

Chapter 2

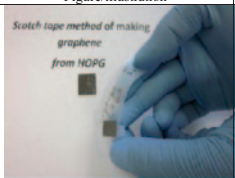

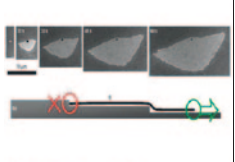
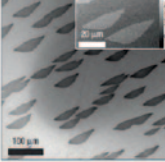
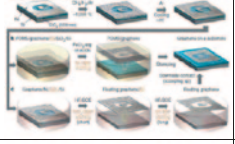

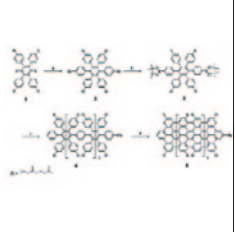
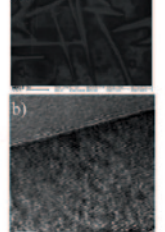
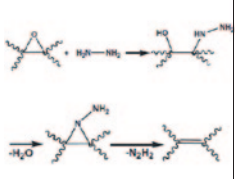
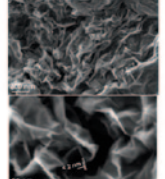
Synthesis, Structure, and Properties of Graphene and Graphene Oxide

2.1 Introduction

To develop large-area graphene-based TCFs, one of the foremost challenges is to produce sufficient amounts of high-quality graphene sheets [1]. The techniques developed for synthesizing graphene can be grouped into six major methods, i.e., mechanical cleavage, epitaxial growth, chemical vapor deposition (CVD), total organic synthesis, and chemical method. The first attempt to produce graphene can go back to 1960, when the electron microscopist, Fernandez-Moran, was looking for a robust, electron-beam transparent, and uniform support membrane [2]. Millimeter-sized graphene sheets as thin as 5 nm (~15 layers of graphene) were produced by micromechanical exfoliation from graphite [2]. Single layers and bilayers of colloidal graphite oxide were observed by electron microscopy by Boehm et al. in 1962 [3]. Chemical intercalation and exfoliation of oxidized graphite were extensively investigated in the next decade [4]. Since the discovery of fullerenes and nanotubes in the early 1990s, great interests were attracted to study all kinds of carbon materials including graphene [4]. Nanoscale origami-like structures of one-graphene thickness were observed by atomic force microscopy (AFM) manipulation of freshly cleaved pyrolytic graphite [5]. Sub-10 nm stacks of graphite were obtained by rubbing micro fabricated graphite pillars on a substrate in 1999 [6], suggesting a possibility to produce single layer using this technique [7]. In 2004, Geim's group successfully extracted monolayer graphene sheets by repeatedly cleaving a graphite crystal with an adhesive tape to its limit [8].

The success in mechanical cleavage led to the synthesis of graphene using other techniques that had reputedly failed in the past [4]. Among others, epitaxial growth [9] and CVD [10] were shown to produce high-quality graphene. New methods have emerged to transfer CVD-grown graphene to other substrates for applications in devices [11, 12]. In order to produce large quantities of graphene for industry applications, developing large-scale and mass production methods became necessary [13]. Among those feasible for large-scale production include the

Table 2.1 Synthesis of graphene [15] (Reprinted with permission from [15]. copyright (2014) by Elsevier.)

Method	Figure/illustration	Images	Advantages	Disadvantages	References
Mechanical cleavage			Less defects	Neither scalable nor capable for mass production	Novoselov et al. ^{8, 16} , Singh et al. ¹⁴
Epitaxial growth			No defects for every single graphene island	Discontinuous	Sutter et al. ¹⁷
CVD			Compatible with the current CMOS technologies	High cost and complex transfer process	Kim et al. ¹⁸
Total organic synthesis			Potentially suitable for mass production	Many defects	Yang et al. ¹⁹
Chemical method			Low cost and suitable for mass production	The majority of defects can be removed	Stankovich et al. ²⁰

total organic synthesis of polyaromatic hydrocarbons (PAH) [14] and the chemical route to produce reduced graphene oxide (rGO) sheets. At present, the chemical method has emerged to be a viable route to afford graphene-based single sheets in considerable quantities [14].

Table 2.1 summarizes the relative advantages and disadvantages of the above synthesis methods in term of the feasibility to scale-up the process for mass production, materials and production costs, and the presence of defects. The detailed fabrication processes of these methods are described in Sect. 2.2.

2.2 Synthesis Methods of Graphene and Graphene Oxide

2.2.1 Mechanical Cleavage

Mechanical cleavage is the method developed to isolate graphene by peeling it off from graphite flakes using a Scotch tape. As shown in Fig. 2.1, the presence of graphene was optically identified by transferring it to a silicon dioxide layer on Si [4, 8]. Since the interlayer van der Waals force in graphite is very weak with interaction energy of ~ 2 eV/nm [2], graphite can be easily exfoliated using an adhesive tape [21]. The graphene and graphite pieces can be transferred onto the cleaned substrate by a gentle press of the tape after checking for smooth and thin fragments on the tape with optical microscopy [8, 16]. The method involves manual searching for single graphene sheets among a myriad of multilayer flakes, and after likely specimens are identified with an optical microscope, conclusive evidence of their thicknesses must be provided by performing AFM or Raman techniques [16]. As such, the yields of this approach are extremely low due to the manual operation.

The choice of substrate is critically important and the apparent contrast of graphene monolayer on a SiO_2/Si substrate (with an oxide thickness of either 300 or 90 nm) was maximized at about 12 % at 550 nm. This observation was explained by considering a Fabry–Perot multilayer cavity in which the optical path added by graphene to the interference of the SiO_2/Si system became maximum for specific oxide thicknesses [22–24]. Thicker graphite flakes deposited on a 300 nm SiO_2 appeared yellow to bluish as the thickness decreased (Fig. 2.1a), while few- or one-layer graphene appeared darker to lighter shades of purple (Fig. 2.1b) [4]. It should be noticed that the tape technique can leave glue residues on the substrate

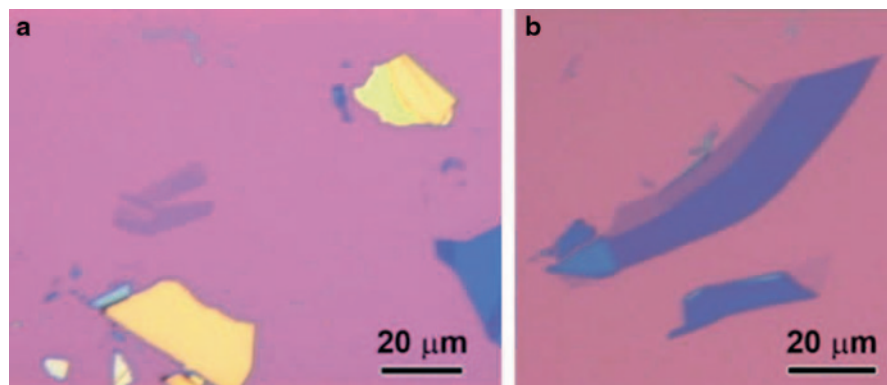


Fig. 2.1 Micromechanically exfoliated graphene: optical images of **a** thin graphite, and **b** few-layer graphene and single-layer graphene (*lighter purple contrast*) on a ~ 300 nm SiO_2 layer. *Yellow color* indicates thicker samples whereas *bluish* and *lighter contrast* indicates thinner samples [4] (Reprinted with permission from [4], copyright (2010) by Elsevier.)

surface, which may limit the carrier mobility [25]. This technique is neither scalable nor capable of mass production, even though the samples of graphene thereby obtained could be useful for fundamental studies to characterize their chemistries and properties.

2.2.2 *Epitaxial Growth*

Epitaxial growth is a substrate-based method, where isolated monolayer of graphene is grown on a single-crystal silicon carbide (SiC) by vacuum graphitization. Since the thermal treatment of silicon carbide at $\sim 1300^\circ\text{C}$ under vacuum results in sublimation of the silicon atoms while the carbon-enriched surface undergoes reorganization and graphitization, graphene islands over the entire surface of SiC wafers were obtained through careful control of the sublimation (Table 2.2) [4, 26–29]. The thickness of graphene layers was controlled mainly by annealing temperature and time, and the uniformity of thickness was improved by vapor-phase annealing [30, 31]. A major advantage is that epitaxial-grown graphene can be patterned using standard lithography methods, a useful property for nanoelectronics. The physical properties of graphene varied significantly between those grown epitaxially and exfoliated mechanically, due mainly to the influence of interfacial effects in epitaxial graphene. Similar approach was applied to other metallic substrates, such as ruthenium (Ru), to produce graphene layers [17, 32]. It is found that the (0001) faces of Ru crystals were able to grow epitaxial graphene layers, where a very sparse graphene nucleated at high temperatures. The first graphene layer coupled strongly to the Ru substrate and the second layer was free of the substrate interaction, which had an electronic structure similar to freestanding graphene. However, several hurdles must be overcome before real applications are found [14]. First of all, it is very hard to control the thickness of graphene in the routine production. Second, unusual rotational graphene stacking were observed in multilayer graphene due to the different epitaxial growth patterns on different SiC polar faces, which had profound effects on the physical and electronic properties of epitaxial graphene [33]. The growth mechanisms need to be further investigated. Third, the relationship between the structure and electronic properties of the interface layer between graphene and the substrate needs to be clearly understood.

2.2.3 *Chemical Vapor Deposition (CVD)*

In CVD methods, graphene is grown directly on a transition metal substrate via saturation of carbon upon exposure to a hydrocarbon gas at a high temperature [12, 45–50]. Ni or Cu films are typically used as the substrate with methane as the precursor gas. When the substrate is cooled, the solubility of carbon on the substrate decreases and the carbon precipitates to form mono- to multilayer graphene sheets

Table 2.2 Epitaxial growth of graphene on SiC substrates [34]

SiC substrates	Fabrication method	Characterization	References
Si-face 6 H-SiC	CVD reactor, Ar atmosphere (1500–1600°C, 90 min)	Thickness between 0.25 and 1 nm having a mobility of 860 cm ² /(V·s) for an electron concentration of 1.13×10^{13} cm ⁻³	VanMil et al. [35]
C-face 6 H-SiC	SiC sample covered with a graphite cap. RF-heated furnace under high vacuum (1700°C, 15 min)	Large, homogeneous, mono-layer or bilayer graphene ribbons (5×600 μm)	Camara et al. [36]
C-face 6 H-SiC	AlN mask on the substrate. RF under high vacuum ($\sim 1.33 \times 10^{-4}$ Pa, 1550°C, 5 min)	A few-layer graphene (FLG)	Camara et al. [37]
6 H-SiC (0001)	Inductively heated furnace, 2000°C at an ambient argon pressure of 1.013×10^5 Pa.	Homogeneous large-area graphene layers	Virojanadara et al. [38]
6 H-SiC (0001)	UHV chamber (1.33×10^{-8} Pa), 1550°C	Bilayer graphene	Unarunotai et al. [39]
C-face 6 H-SiC (0001)	UHV MBE chamber ((1030–1050°C), (10–60 min))	Non-Bernal rotated graphene planes, single-layer or few-layer graphene	Moreau et al. [40]
4 H-SiC(0001)	LEEM instrument, 1300–1500°C	Bilayer and few-layer graphene	Hibino et al. [41]
C-face 4 H-SiC(0001)	Heated for 10 min to temperature $T > 1350^\circ\text{C}$ in vacuum	A mesh-like network of ridges with high curvature that bound atomically flat, tile-like facets of few-layer graphene	Prakash et al. [42]
Si-face 4 H-SiC	UHV (pressure $< 10^{-6}$ Pa) (1200–1600°C, 10–40 min)	Single-layer or few-layer graphene	Jernigan et al. [43]
3 C-SiC(111)/Si(111)	Resistively heated hot wall reactor (1250–1350°C, 10 min)	Continuity on terraces and step edges suggesting the possibility of growing large-scale graphene suitable for industrial applications	Ouerghi et al. [44]

CVD chemical vapor deposition, UHV ultrahigh vacuum

on the substrate. One of the major advantages of the epitaxial and CVD growth techniques is their high compatibility with the current complementary metal–oxide–semiconductor (CMOS) technology. A typical weakness is that controlling the film thickness is difficult and secondary crystals are easily formed [51], although some progress has been made to grow uniform graphene layers using the CVD method [52]. Another important disadvantage is the need of expensive substrate materials for graphene growth, considerably limiting its applications for large-scale production. Nevertheless, the CVD approach has emerged as an important method for mass production of graphene with less structural and electronic disorder or defects, making it an excellent potential for TC applications.

Graphene Grown on Ni

The formation of FLG on transition metal surfaces has been known for nearly a half century [53, 54]. The typical process for CVD of graphene onto Ni film is shown in Fig. 2.2a. In general, the polycrystalline Ni films deposited on SiO₂/Si are first annealed at 900–1000 °C under H₂ and Ar flow to grow a smooth surface. The Ni films are then exposed to a H₂ and CH₄ mixture so that the carbon atoms can dissolve into the Ni film to form a solid solution. Finally, the substrate is cooled down in an Ar atmosphere. As the solubility of carbon atoms decreases as the temperature goes down, the carbon atoms diffuse out from the Ni–C solid solution during cooling and precipitate onto the Ni surface to form graphene films.

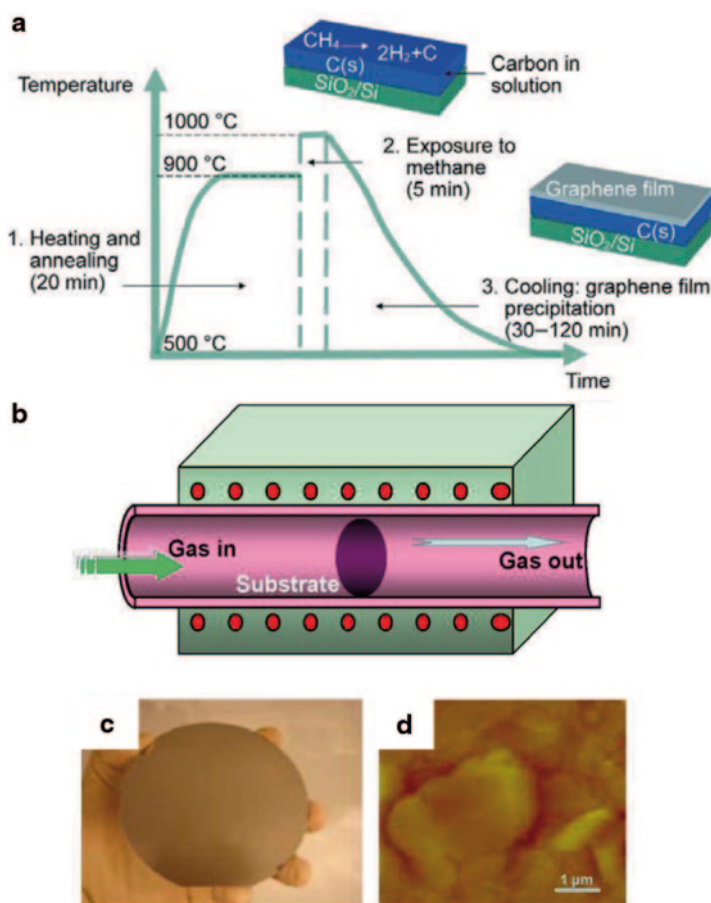


Fig. 2.2 Graphene grown on a Ni substrate. **a** Illustration of graphene growth in three different stages [56]. **b** Schematic of full-wafer scale deposition of graphene layers on polycrystalline Ni by chemical vapor deposition (CVD). **c** E-beam-evaporated Ni film of thickness 100 nm on a 10 cm diameter Si/SiO₂ wafer. **d** Atomic force microscopy (AFM) image of a Ni film after CVD of graphene layers [55] (Reprinted with permission from [56, 58]. copyright (2009, 2013) by Springer and ACS.)

Figure 2.2b shows the wafer-scale graphene synthesis on evaporated Ni films [55]. About 10 cm diameter Si/SiO₂ wafers were used as the substrate to deposit 100-nm-thick Ni films (Fig. 2.2c). It is found that using diluted methane was key to the growth of single-layer graphene (Fig. 2.2d), whereas concentrated methane led to the growth of multilayer graphene.

Graphene Grown on Pd

Graphene islands can also be in situ grown on another metal surface, such as Pd(111), using the CVD method [57]. Figure 2.3a, b shows the scanning tunneling microscope (STM) images of graphene islands grown on a Pd(111) surface using ethylene at 968 K. The size of the graphene islands largely varied between 200 and 2000 Å, which are common, especially near the Pd step edges or spanning across the multiple terraces. The STM image in Fig. 2.3c presents the ordered honeycomb structure in the graphene island formed by the precipitation of carbon atoms. A periodicity of ~20 Å was observed from the surface height profile (Fig. 2.3d), which was measured along the white line in Fig. 2.3c. Due to the superposition of the

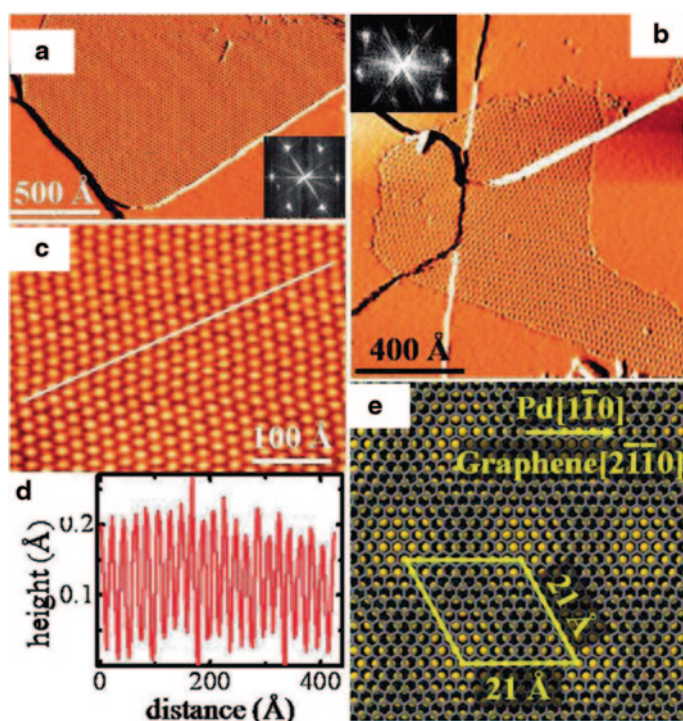


Fig. 2.3 a–c Scanning tunneling microscope (STM) images of graphene on Pd(111) acquired in situ during growth. **d** Surface height profile along the *white line* shown in (c); and (e) atomic model showing the orientation of graphene [57] (Reprinted with permission from [57]. Copyright (2009) by ACS)

honeycomb lattice of graphene and the hexagonal lattice of Pd (111), these superstructures are of Moiré patterns [57]. Figure 2.3e shows the atomic model of such a commensurate Moiré superstructure and the determined epitaxial relationship between the monolayer graphene and Pd(111). The method of growing graphene islands on a Pd surface opened up a new avenue of preparing metal-semiconducting graphene structures and metal-doped graphene-based devices.

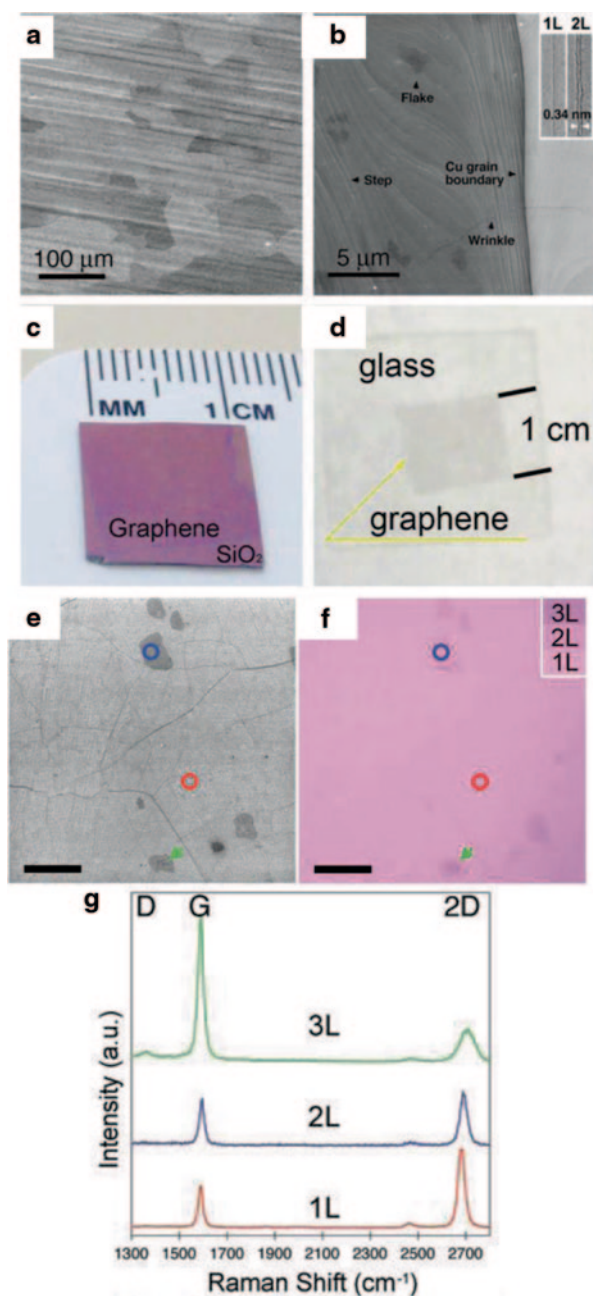
Graphene Grown on Cu

Due to the grain boundaries of Ni or Pd surface, the grown graphene films usually contain both monolayer and few-layer graphene [58]. Because carbon has extremely low solubility in Cu, Cu has become a potentially outstanding substrate for the growth of monolayer graphene [54]. Ruoff's group at the University of Texas at Austin first reported the growth of high-quality monolayer graphene on polycrystalline Cu foils, which attracted great attention due to the advantages of good control of graphene layers, low cost, and ability to transfer [10]. The Cu foil was annealed at 1000 °C in a hydrogen atmosphere. A mixture of H_2/CH_4 was then introduced into the system to initiate graphene growth on the Cu foil. The system was cooled down to room temperature after a continuous graphene layer was formed [10]. The SEM image in Fig. 2.4a clearly shows Cu grains with color contrast. The high-resolution SEM in Fig. 2.4b indicates that these Cu surface steps were formed during thermal annealing. The darker flakes indicate multilayer graphene, while the wrinkles originated from the different thermal expansion coefficients between graphene and Cu. The wrinkles went across the Cu grain boundaries, confirming that the graphene film was continuous. The inset of Fig. 2.4b shows TEM images of single and bilayer graphene. The grown graphene films can be transferred to another substrate using various transfer methods. Figure 2.4c, d shows the transferred graphene film on a SiO_2/Si or glass substrate. It is seen that the graphene film on the glass substrate was optically uniform. The quality and uniformity were evaluated by Raman spectroscopy and Fig. 2.4e–g shows the SEM and optical images with the corresponding Raman spectra. The Raman spectra (Fig. 2.4g) indicated by a red circle has a G-to-2D intensity ratio (I_G/I_{2D}) of ~ 0.5 and a symmetric 2D band centered at $\sim 2680\text{ cm}^{-1}$ with a full width at half maximum (FWHM) of $\sim 33\text{ cm}^{-1}$, confirming the monolayer graphene [10]. The blue circle and green arrow represent bilayer- and trilayer-graphene sheets, respectively.

2.2.4 Total Organic Synthesis

The graphene-like polyacrylic hydrocarbons (PAHs) are another alternative route to produce graphene. PAHs are known to have an intermediate structure between the molecular and micromolecular phases; they are highly versatile and can be substituted with a range of aliphatic chains to modify the solubility. Yang et al. [19]

Fig. 2.4 CVD-grown graphene on Cu foil [10]. **a** SEM image of graphene grown for 30 min. **b** High-resolution SEM image showing a *Cu grain boundary* and *steps*, one- and two-layer graphene, and graphene *wrinkles* (Inset shows TEM images of folded graphene edges). **c, d** Graphene films transferred onto a SiO_2/Si substrate (**c**) and a *glass plate* (**d**), respectively. **e** SEM image of graphene transferred onto SiO_2/Si showing *wrinkles*, as well as one-, two- and three-layer regions. **f** Optical microscope image of the same regions as in (**e**). **g** Raman spectra for the marked spots with corresponding colored circles in (**e**) and (**f**) showing the presence of one, two, and three layers of graphene [10]. *CVD* chemical vapor deposition, *SEM* scanning electron microscope, *TEM* transmission electron microscope



reported the synthesis of nanoribbon-like PAHs up to 12 nm in length. Although the electrical properties of these graphene nanoribbons (GNRs) are unknown, they may indeed exhibit graphene-like properties (Table 2.1). If their size can be further extended, PAHs may offer a new route for graphene synthesis. However, it may be very difficult to totally eliminate the defects present along the boundaries between the molecules.

Another bottom-up method was reported to fabricate GNRs on gold surfaces using 10,10'-dibromo-9,9'-bianthryl precursor monomers [59]. The monomers were thermally deposited onto a gold surface to remove the halogen substituents from the precursors and provide the molecular building blocks for the targeted graphene ribbons, as shown in Fig. 2.5a. The biradical species diffused across the surface and underwent radical addition reactions to form linear polymer chains during the first thermal activation step. Then, a surface-assisted cyclodehydrogenation created an extended fully aromatic system during the second thermal activation step (Fig. 2.5b–e) [59].

2.2.5 Chemical Methods

The most common source of graphite used for oxidation is flake graphite, which can be produced by removing heteroatomic contaminations from naturally occurring graphite [60]. Due to the spaces between graphene layers in graphite, the intercalating agents are able to reside between the graphene layers under chemical reactions, forming graphite intercalation compound (GIC) [61]. The experiments to investigate the insertion of additional chemical species between the basal planes have been performed extensively since the successful formation of the first intercalation compound using potassium [51]. GICs have layered compounds with different stages, which are defined as the number of graphitic layers in between adjacent planes of intercalant [51]. Figure 2.6a–d shows the structures of second- to fifth-stage bromide GICs, which correspond to approximate compositions of $C_{16}Br_2$, $C_{24}Br_2$, $C_{32}Br_2$, and $C_{40}Br_2$ [62].

The interlayer spacing of GIC can increase from 0.34 nm to more than 1 nm depending on the intercalant, leading to a significant reduction in the van der Waals forces between adjacent sheets [61]. The weak van der Waals forces make GICs much easier to be further exfoliated, offering a possible route to fabricate single layer graphene or graphene oxide (GO). The interlayer spacing in GICs can be expanded by thermal shock ($\sim 1000^\circ\text{C}$) to produce expanded graphite (EG). As shown in Fig. 2.6e, the halogen intercalants, such as iodine chloride (ICl) (to form Stage-2 ionic GIC) and iodine bromide (IBr) (to form Stage-3 ionic GIC), can be introduced into the host material of highly ordered pyrolytic graphite (HOPG) and sequentially to form layered structures [63]. Upon high-temperature annealing, the volume of the obtained Stage-2 and Stage-3 GICs (Fig. 2.6f, g) increases rapidly due to the volatilization of the IBr or ICl intercalants between the graphene layers [63].

Graphite oxide was first prepared almost 150 years ago by Brodie, who treated graphite repeatedly with potassium chlorate and nitric acid [64]. The oxidizing agent

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