries and other defects, giving 50-nm-thick MLG a mobility of $550 \text{ cm}^2\text{V}^{-1}\text{s}^{-1}$ and a conductivity of $2700 \text{ S}\cdot\text{cm}^{-1}$, suitable for transparent electrodes and low-resistance interconnects [172]. Defect control also enhances interlayer charge transport; random stacking avoids semimetallic behaviour while retaining high mobility, yielding both high conductivity and stability [112].

In dielectric/barrier applications, 0.5 wt.%–1 wt.% MLG with few and uniformly distributed lattice defects suppresses negative impacts on dielectric, mechanical, and thermal properties, achieving low dielectric constant, high strength, and thermal stability for 5G base station materials [33]. Interlayer disordered stacking and grain boundaries create interlaced diffusion paths that block Cu ion penetration, making the material effective as a Cu diffusion barrier in integrated circuits [173].

In rhombohedral MLG, bulk electronic states have energy gaps; low-temperature transport is dominated by surface states, enabling the quantum Hall effect and electronic phase separation. A vertical electric field tunes the surface gap, providing a platform for quantum spin Hall phases and strongly correlated states [4]. In rhombohedral graphene moiré superlattices, a vertical electric field drives continuous Chern number transitions ($-1 \rightarrow 1 \rightarrow 2$) in seven-layer graphene. Introducing WSe_2 into ten-layer graphene yields zero-field-quantized anomalous Hall resistance, revealing topological phase transition mechanisms [174].

For quantum magnetism and superconductivity, a moiré superlattice in rhombohedral MLG separates low-energy surface bands from high-energy dispersion bands. Double-gate control of carrier density and displacement field produces tunable layer-polarized ferromagnetism with a hysteretic anomalous Hall effect [175]. Interlayer orientation differences and lattice defects act as key sites for carrier aggregation and superconducting coupling. Gate-voltage-induced carrier density changes can trigger superconducting-like behaviour in otherwise non-superconducting MLG, offering a model system for studying superconducting mechanisms [176].

This section reviews defect engineering in MLG and GF. First, it introduces the controlled creation of desired defects through methods such as ion implantation, plasma treatment, laser

irradiation, and mechanical sliding. Defect repair and removal are achieved via high-temperature annealing and chemical repair, while improved transfer methods help minimize the generation of new defects. Next, the preparation of nearly defect-free single-crystal MLG and GF is discussed, using techniques such as isothermal carbon diffusion on nickel substrates. Finally, applications of defect engineering are presented, including corrosion protection, thermal management, energy storage (lithium/sodium/sulfur batteries and supercapacitors), sensors, electromagnetic shielding, and quantum physics (moiré superlattices, flat bands, ferromagnetism, and superconductivity). The research paradigm has shifted from passive defect tolerance to active design and utilization. However, key challenges remain: the lack of quantitative models correlating defect parameters with material properties, and the need for scalable transfer methods that avoid generating new defects. Future research should prioritize multi-objective optimization (e.g., balancing defect density to achieve both high electrical conductivity and high catalytic activity), scalable manufacturing of defect-engineered MLG/GF, and quantitative assessment of the effects of defect engineering.

5 Conclusions and outlook

The preparation methods for MLG and GF each have their own characteristics. Mechanical exfoliation yields high quality but low scalability. CVD offers both high quality and high scalability, making it suitable for large-scale production of high-quality material with high demand, although its cost is high. The redox method features low cost and high yield, making it suitable for large-scale applications that require low quality. Layer-by-layer stacking enables precise control of the number of layers, which is useful for studying the relationship between layer number and other properties. Flash Joule heating, which has low cost, relatively high quality, and good scalability, is a potential method to replace CVD in the future.

Defects in MLG and GF are generated during preparation and transfer. Defects can be either beneficial or detrimental. For example, point defects (vacancies and heteroatom dopants) can provide active sites and enhance catalytic, energy-storage, and sensing performance, but they also have negative effects, such as reducing tensile strength and electrical conductivity. Therefore, one can choose to maximize benefits and minimize harm according to needs.

Defect engineering can follow a complete strategy chain of “introduction–regulation/repair–application”. Controllable defects can be precisely introduced by methods such as ion implantation, plasma treatment, and laser irradiation. Existing defects can be repaired by annealing at different temperatures, with SLG-assisted repair giving better results. Wet transfer is currently the mainstream transfer method. The application of defect engineering has expanded from single-performance optimization to multi-function integration, demonstrating significant value in corrosion protection, thermal management, energy storage, sensing, electromagnetic shielding, and quantum physics.

Despite significant progress in defect engineering, several key scientific problems and technical bottlenecks must be solved to realize practical applications of MLG/GF in high-performance electronic devices, energy systems, and quantum devices.

To begin with, precise control of the layer number in large-scale single-crystal MLG/GF remains a challenge. At present, the

preparation of single-crystal MLG and GF is mainly limited to thin films of fewer than five layers or very thick films of tens of thousands of layers. There are few studies on the precise preparation of uniform films with five to several hundred layers, mainly due to substrate limitations. Current substrates are mainly single-crystal copper (which easily produces few-layer graphene) and single-crystal nickel (which easily produces thick graphene). Therefore, further research is needed on preparation methods for intermediate layer numbers and on new substrates. Another key issue is the lack of a quantitative relationship between defect type and performance. Most existing studies remain at a qualitative level (e.g., “defects enhance catalytic activity”) and lack quantitative models linking specific defect type, density, and spatial distribution to concrete performance indicators such as electrical conductivity, thermal conductivity, mechanical strength, and catalytic turnover frequency. It is recommended to establish a “defect parameter–performance” database, combined with high-throughput computation and machine learning, to predict optimal defect configurations and provide a quantitative design basis for defect engineering. A further consideration is the feedback from performance to application effectiveness, ultimately establishing a relationship from defect parameters to performance to application outcomes.

Data availability

Not applicable.

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Declaration of competing interest

All the contributing authors report no conflicts of interest in this work.

Author contribution statement

Q. C. H.: Data curation, project administration, validation. C. D.: Data curation, validation, writing manuscript. X. Z.: Project administration. F. W. L.: Project administration. S. L. C.: Project administration. S. H. Y.: Data curation. Q. K. H.: Data curation. X. A. L.: Validation. S. Y. L.: Data curation, validation. All the authors have approved the final manuscript.

Use of AI statement

None.

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