

# Graphene transfer methods: A review

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## ABSTRACT

Graphene is a material with unique properties that can be exploited in electronics, catalysis, energy, and bio-related fields. Although, for maximal utilization of this material, high-quality graphene is required at both the growth process and after transfer of the graphene film to the application-compatible substrate. Chemical vapor deposition (CVD) is an important method for growing high-quality graphene on non-technological substrates (as, metal substrates, e.g., copper foil). Thus, there are also considerable efforts toward the efficient and non-damaging transfer of quality of graphene on to technologically relevant materials and systems. In this review article, a range of graphene current transfer techniques are reviewed from the standpoint of their impact on contamination control and structural integrity preservation of the as-produced graphene. In addition, their scalability, cost- and time-effectiveness are discussed. We summarize with a perspective on the transfer challenges, alternative options and future developments toward graphene technology.

## KEYWORDS

high-quality transfer, application-compatible substrate, graphene technology

## 1 Introduction

Graphene is a unique material with distinctive characteristics, which has shown great potential for a wide range of applications in electrical, catalytic, energy, and bio-related fields [1–3]. However, to effectively take advantage of the special properties of graphene and enable its use for practical applications and subsequent commercialization, the availability of high-quality pristine graphene is an ongoing priority [4, 5]. High-quality graphene implies single crystalline material without contamination, wrinkle, cracks, or other defects. There have been considerable advancements in graphene synthesis methods. In particular, chemical vapor deposition (CVD) can produce graphene films with high structural integrity on transition-metal substrates (Cu is commonly used), although such substrates are not suitable for most applications [6–8]. However, many technologies involving graphene require application-specific substrates, such as semiconductors and metal oxides; therefore, a subsequent process is often required to transfer the CVD graphene to the desired technological substrate [9, 10]. Accordingly, immense care and good process control is imperative to preserve the attributes of the as-deposited high-quality graphene.

After graphene transfer, cracks, wrinkles, residue, and

contamination are commonly observed, which degrade the quality of the graphene available for the application [11, 12]. The sources of the residue and contamination are the sacrificial substrate (e.g., Cu foil); etchant used to dissolve the sacrificial substrate (e.g., ammonium persulfate (APS)); and the support layer (usually organic polymers such as polymethyl methacrylate (PMMA)) that also favors wrinkle formations and produces the most undesirable type of residue owing to the compatible interaction of the polymers with graphene [13–16]. These impurities have a detrimental effect on graphene, mainly related to undesired doping that degrades the electrical and catalytic properties of graphene by creating charge-scattering centers and charge gradients [17, 18]. Graphene sheets are usually one atom thick; thus, cracking easily occurs as a result of mechanical strain applied during cleaning and repeated transfer, and damage from sharp tools. Such damage degrades the electrical properties and mechanical stability of the graphene, resulting in subsequent operational inefficiency or even failure [19–21]. In addition, analysis of impure and damaged graphene makes it challenging to develop correct structure–property relationships [22–24].

There has been significant development in research aiming at achieving application-quality transfer of defect-free graphene, and various strategies have been proposed to ensure effective

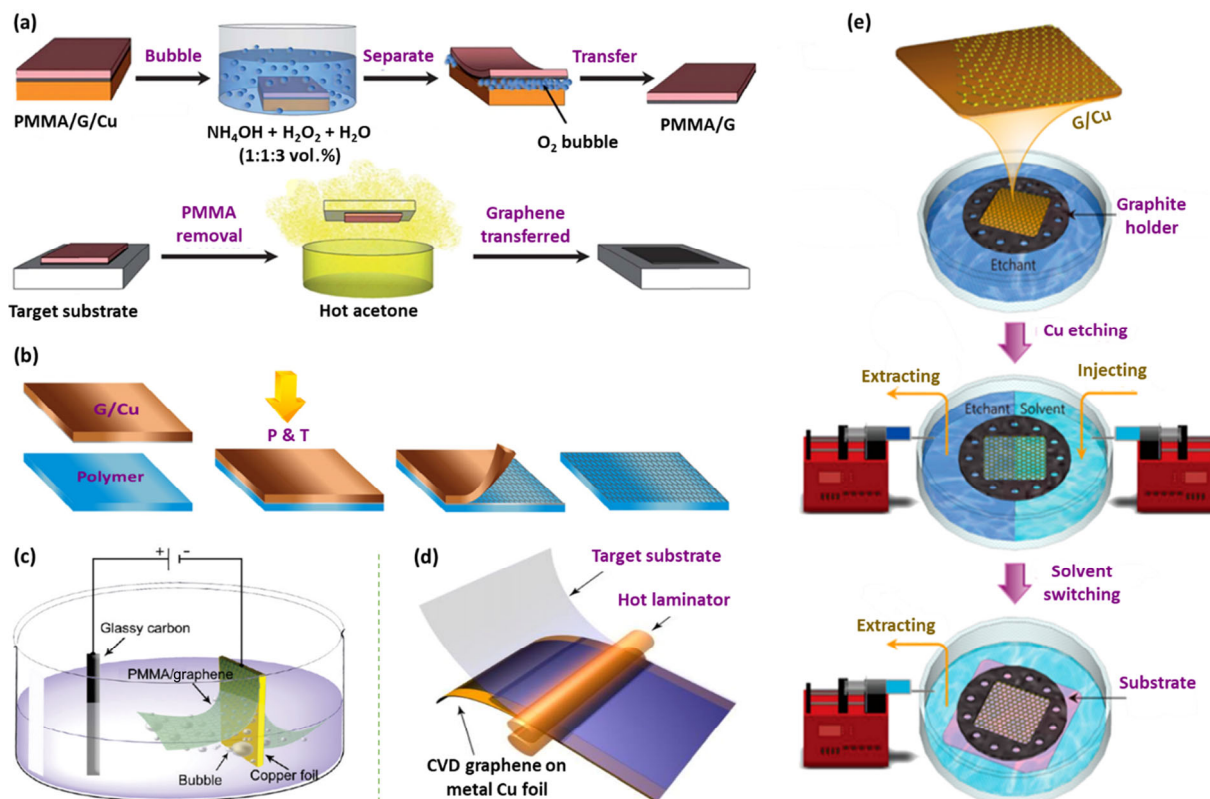
graphene transfer and preservation of the unique properties of graphene by maintaining its structural integrity [25–27]. The transfer methods can also successfully flatten graphene wrinkles generated during synthesis as a result of the differences in the thermal expansion coefficients between the metal substrate and graphene, e.g., by paraffin-supported transfer. Moreover, the cost, processing time, scalability, and environmental impact are also considered when evaluating a graphene transfer technique [7, 9, 28]. Some of the common methods, including the PMMA-supported wet route, dry transfer, and bubble-assisted delamination, are presented in Figs. 1(a)–1(e). Each method has its own advantages and disadvantages, as listed in Table 1.

In this review article, we discuss the different approaches that have been proposed to address the various challenges

encountered during transfer that limit the practical application of graphene. Finally, we highlight the future perspectives and alternative routes which could be followed to establish the efficient and scalable transfer routes which are industrially relevant to graphene technology.

## 2 Transfer methods

The conventional method of graphene growth with CVD uses metal substrates that are not technologically appropriate, making a subsequent transfer process necessary [9, 29]. To prepare the graphene for transfer, the growth substrate is removed either by dissolution in a liquid etchant, bubble delamination, or thermal peel off. To prevent damage of the graphene during



**Figure 1** Schematic diagrams of typical transfer routes. (a) Non-electrochemical reaction-based bubble-mediated transfer. Adapted with permission from Ref. [57], © The Royal Society of Chemistry 2014. (b) Dry transfer route. Adapted with permission from Ref. [66], © Elsevier Ltd. 2014. (c) Electrochemical delamination. Adapted with permission from Ref. [31], © American Chemical Society 2011. (d) Scalable roller-assisted delamination transfer method. Adapted with permission from Ref. [32], © The Royal Society of Chemistry 2015. (e) Support-free transfer route. Adapted with permission from Ref. [78], © American Chemical Society 2014.

**Table 1** The advantages and disadvantages of different transfer approaches

Transfer approach	Advantages	Disadvantages	Refs.
Wet transfer	Non-destructive, successful up to laboratory scale	High chance of contamination, time consuming, expensive	[16, 17, 34, 36–39, 42–45, 47, 48]
Electrochemical bubble transfer	Growth substrate repeatability, scalable, minimal use of etching/cleaning chemicals, fast and efficient removal of contaminants, growth substrate self-polishing	Limited to conducting substrates, complicated voltage optimization	[31, 49, 52–54, 56]
Non-electrochemical bubble transfer	Can be applied to both metallic and non-metallic substrates	Relatively slow	[57, 58]
Dry transfer	High-quality, scalable, growth substrate repeatability, short processing time	Appearance of cracks due to interaction with hard surfaces	[19, 59, 60, 62, 64–66]
Roll-to-roll transfer	Application compatible, low cost, short processing time	Limited to flexible substrates, appearance of cracks	[6, 69, 72, 73]
Support-free transfer	No organic residue, low cost, short processing time	Growth substrate/etchant residues, high risk of damage	[75, 77–80]

the transfer process, support/protective layers (often organic polymers such as camphor) are used to minimize wrinkles, cracks, and other mechanical damage, which are finally removed after transfer [18, 27]. During the transfer process; cleaning steps, removal of the growth substrate and protective layer, the pristine graphene structure can be damaged by the introduction of cracks, undesired doping, and wrinkles [30–32]. To address these concerns, different transfer techniques have been developed and evaluated, as reviewed in this section.

## 2.1 Wet transfer

In wet transfer methods, ionic etchants (e.g., ammonium persulfate aqueous solution, Table 2 lists some of the typical etchants with the reported concentrations) are used to dissolve the growth substrate, and then the graphene is transferred from the liquid cleaning solvent (often water) to the target substrate without drying. Various support layers are used to achieve clean and residue-free transfer of graphene. An interesting new transfer route was recently proposed using Cytop, which is an amorphous fluororesin that has been attracting attention from researchers due to its potential application as an optical thin film [33]. In this case, Cytop was used as the support layer and more excitingly, it lead to the simultaneous p-type doping of the graphene layer by introduction of fluorine. This technique is simple, and also demonstrates that simultaneous chemical doping can be achieved during transfer, highlighting the possibility for the introduction of various chemical dopants, e.g., nitrogen, boron, or metal doping [34]. A similar method was proposed, where the transfer layer is used to tune the graphene properties [35]. For example, PMMA residues can result in p-type doping, which is restored by treatment with formamide. These studies indicate that transfer-layer impurities are not always detrimental, and can be used to obtain graphene with special behavior, while achieving high-quality transfer.

Both small- and large-molecular polymers have been used as support layers to achieve residue-free graphene transfer and avoid doping effects. A study of the role of different support layers showed that low-molecular-weight polymers-based support material are preferable than high-molecular weight polymer support layers for clean and contamination-free transfer; e.g., poly(bisphenol A carbonate) is superior to PMMA [36]. Similarly, another group proposed the use of naphthalene as a small-molecular support layer [37], where naphthalene showed

remarkable performance, such as facile sublimation and clean removal without affecting the electronic properties of graphene, which are often degraded by residue from organic support layers. In addition, camphor was used as a lifting laminate due to its sublimation behavior; it can be removed in air with mild heating and enabled the transfer of graphene to a hollow substrate over a large area [38].

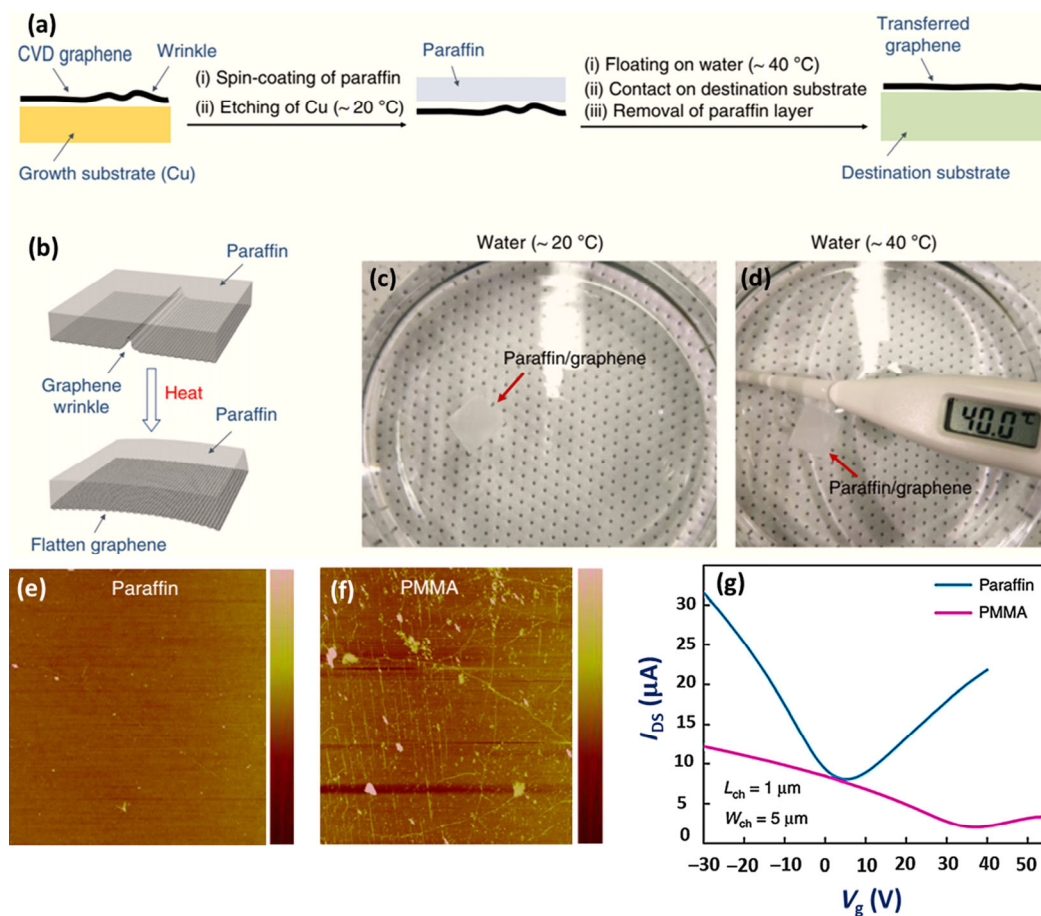
The graphene quality can be preserved by using a transfer film that does not need to be removed, i.e., a functional substrate [39]. In this method, a polymer blend of ethylene propylene diene monomer (EPDM) and polyaniline (PAni) was used as a lifting layer with mechanical adaptability, transparency, and conductivity. The graphene and conducting polymer were used to prepare an electrode for a photovoltaic device that showed similar performance to indium-tin oxide (ITO)/glass-based electrodes. In contrast to conventional methods that leave significant amounts of PMMA residue on the graphene, this new transfer procedure simplifies the process as support-layer removal and cleaning steps are avoided. This process has great potential as an economic transfer route that can preserve the desired properties of the graphene. Another similar method demonstrated that, the transferred graphene had enhanced electrical performance compared to graphene transferred using the polymer removal approach, which resulted in cracks in the graphene layer [21].

Considering the challenge of permanent residues from the polymer support remaining on the graphene Park et al. [40] proposed a novel idea of using a metallic growth substrate (e.g., copper film in this case) that also acts as a support layer. The transferred graphene had fewer lees and defects compared to other counterparts and avoids the costs and time related to the use of an additional polymer support layer and the solvent required to dissolve it. Similarly, an Au (gold) thin film was used as the transfer layer to avoid the polymer contamination. In comparison to PMMA-enabled transfer, the graphene transferred using the Au-assisted process was clean, uniform, and had better electrical performance. Therefore, the Au transfer method for CVD graphene is a promising alternative for various applications of high-quality graphene, which could be extended to more cost-effective metals [41].

Zhang et al. introduced a novel wet method of biphasic organic/aqueous (hexane/APS) interface treatment for high-quality graphene transfer [42]. The major advantage of this procedure is polymer-free transfer to avoid contamination. In addition, this approach is very successful for transferring graphene to a more complex substrate. Such as, an atomic force microscope (AFM) tip or transmission electron microscope (TEM) grid, which further strengthens the analysis potential of these techniques. This method also allowed the fabrication of a suspended graphene layer that is useful for studying its properties and developing accurate structure–property relationships. There are a number of novel ways used to achieve clean transfer, such as a dual cleaning method, where acetic acid is used as a strong solvent to dissolve PMMA, followed by annealing to remove traces of PMMA and flatten wrinkles without reducing the graphene quality [43]. An interesting transfer method was proposed, which simultaneously achieves residue-free lifting and flattens wrinkles formed during graphene growth (see Fig. 2(a)) [17]. They used paraffin as the support layer as it has suitable thermal properties and low chemical/covalent interaction with graphene. Paraffin thermally expands during low-temperature treatment (paraffin expand ca. 40 °C, provided when floated on top of water for cleaning while at 20 °C it cannot be expanded) on top of graphene (Figs. 2(b)–2(d)), which stretches out the graphene and flattens the wrinkles compared to PMMA-assisted lift-off, as observed using AFM imaging (Figs. 2(e)

**Table 2** List of the typical growth substrate etchants and the corresponding reported concentrations

Growth substrate	Growth substrate etchants	Concentration	Refs.
Copper foil	Ammonium persulfate ((NH <sub>4</sub> ) <sub>2</sub> S <sub>2</sub> O <sub>8</sub> ) solution	0.02 M	[43]
Copper foil	Ammonium persulfate solution	0.05 M	[34]
Copper foil	Ammonium persulfate solution	0.08 M	[98]
Copper foil	Ammonium persulfate solution	0.1 M	[42]
Copper foil	Ammonium persulfate solution	1 M	[45]
Nickel foil	Ferric chloride (FeCl <sub>3</sub> ) solution	0.1 g·mL <sup>-1</sup>	[16]
Copper foil	Ferric chloride solution	1 mol·L <sup>-1</sup>	[39]
Copper foil	Ferric chloride solution	2 mol·L <sup>-1</sup>	[21]
Copper foil	H <sub>2</sub> O <sub>2</sub> :HCl	1 M:2 M	[37]
Copper foil	HCl:H <sub>2</sub> O:CuSO <sub>4</sub> ·5H <sub>2</sub> O	50 mL:50 mL:10 g	[46]



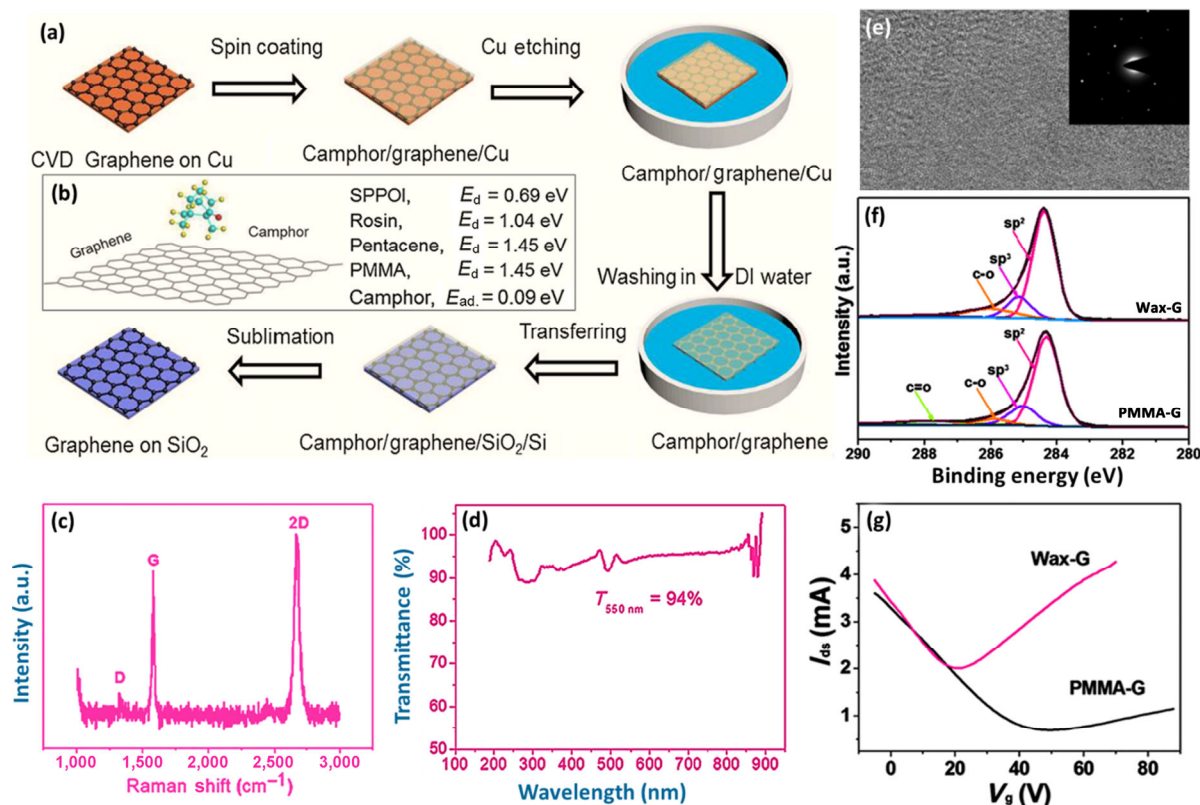
**Figure 2** (a) Schematic of paraffin-supported graphene transfer. (b) Schematic showing the flattening of graphene wrinkles by the thermal expansion of paraffin. (c) and (d) Photographs of the paraffin-supported graphene film in water at ~20 and ~40 °C respectively. At ~40 °C, flattening of the wrinkles in the graphene layer occurs because of the thermal expansion of paraffin from heat provided by the underlying water. (e) and (f) AFM images of graphene transferred using either paraffin and PMMA, respectively, demonstrating that the paraffin support layer resulted in the reduction of wrinkles. (g) Comparison of the transfer characteristics of two field-effect transistors fabricated with PMMA- and paraffin-transferred graphene. The Dirac voltage of the device fabricated on paraffin-transferred graphene is much smaller and closer to zero, attributed to less residue/doping compared to the PMMA-supported route. Adapted from Ref. [17], © Leong, W. S. et al. 2019.

and 2(f)). The weak interaction between paraffin and graphene results in poor adhesion, allowing the paraffin to be easily dissolved using an organic cleaning solvent (hexane), which minimizes the organic residue on the graphene. This was evidenced by the electrical properties, which demonstrated weak doping/hole carrier mobility as the Dirac point of the graphene was closer to zero than that of the sample prepared using PMMA-associated transfer (Fig. 2(g)). Similarly, paraffin-facilitated transfer was demonstrated where the paraffin was removed thermally (instead of being dissolved by hexane), which maintained the excellent structural integrity of the graphene and allowed large-area transfer without forming defects [30].

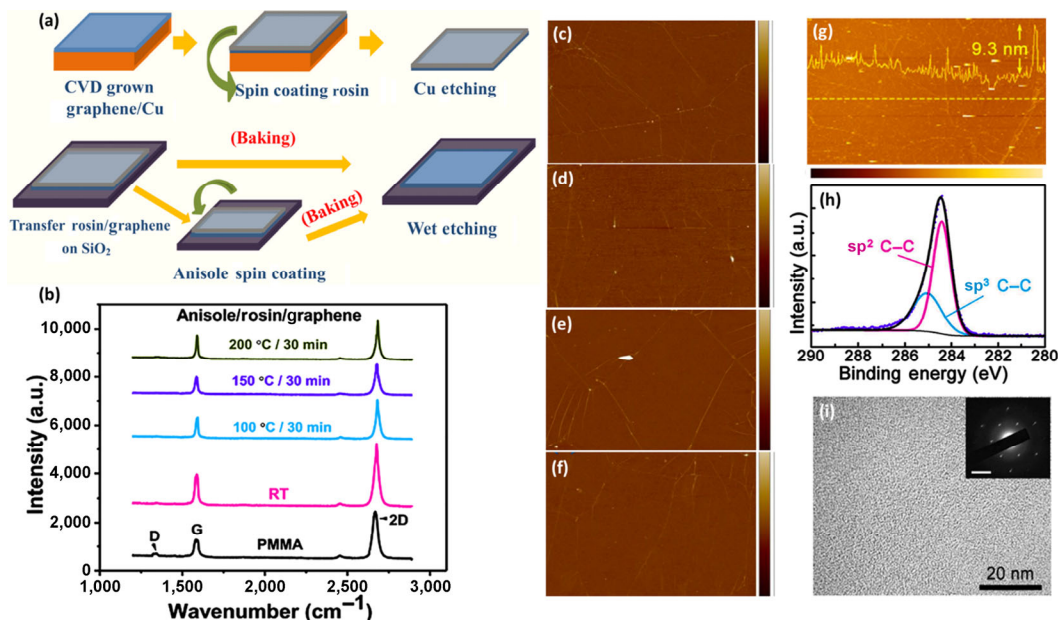
Unlike other polymer-mediated graphene wet transfer methods, in which the polymeric transfer agent has to be eventually removed via extensive washing in harmful organic solvents (e.g., acetone), or high temperature annealing; residues in camphor-mediated transfer will sublime under low temperature in a dry atmosphere, or can be effectively removed by mild rinsing in common safe alcohol-based solvents (Fig. 3(a)). This is offered by the low interaction energy (adsorption energy,  $E_{ad}$ ) between camphor and graphene, unlike other standard support materials (Fig. 3(b)). Effective transfer is evidenced by the small D peak in the Raman spectrum (the D peak is related to the presence of defects in the graphene structure) and high transmittance (Figs. 3(c) and 3(d), respectively) [44]. PMMA generally disrupts the  $sp^2$  nature of graphitic carbon (facilitating  $sp^3$  hybridization), which results in strong PMMA-

graphene interactions. This results in stable residues and doping of the as-transferred graphene. Therefore, wax-assisted transfer is preferable as it does not bond well with the graphene and favors clean and crack-free transfer (Figs. 3(e)–3(g)) [45]. Impurities from the growth substrate and their etchants are also responsible for unintentional doping. However, a solution to this was proposed, where an extra cleaning step was introduced after Cu etching [14]. Etching of the sample with ammonia aqueous solution significantly eliminated both Cu and etchant leftovers. The effectiveness of the washing was evaluated by studying the electrical properties, where ammonia-treated graphene had a Dirac voltage close to zero, in contrast to graphene produced using the conventional cleaning route.

Optimal anisole/rosin-assisted transfer established the fabrication of a clean and smooth graphene surface with improved quality than PMMA-carried transfer (Figs. 4(a)–4(f)) [46]. In contrast, Zhang et al. presented an alternative route that does not require a regular polymer support [47], and instead took the services of joint three protective measures; a use of liquid protection layer (LPL) e.g. n-heptane, use of an anti-wrinkle agents (blend of cellulose and polyester that expands and flattens wrinkles), and lastly the application of glass frame to curve the etchant/LPL surface. After copper etching the graphene layer is stamped onto target substrate from the top side, unlike conventional routes where the bottom side is deposited onto a destination substrate. This method successfully transferred clean, wrinkle-free graphene onto a desired surface (Figs. 4(g)–4(i)).



**Figure 3** (a) Schematic of camphor-supported graphene transfer. (b) Camphor has a low adsorption energy compared to other molecules, indicating minimal interaction with graphene and easy subsequent removal after transfer. (c) Raman spectrum with small D peak and (d) FTIR spectrum with high transmittance of single-layer graphene, demonstrating the effective transfer of high-quality graphene. Adapted with permission from Ref. [44], © Elsevier Inc. 2019. (e) TEM micrograph of wax-assisted transferred sample free of contamination. (f) XPS spectra and (g) current–voltage curves demonstrating graphene transfer without residue/doping, indicated by a Dirac point closer to zero than the PMMA equivalent. Adapted with permission from Ref. [45], © Elsevier B.V. 2019.



**Figure 4** (a) Schematic of the anisole/rosin-supported transfer route. (b) Raman spectra of the graphene transferred at anisole/rosin (baked at different temperatures; room temperature (RT), 100 °C, 150 °C, and 200 °C, respectively) and PMMA mediated routes. (c)–(f) AFM micrographs showing the smooth surfaces of the graphene produced using anisole/rosin-supported transfer at the corresponding temperatures window. Adapted with permission from Ref. [46], © Shahzad, K. et al. 2020. (g) AFM image, (h) XPS spectrum, and (i) TEM image indicating the clean transfer of graphene with minimal PMMA residues. Adapted with permission from Ref. [47], © Elsevier Ltd. 2020.

The role of the growth substrate in achieving clean and high-quality transfer is rarely reported. One study showed that the topographical features of the Cu substrate strongly affect the flatness and smoothness of the transferred graphene [48];

this suggests that the features of the Cu substrate should be considered in addition to improving the transfer strategy to achieve transferred graphene layers with excellent integrity, and minimal unintentional doping and cracking.

Wet transfer routes are still the most common and conventional transfer methods, which are successfully used at laboratory scale. However, these methods have many limitations, which have motivated scientists to explore alternative routes that can achieve large-area, contamination-free transfer of graphene. Such research includes optimization of the growth substrate, etchant, support layer, and support layer dissolving solvents, which all contribute to high transfer cost. In addition, it is important to minimize the number of cleaning steps to reduce residue deposition and damage to the graphene layer (such as folds, cracks, tears, and wrinkles).

## 2.2 Bubble-mediated transfer

### 2.2.1 Electrochemical-reaction-based transfer

In this approach,  $O_2$  and  $H_2$  bubbles are produced via electrochemical reactions in which the graphene on the Cu growth substrate acts as one of the electrodes (either cathode or anode). The bubbles apply a peeling force and eventually delaminate the graphene from the growth substrate (Fig. 1(c)). This method can only be used with conducting substrates that are appropriate for use as electrodes. Clean removal of the graphene from the growth substrate can be achieved, allowing the substrate to be recycled, unlike the conventional wet transfer methods that chemically etch the metal substrate [49]. This method is economical as it minimizes the use of etchants or cleaning agents, and is scalable. Taking advantage of these distinctive benefits, Wang et al. developed the electrochemical route for high-quality graphene transfer (Fig. 1(c)) [31]. The Cu foil growth substrate is self-polished during delamination and can be reused without further treatment. Morphological surface features of the Cu substrate, such as ripples, are imprinted on the transferred graphene, which highlights the opportunity for patterning of graphene and other materials. Electrochemical transfer procedures eliminate Fe deposits that are challenging to remove, and are faster than conventional methods [50]. Another, remarkable, non-destructive bubble-mediated route was developed by Gao et al. which enabled the repeated use (up to 100 times) of the growth substrate (in this work platinum served as the growth substrate). Interestingly, the graphene quality is preserved despite repetitive usage of the substrate. The as-produced graphene had minimal wrinkles and a high carrier mobility after transfer [51]. One study used PMMA/graphene/Cu as both the cathode and anode to simultaneously delaminate two graphene sheets using bubble delamination, which resulted in high-quality transfer [52]. This method is considered scalable with catalyst repeatability, and provides fast and economical transfer by using both electrodes to scale up lift-off. Another study was able to reduce the use of organic solvents and recycle the growth substrate for continual use, while demonstrating the use of a solid electrolyte (agarose gel) which additionally acted as the support layer for the graphene sheet and was completely removed in hot water treatment after graphene transfer [53]. All of these advantages are beneficial for industrial-scale transfer of graphene.

Multi-functional transfer methods are becoming more common because of their various advantages. One study developed a transfer method in which a protective interlayer (poly(9,9-di-n-octylfluorene-alt-(1,4-phenylene)-((4-sec-butylphenyl)imino)-1,4-phenylene), short form is TFB) between PMMA and graphene resulted in p-type doping of the graphene [54]. In this two-in-one method, the TFP interlayer minimizes PMMA residue on the graphene, which showed improved performance when used in organic light emitting diodes. In addition, a dual-layer transfer method was developed where the PMMA was coated with polystyrene (PS), which strengthened the

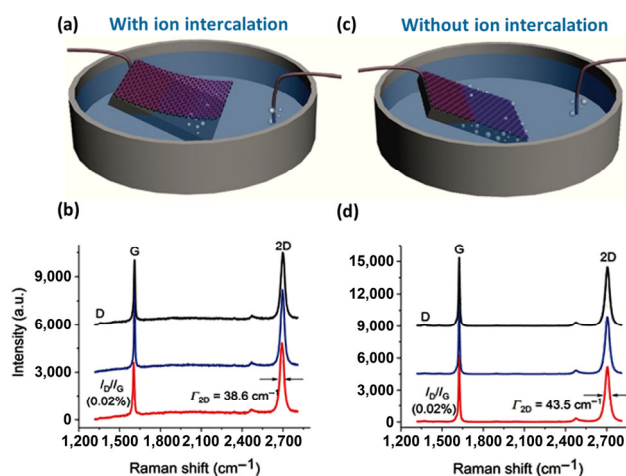
support layer and assisted graphene transfer onto the target substrate [55]. Moreover, in contrary to regular transfer methods, wrinkles, holes, and residues are eliminated, confirmed by the low-intensity D peak in the Raman spectra, which indicates the excellent crystalline quality of the graphene and success of this technique. In another study, an electrochemical stamping method was developed for producing high-quality graphene suitable for flexible and wearable applications [20]. Clean and crack-free graphene was successfully transferred to different target polymer substrates, whereas, growth substrate is recovered for multiple reuse.

In contradiction, Verguts et al. argued that in the case of electrochemical bubble-mediated delamination, the  $H_2$  and  $O_2$  bubbles are not the foremost reason for the separation of graphene from the Cu substrate, and proposed that ion intercalation is responsible for the rapid delamination (in this case, graphene is grown on platinum substrate) [56]. This study demonstrates that alkali-based electrolytes which cause contaminations (for instance,  $Na^+$  and  $K^+$ ), can be avoided with alternative electrolytes (such as, ammonium hydroxide and tetraethylammonium hydroxide) which can immediately intercalate and rapidly assist delamination (Figs. 5(a)–5(d)).

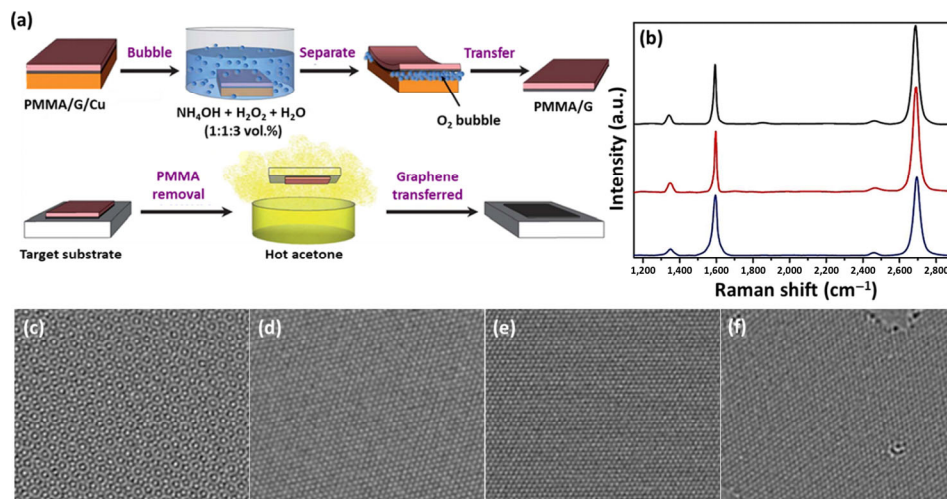
In short, electrochemical method is fast, effective and offers multiple reuses of growth substrate.

### 2.2.2 Non-electrochemical bubble-assisted transfer

Generally, electrochemical bubble-assisted transfer is complex and aggressive. Moreover, optimization of the operating potentials is required, which is challenging. Nonetheless, electrochemical bubble-based transfer is suitable only for conducting substrates which makes this method less ideal for graphene transfer. Therefore, a gentle and facile bubble-assisted transfer method is highly desirable. Gorantla et al. [57] proposed the idea that bubbles can be produced even by normal chemical reactions which enable synthetic graphene delamination from the substrate (even for non-electrically conductive substrates). They used the following simple wet chemical reaction:  $NH_4OH + H_2O_2 + H_2O$  (1:1:3 vol.%), which forms  $O_2$  bubbles that help delaminate the PMMA/graphene from the Cu foil (Fig. 6(a)). The transferred graphene sheets were clean, with minimal defects, as verified by the results shown in Figs. 6(b)–6(f). These findings indicate that such approaches could be successfully



**Figure 5** (a) and (b) Illustrations and the corresponding Raman spectra of electrochemical transfer with intercalation of ions to provide the peeling force. (c) and (d) Illustrations and the corresponding Raman spectra of electrochemical transfer without intercalation of ions. Ion intercalation greatly increased the quality of the transferred graphene compared to electrochemical bubble-assisted delamination. Adapted with permission from Ref. [56], © The Royal Society of Chemistry 2018.



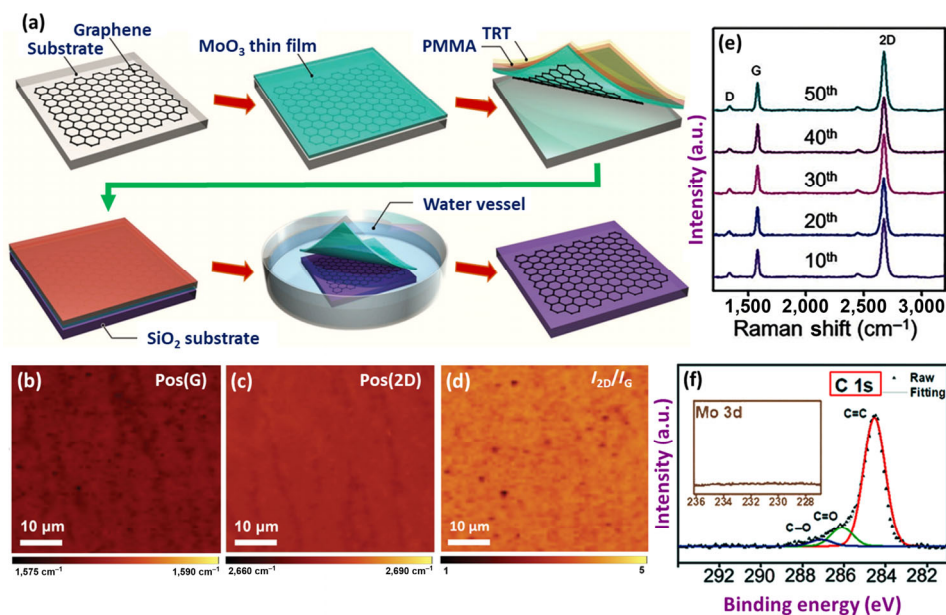
**Figure 6** (a) Schematic diagram of chemically generated bubble-assisted transfer, which is a universal transfer route that can be applied to any substrate, unlike electrochemical routes that require conducting substrates. (b) Corresponding Raman spectra of high-quality transferred graphene from different growth substrates (Cu foil, MoNi, and  $\text{Al}_2\text{O}_3$  from bottom to top respectively) to a Si/SiO<sub>2</sub> wafer. (c)–(f) TEM micrographs of the corresponding transferred graphene with super clean and residue-free surface, demonstrating the successful transfer from a range of substrates (Cu foil, MoNi,  $\text{Al}_2\text{O}_3$ , and SiC, respectively, to TEM grids). Adapted with permission from Ref. [57], © The Royal Society of Chemistry 2014.

scaled up for commercial production of graphene. Interestingly, unlike the regular electrochemically generated bubble approach this method can be used for both conducting and non-conducting substrate which demonstrates the universality of this method. Similarly, Gao and his coworker proposed the idea of bubble formation by a normal chemical reaction without requiring an electrochemical reaction. Interestingly, this work proposed that bubbles not only operate as delamination force between the graphene and underlying substrate but also create the holding force between graphene and under substrate that stops graphene detachment from the substrate (silicon wafer in this case) [58].

### 2.3 Dry transfer

In transfer techniques which extensively use ionic liquids and

repeated transfer steps, there is a high chance of contamination and defects, where these multiple cleaning steps make it challenging to achieve application-grade graphene. Moreover, it is common that the growth substrate is not reusable in such procedures, which increases the net cost. Therefore, dry transfer techniques have been developed as alternative, economical, and feasible routes to transfer clean, high-quality graphene to device-compatible surfaces, where delamination methods are used to allow reuse of the growth substrate [16]. A dry transfer method was developed using an inorganic metal oxide lifting layer ( $\text{MoO}_3$ ) with a low binding energy, which is completely washed away by water treatment (Fig. 7(a)) [59]. This approach leads to high-quality graphene transfer, as demonstrated by the Raman maps shown in Figs. 7(b)–7(d). Furthermore, Raman spectra demonstrate that multiple reuse



**Figure 7** (a) Schematic diagram describing the use of  $\text{MoO}_3$  as a protective layer for graphene transfer. (b)–(d) Raman maps corresponding to the G, 2D peaks, and  $I_{2D}/I_G$  ratio, respectively, indicating clean, homogenous, and high-quality transferred graphene. (e) Raman spectra of graphene films grown repeatedly on the same recycled Cu foil substrate, indicating good reproducibility of the structural integrity and preservation of topographic features up to the 50<sup>th</sup> reuse. (f) XPS spectrum indicating that the transferred graphene surface was not contaminated; the inset shows that no significant Mo signal was measured, which confirms the effective removal of the Mo post transfer. Adapted with permission from Ref. [59], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2019.

(up to 50 times) of the growth substrate produced graphene with high quality (Fig. 7(e)). X-ray photoelectron spectroscopy (XPS) study confirmed the clean transfer without metal remnants (Fig. 7(f)). Hence, laminar metal oxides can be used for improved transfer of flat graphene layers and facilitate application of graphene.

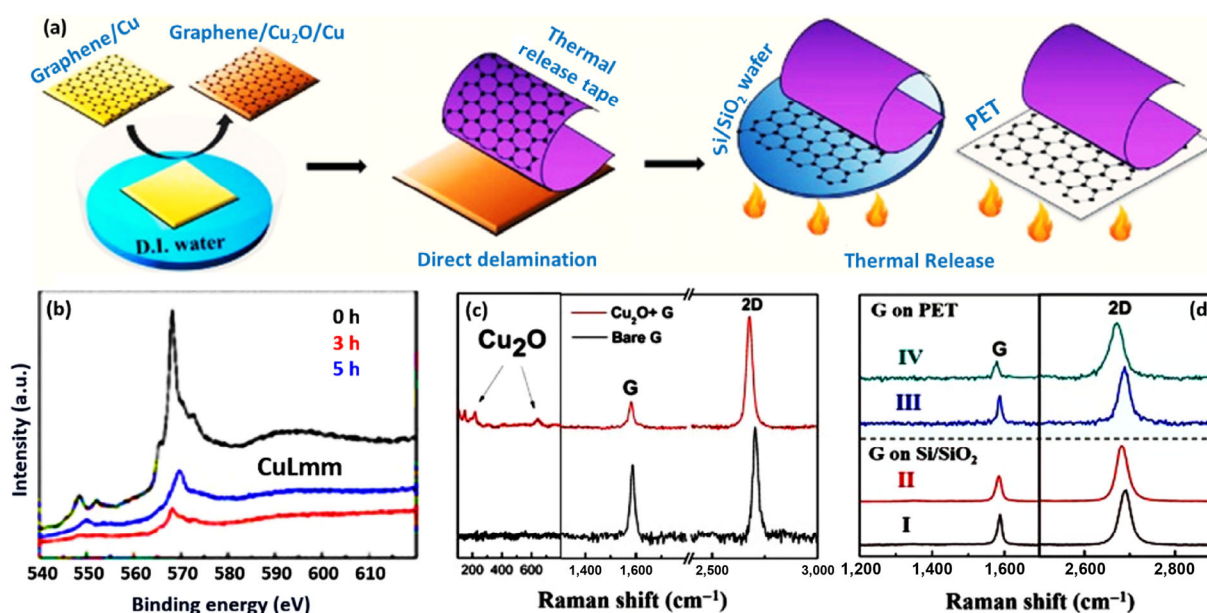
Similarly, following the aim of recycling the growth substrate, a simple, inexpensive, large-area, and scalable dry transfer method was proposed using a standard office laminator to bind the graphene to a polyvinyl alcohol carrier substrate [60]. The Cu substrate can be used multiple times with no significant degradation in graphene quality. Continuous sheets of graphene were transferred, where tears, holes, and polymer leftover are occasionally observed. In addition, the effect of doping on the electrical behavior was studied, which clearly showed that the charge neutrality point for all devices was close to the zero Dirac point, corresponding to low residual doping levels. One route based on hot pressing and lamination was demonstrated with an additional step of introducing intermediate layers (3-aminopropyltrimethoxysilane (APTMS) and polyimide (PI)) between the transferred graphene and target substrate that played an imperative role in avoiding the effects of residues [61]. In particular, this method is fast, simple, and enables substrate recycling. This transfer approach can be used for simultaneous graphene transfer, along with scale-up and large-area transfer. Sometimes chambered or perforated substrates (substrates with mini slits or trenches) are used in application-grade devices, which complicate graphene transfer. To address this, an innovative method was developed that enables graphene transfer to the chamber substrate without trapping liquid [62]. This was achieved using a polydimethylsiloxane (PDMS) block to transfer the PMMA/graphene to the target substrate and retain the graphene properties. This procedure enables the development of devices based on graphene and perforated surfaces interface.

As some target substrates are liquid sensitive, transfer methods that help protect the substrate from damage by cleaning fluids are required. One such method combines an initial wet process with a following dry transfer process to ensure high-quality continuous transfer of graphene and avoids contact between any

liquid and the final substrate [63]. Delamination of graphene from the Cu foil using thermal release tape (TRT) is possible when the binding forces between the layers are weak, which is achieved by a facile and economical water-assisted method [64]. In this method, graphene/Cu is soaked in water for 5 h at 90–95 °C to form a uniform  $\text{Cu}_2\text{O}$  layer; water molecules enter via the graphene grain boundaries and form an oxide layer over the Cu foil, without damaging the graphene. The growth of the oxide layer provides a delamination force between the Cu and graphene, which is finally removed by TRT (Fig. 8(a)). The presence of the  $\text{Cu}_2\text{O}$  layer was confirmed by both XPS and Raman analyses (Figs. 8(b) and 8(c)), while the lack of the D peak in the Raman spectra indicates that this process did not damage the structural integrity of the graphene (Figs. 8(c) and 8(d)), which is a major advantage of this transfer method.

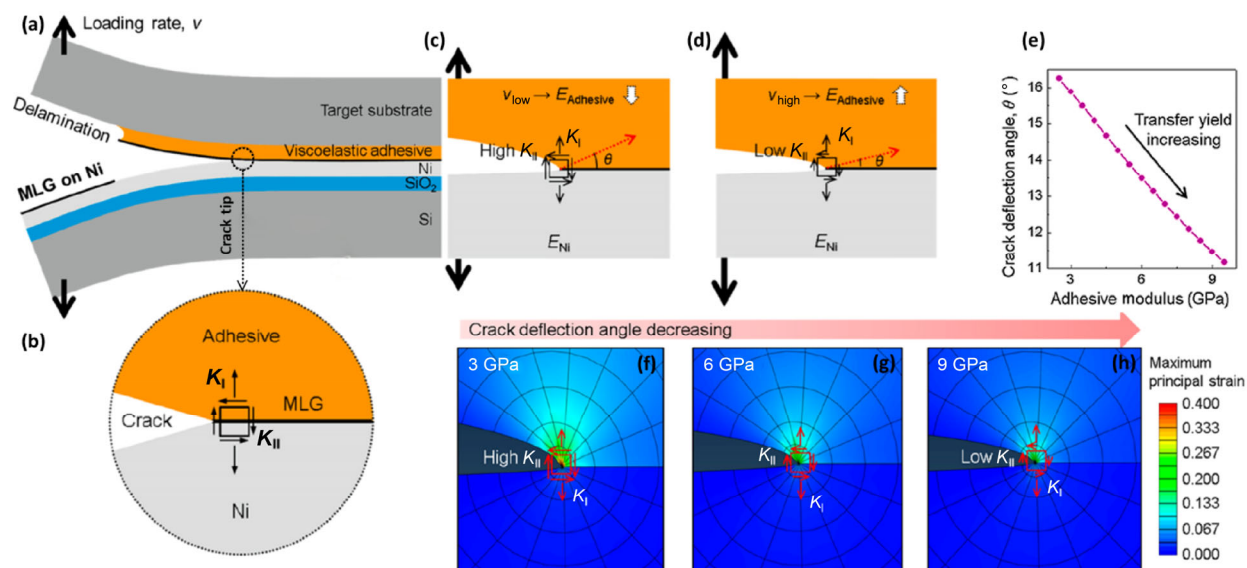
Another dry route uses a bilayer support with polybutadiene (PBU) at the bottom and PMMA at the top, which successfully transferred graphene to liquid-sensitive substrates with minimal performance loss of the graphene [65]. Another mechanical dry transfer route was proposed, in which a polymer is hot pressed onto the graphene surface, which is delaminated after cooling (Fig. (1b)) [66]. This method is simple and contains few washing steps. Both theoretical and experimental analyses demonstrated that successful hot-pressing transfer can be achieved by applying the optimal pressure and temperature, including graphene proper interaction with supporting polymer layer is critical. In the case of dry transfer methods, the peeling mechanism is rarely reported, although it is highly significant for improving graphene transfer. One study addressed this knowledge gap and proposed a delamination mechanism for graphene transfer from the growth substrate [19]. In contrast to previous study that investigated transferred graphene properties with respect to the loading rate, this group focused on crack deflection angle during peeling off (Figs. 9(a)–9(d)), and showed the significance of crack deflection angle on transfer yield. They reported that small crack deflection angle is helpful for greater transfer yield (Fig. 9(e)–9(h)).

An interesting method using *in-situ* photo-polymerization of the support layer was reported, where a support layer composed of two different resins, is spin coated onto the



**Figure 8** (a) Illustration of  $\text{Cu}_2\text{O}$  facilitated graphene-substrate delamination. (b) XPS spectra of CuLmm, exhibiting the presence and development of  $\text{Cu}_2\text{O}$  layer which behave as the peeling force. (c) Raman spectra of transferred graphene to different substrates successfully. (d) Raman spectra of graphene and  $\text{Cu}_2\text{O}$  mediated graphene, even confirming the presence of  $\text{Cu}_2\text{O}$  signature peak which became the ultimate force to drive the peeling. Adapted with permission from Ref. [64], © Elsevier B.V. 2019.





**Figure 9** (a) Schematic of the peeling and delamination of graphene from the growth substrate. (b) Magnified view of the crack tip that propagates during the mechanical delamination. (c) and (d) Definitions of the high and low deflection angle at the delamination point. (e) Crack deflection angle as a function of adhesive modulus. (f)–(h) Maps showing the reduction in the crack deflection angle with increasing adhesive modulus. Adapted with permission from Ref. [19], © American Chemical Society 2019.

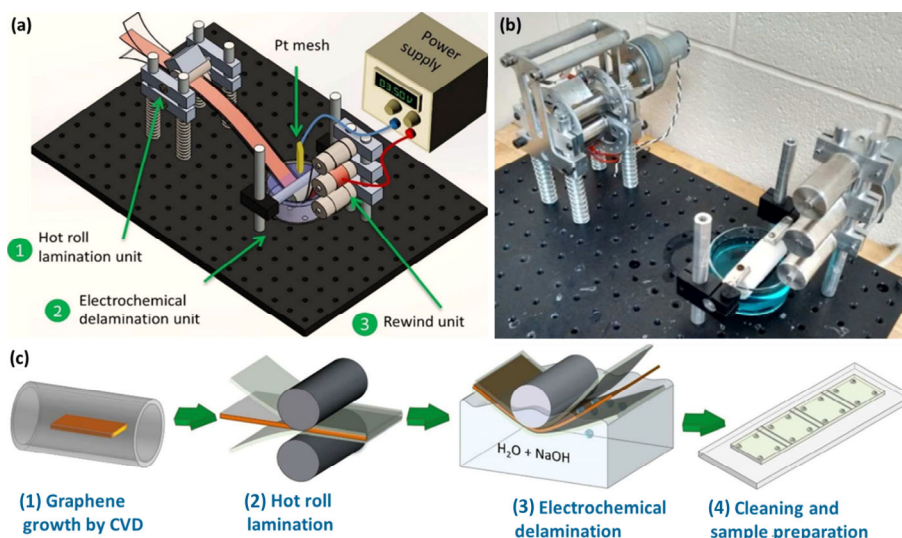
graphene layer and simultaneously exposed to light to achieve polymerization [67]. The quality of the transferred graphene was dependent on the viscosity of the resins, where higher viscosities resulted in fewer graphene defects. This study is inspired by photo-mendable polymers that are used to form self-healing substrates that facilitate successful transfer. This method has great potential for upscaling graphene transfer from the laboratory scale to a device-compatible grade, implying clean, large-area graphene transfer with reduced cleaning steps. However, a standard method has not yet been developed and cracks still tend to develop in the graphene during delamination. Therefore, further insight into the delamination mechanism and control of various significant parameters could aid in the development of a standard and universal transfer route to facilitate commercialization of graphene.

## 2.4 Roll-to-roll transfer

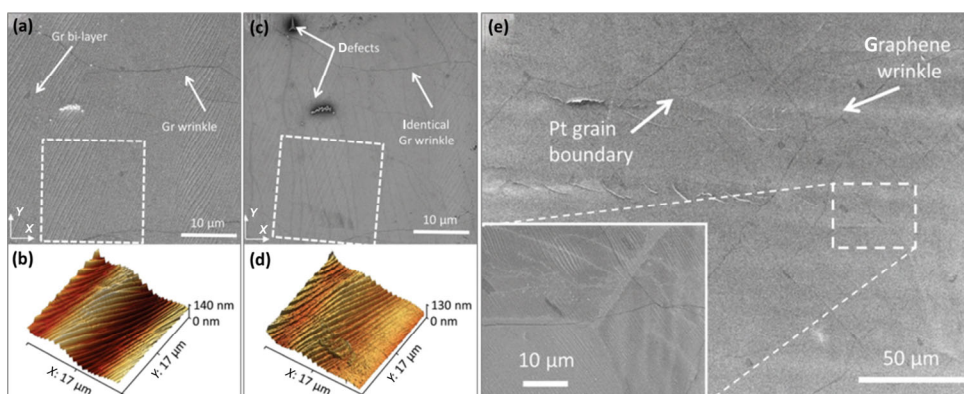
To meet the market demand for large-scale graphene and enable the various applications of graphene, high-quality industrial-scale transfer is of prime importance. To achieve this, the roll-to-roll (R2R) graphene transfer was developed. Moreover, this method was extended to the transfer of other two-dimensional (2D) materials, including R2R stacking of heterostructures [6, 68]. Recently, such an R2R transfer process was developed, which is benign, polymer-residue free, and enables recycling of the growth substrate to minimize the cost [69]. Another important factor that added to the scalability of this method is the use of hot deionized water permeation between the graphene and substrate as the major driving force for delamination. The three most important R2R process parameters are the transfer rate, temperature, and roller pressure. Low transfer rates, gentle heating, and high pressure facilitate high-quality transfer in the case of lamination-assisted R2R transfer. Interestingly, this group used their R2R transfer method to coat antique paintings with graphene to protect them from moisture and light that results in fading and discoloration over time [70]. The role of other parameters, such as the linear film speed, guiding roller diameter at the delamination point, and separation angle was investigated [71]. It is observed that the film speed and roller diameter have a significant effect on the transferred graphene coverage, and it is concluded that, a high speed and

large roller diameter are favorable for effective transfer; 98% graphene coverage was achieved by optimizing the parameters (3 m/min speed and 51 mm roller diameter in this case). However, the influence of the separation angle was insignificant. Hence, industrial-scale fabrication of graphene is expected to be possible with careful optimization of the processing parameters and setup.

To fulfill the vision of cost-effective, scalable, continuous growth, and subsequent transfer of graphene, an electrochemical R2R transfer method was developed (Figs. 10(a)–10(c)) [72]. The effect of pressure, heating rate, and lamination/delamination speed on the R2R transfer method was extensively studied, resulting in high-quality transfer under optimal conditions (Figs. 11(a)–11(d)). More significantly, using this approach, the transfer of other 2D materials (e.g., hexagonal boron nitride (hBN)) and continuous stacking of heterolayers were also accomplished with controlled restacking (graphene over hBN sheets), as shown in Fig. 11(e). This indicates that R2R methods are not limited to graphene transfer, but also appropriate for successful transfer of heterostructures, which is an important step toward the revolution of economical and scaled-up 2D material technology. Similar to conventional methods, continuous transfer also suffers from challenges such as mechanical damage to the graphene that negatively affects its electrical properties. The main cause of the mechanical damage to transferred graphene (and ultimate failure of the transfer mechanism) is the roughness of the graphene on the carrier substrate and the presence of unwanted particles. Such limitations are being overcome by using a force-control system on the roller that successfully reduces the damage [73]. Interestingly, Ma et al. proposed a simultaneous roll-to-roll transfer and doping approach. They used an UV-epoxy (on top of polyethylene terephthalate (PET) support layer) as an adhesive layer which offers robust lifting strength and also the potential for p-type doping by generating super p-dopant (HSbF<sub>6</sub>) through ultraviolet light treatment. Consequently, the hole concentration could be boosted up to ten times, with a drop in sheet resistance of up to 95%. This dual feature enabled the continuous production of flexible graphene transparent conductive films with overall performances superior to those produced by common transfer methods and typical dopants [74].



**Figure 10** (a) Schematic of the R2R transfer setup consisting of a hot roll lamination unit, electrochemical delamination unit, and rewind unit. (b) Photograph of the experimental transfer setup. (c) Schematics of the transfer process, starting with: (1) graphene growth on a metal film, (2) hot roll lamination of the graphene/metal between polymer substrates, (3) electrochemical delamination of the graphene/polymer support from the metal surface, and (4) cleaning the polymer substrates and gluing them on glass slides for further characterization. Adapted from Ref. [72], © Hempel, M. et al. 2018.



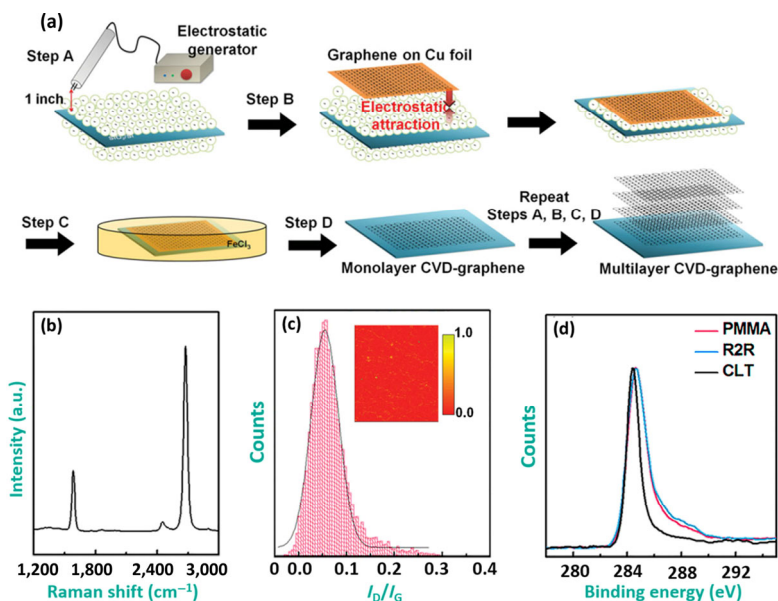
**Figure 11** (a) SEM of a Cu surface after graphene growth. (b) AFM image of the white outlined area in (a). (c) SEM image of the graphene transferred to PET coated with ethylene-vinyl acetate (EVA) surface after lamination with a Cu film and electrochemical delamination. (d) AFM image of the white outlined area in (c). Both the SEM and AFM images after transfer indicate a reduction in wrinkles. (e) SEM image of co-transferred stacked graphene/hBN heteromaterials to EVA/PET flexible surface. Adapted from Ref. [72], © Hempel, M. et al. 2018.

## 2.5 Support-free transfer

Although support-aided graphene transfer is the traditional method of transferring high-quality clean graphene to a target substrate. Unfortunately, impurities from the support are still very common and cannot be eliminated completely without compromising the properties of the graphene. Thus, alternative routes are being developed that avoid the use of the support layer and subsequently reduce the cost related to the support layer, the solvent required to dissolve it, and the additional cleaning steps and equipment [75]. In one support-free transfer route, an electrostatic charge accumulated on the target substrate is used to lift the Cu/graphene, followed by wet etching of the Cu (Fig. 12(a)). The approach is scalable and showed high-quality graphene transfer with fewer defects (Figs. 12(b) and 12(c)). Compared with PMMA-supported and R2R approaches, static-charge-mediated transfer showed higher quality, residue-free graphene, as evidenced by the narrower XPS peak (Fig. 12(d)) [76].

Another group achieved support-free transfer mediated by three concurrent processes (mechanical, electrical, and thermal), where the target substrate (as one electrode) is hot pressed to the as-grown graphene (as the other electrode) to transfer the graphene to the target substrate. This method is clean, fast,

inexpensive, and has a low environmental impact, while the graphene has excellent conformal contact with the target substrate and is free of remnants, making it suitable for various applications [77]. Support-free processes that do not require additional steps to remove polymer residues are becoming increasingly popular. In one method, a system of switching is used in which the etchant is constantly replaced with fresh one to cleanly remove the copper growth substrate and protect the graphene from damage before it is transferred to the destination substrate (Fig. 1(e)) [78]. The clean and residue-free graphene presented better optical and conducting properties than that transferred by common methods. Two other groups used similar transfer procedures based on hot pressing the graphene directly on the intended substrate, followed by etching of the Cu foil [75, 79]. Both groups observed satisfactory results and achieved low-contamination graphene transfer, demonstrating the potential for upscaling. Notably, one such study showed that graphene is under mechanical strain when deposited onto copper substrate, and the strain disappears when the graphene is in contact with the cleaning liquid [80]. This study further proposes that an interesting phenomenon can be observed between graphene and other liquids, which may favor transfer and cleaning mechanism, and facilitate new exciting applications.

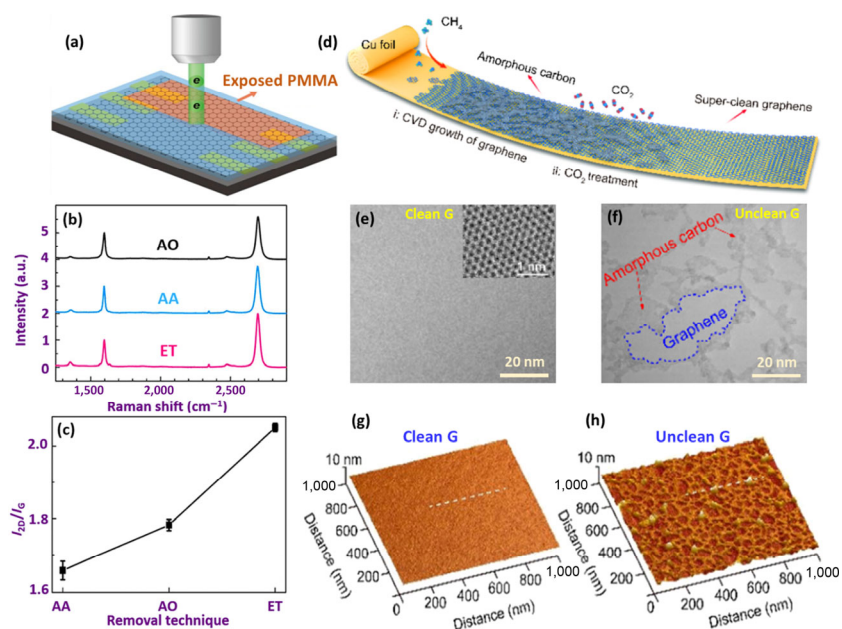


**Figure 12** (a) Schematic illustration of clean-lifting transfer (CLT) process of as-grown graphene on Cu foil onto a substrate. (b) Raman spectrum of the monolayer graphene transferred using the CLT technique. (c) The distribution of  $I_D/I_G$  ratios of the monolayer graphene over an area of  $100\text{ cm} \times 100\text{ cm}$ , where the inset shows the corresponding  $I_D/I_G$  ratio map of the graphene film. (d) XPS spectra of monolayer graphene transferred by the CLT, PMMA-supported, and R2R-transfer techniques. Adapted with permission from Ref. [76], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2013.

### 3 Cleaning methods

Technological-grade graphene must be uniform and free from residues (either from the growth or transfer process). Apart from conventional cleaning methods, there are also additional cleaning processes that can increase the graphene purity. As PMMA-supported transfer is the most common, and also the most problematic with respect to impurities that damage the graphene properties, cleaning methods to follow this transfer process are being developed. One theoretical study proposed that PMMA coated on graphene comprises of two layers, an

inner layer mixed with graphene and a thick outer layer composed of pure PMMA [81]. After cleaning, the outer layer turn thinner and smoother, while the inner layer insignificantly affected. This effect demonstrates that, PMMA is hard to removed completely, and the residual polymer affects the graphene performance. Despite, PMMA can be eliminated by breaking their molecular backbone bond. In addition to it, reducing the PMMA carboxyl bond, leads to a decrease in the p-type behavior [28]. It was also shown that PMMA can be eliminated by annealing but this caused structural defects and subsequently changes in the electronic properties of graphene. Removal of



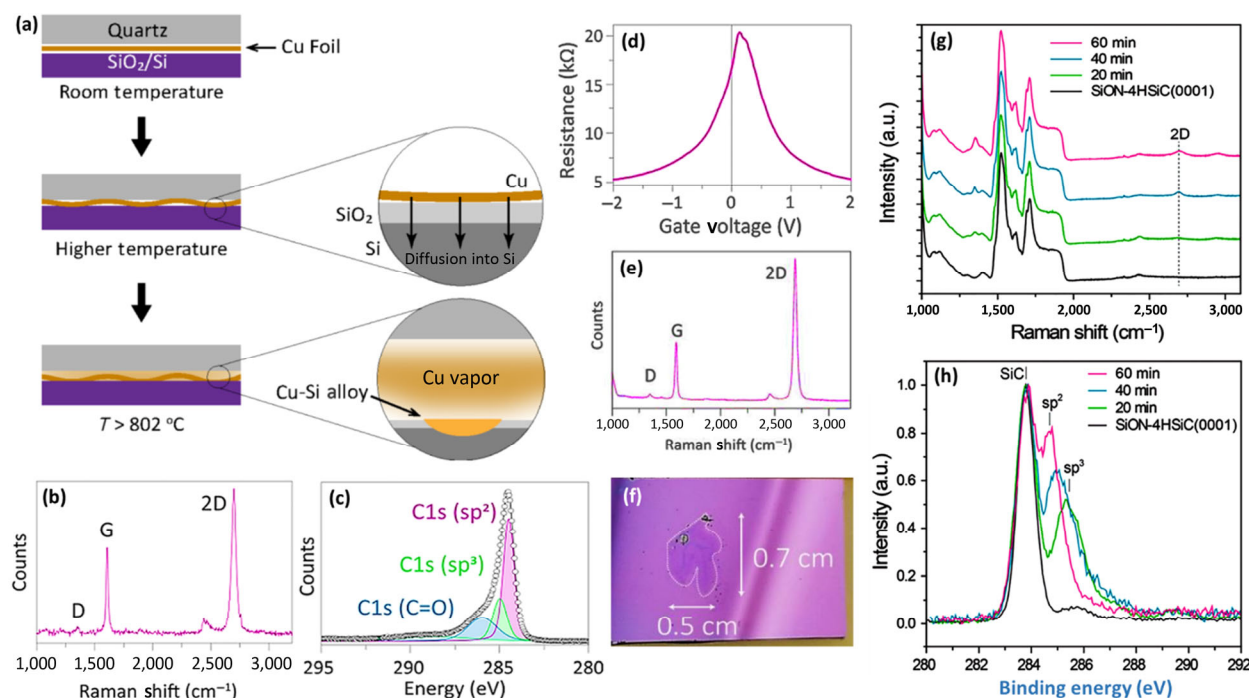
**Figure 13** (a) Schematic illustration of the e-beam cleaning method to remove PMMA residue. (b) Raman spectrum of e-beam-cleaned graphene compared to that cleaned using other approaches. (c) Comparison of the Raman 2D and G peaks ( $I_{2D}/I_G$ ) for different cleaning methods. (AA, AO and ET stand for acetic acid, acetone overnight, and electron beam treatment of PMMA deposited graphene samples respectively for comparative reasons; the ET technique clearly is more favorable). Adapted from Ref. [82], © Son, B. et al. 2017. (d) Schematic of the  $\text{CO}_2$ -mediated cleaning method. (e) and (f) TEM micrographs of graphene before and after  $\text{CO}_2$  cleaning, where the unclean graphene clearly has amorphous deposits. (g) and (h) AFM images of clean and unclean graphene, where the clean graphene has a more uniform and smoother surface compared to the untreated sample. Adapted with permission from Ref. [86], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2019.

PMMA residue can also be achieved by irradiating the sample with an electron beam (Fig. 13(a)), which breaks the PMMA bonds, followed by their sublimation, similar to the effect of annealing. In addition, e-beam cleaning is more effective than other methods (Figs. 13(b) and 13(c)) [82]. The use of a laser can also effectively remove PMMA residue and is non-destructive to graphene and position specific, so it can be used to tune the graphene performance [35, 83]. Transfer residues can also be cleaned using supercritical CO<sub>2</sub> treatment as an alternative solvent that can have its solvent power modified by controlling the temperature and pressure [84, 85]. To enable high-quality graphene transfer, the graphene surface must be very clean and free from impurities originating from the growth process. One cleaning method treats the graphene/Cu surface with CO<sub>2</sub> to etch the amorphous carbon that is often deposited along with the crystalline graphitic carbon during CVD and can degrade the graphene properties (Fig. 13(d)) [86]. This process removes weakly bound carbon species and ensures clean and impurities-free transfer (Figs. 13(e)–13(h)). Therefore, pre-cleaning of the graphene before the transfer process can make certain that the graphene has high structural integrity after transfer, to meet successful applications.

#### 4 Direct growth

Direct growth on technologically interesting substrates is the preferred option to avoid the limitations of the transfer and cleaning processes, while reducing the required cost and time of processing. Therefore, achieving direct growth would be a positive step toward scaling up graphene development and the subsequent applications. Generally, it is challenging to deposit graphene on dielectric substrates, such as SiO<sub>2</sub>, quartz, and sapphire, because of their non-catalytic nature. Therefore,

catalytic agents are introduced to help decompose the carbon source and provide nucleation sites for subsequent deposition. Recently, Song et al. presented CVD fabrication of graphene on quartz substrates facilitated by Cu vapor as a catalyst [87]. The vapor was produced by the reaction between the Cu foil and a sacrificial SiO<sub>2</sub>/Si substrate at elevated temperature, where the Cu eventually fully vaporizes, which avoids the subsequent etching step (Fig. 14(a)). This method resulted in high-quality single-layer graphene with limited defects, as demonstrated by Raman, XPS, and electrical studies (Figs. 14(b)–14(d)). The vapor-generation mechanism was confirmed when only the sacrificial substrate and copper foil are subjected to growth which also results in the development of high-quality single layer graphene growth (Figs. 14(e) and 14(f)), that can be extended beyond the current growth substrate. It is also possible to deposit graphene directly on an insulating substrate with the assistance of a coated catalyst rather than vapors, which can be removed by etching while preserving high-quality graphene [88]. One such method was reported by Guo et al., where graphene was deposited on a quartz substrate and the Ni sacrificial substrate was later on dissolved to produce a high-quality single layer of graphene [89]. These direct growth methods on application-relevant substrates still require the use of metal catalysts to feasibly translate graphene growth which again comes with cost-effectiveness. Interestingly, Shin et al. [90] achieved direct growth of graphene on a dielectric substrate (SiON-SiC(0001)) without the use of a metal catalyst due to the hexagonal lattice symmetry of the substrate, which is compatible with graphene and allows its single-crystal growth. In addition, this process is a self-limiting growth without secondary growth once the surface is entirely covered, as verified by both Raman and XPS analyses (Figs. 14(g) and 14(h)). Further, Pang et al. [91] reported a self-limiting growth process



**Figure 14** (a) Schematic illustrations of Cu-vapor formation and its role in graphene direct growth. (b) and (c) Raman and XPS spectra indicating the growth of high-quality graphene with negligible defects. (d) From electrical measurement (resistance vs. gate voltage), the unintentional doping level in directly grown graphene is much less than that of the Cu foil CVD method (Dirac point is close to zero) that produces damaged graphene with unintentional doping. (e) and (f) Raman spectrum and photograph of a large specimen obtained directly after the reaction between the sacrificial SiO<sub>2</sub>/Si substrate and the Cu foil to produce Cu vapor and a subsequent graphene layer on the substrate. Adapted with permission from Ref. [87], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2018. (g) Raman spectra and (h) XPS spectra showing the saturation and self-limiting growth of graphene on the SiON-SiC substrate with increasing growth time, where saturation was reached after 1 h of growth. Adapted with permission from Ref. [90], © American Chemical Society 2019.

and developed high-quality graphene on a technologically relevant substrate (Si/SiO<sub>x</sub>). This is a simplified approach that uses a growth substrate with a sandwich configuration that favors the formation of a single layer of graphene by reducing the gap for feedstock supply, which helps control the flow of the carbon species and subsequent graphene growth, unlike face-up and face-down growth substrate configurations (Figs. 15(a)–15(i)). This is also a self-limiting approach with an optimal growth period for developing a single layer of graphene (Figs. 15(j)–15(m)).

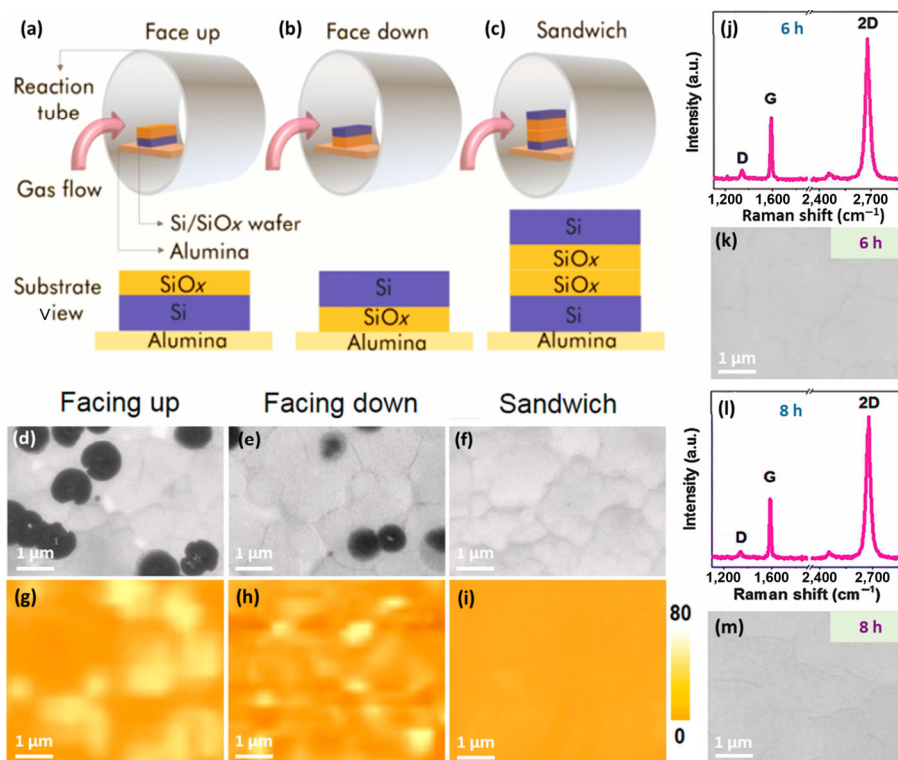
## 5 Summary and future perspectives

In this review article, different strategies for achieving high-quality graphene transfer and cleaning were discussed, and we demonstrated the viability of direct growth on technologically interesting substrates. However, all methods are accompanied by their own challenges, and a universal standard transfer procedure has not yet been developed. Each cleaning and transfer method is associated with challenges which ultimately cause contaminations [45], wrinkles [17], and cracks [21], as shown in Figs. 16(a)–16(c). Cleaning graphene contaminated by residues from the growth or transfer process is the least time- and cost-effective method, and has a high environmental impact. In addition, after cleaning, the graphene yet contains defects that limit its scalability to commercial levels. To fully exploit the advantages of graphene, direct growth on suitable substrates, such as semiconductors and metal oxide, is preferable [5, 10, 91]. Currently, direct growth methods are still in their infancy and limited to the laboratory scale. Cleaning and transfer processes increase the overall cost and time required to produce graphene and subsequently limit commercialization potential [6]. Therefore, future technologies should avoid

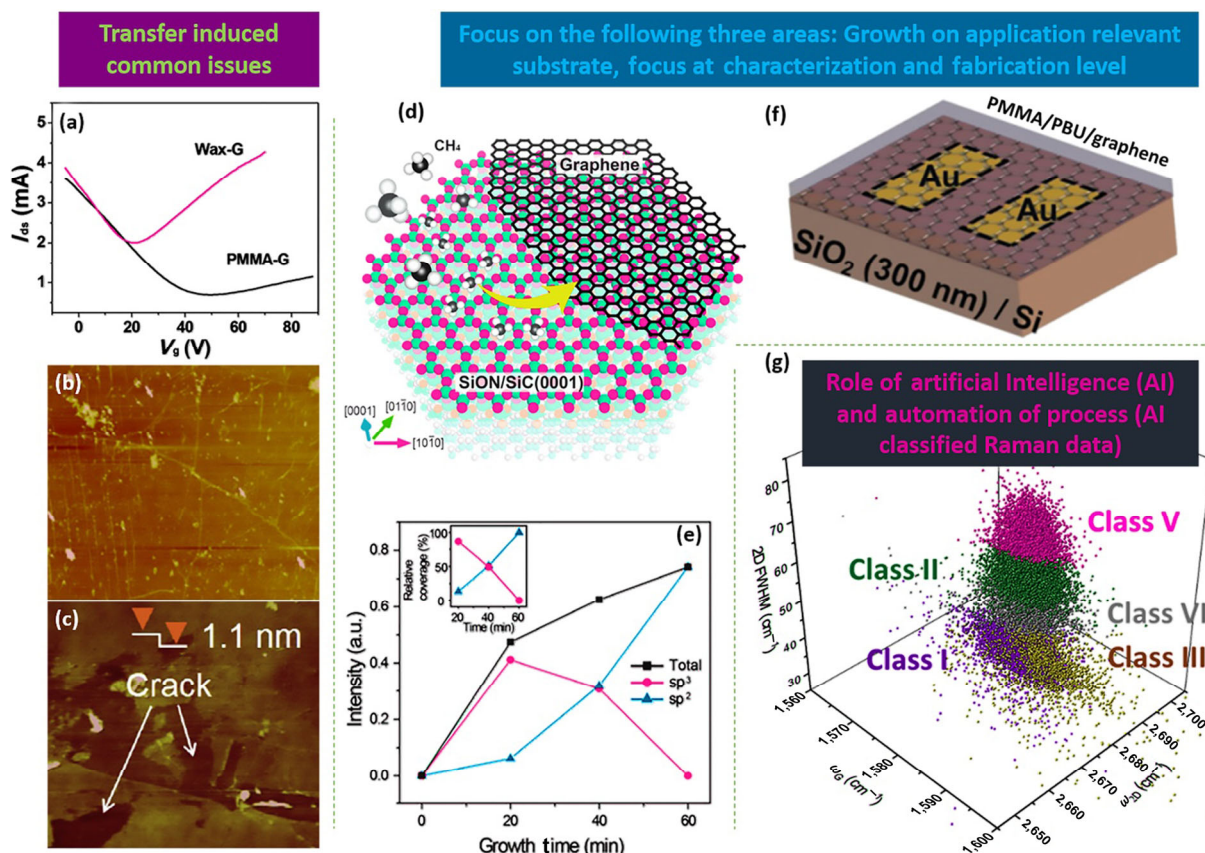
defect formation, and minimize the cost, processing time, and environmental impact [77]. In addition, scalability is a major factor for realizing successful commercialization to revolutionize graphene technology [92, 93].

Transfer techniques should not be limited to graphene but should be optimized for materials beyond graphene such as transition metal dichalcogenides (TMDs). In addition, graphene coupled with other 2D materials to form graphene heterostructures such as hBN/G and MoS<sub>2</sub>/G with stacked and lateral structures should be promoted because of their huge potential [94, 95]. Therefore, proper co-transfer strategies should be encouraged. Hempel et al. reported the first successful roll-to-roll co-transfer and stacking of graphene/hBN (see Fig. 11(e)). Besides, initial success in the stacking of two 2D material layers by R2R transfers in this study, more work is needed to achieve high-quality stacks of 2D materials with R2R transfers in order of 2D material family extension to truly technological level [72].

Graphene-inspired wearable and adaptable technology is highly important to achieve flexible and foldable devices for human-machine interfaces and other technologies [78, 96]. Furthermore, research at the device fabrication and characterization level is important to establish a clear structure–property relationship for graphene [22, 92, 95]. Thus, it is clear that three areas of graphene research should be the focus of future studies to achieve successful, high-quality, and scalable applications: 1) direct growth on application-relevant substrates; 2) appropriate characterizations methods to quickly perform quality-control inspections of graphene produced on a laboratory or industrial scale; and 3) control of device fabrication processes and the necessary steps to protect and isolate the active materials from the effects of the external environment during use of practical devices (Figs. 16(d)–16(f)).



**Figure 15** (a)–(c) Schematic illustrations of different growth-substrate configurations in the self-terminating direct growth method. (d)–(f) SEM and (g)–(i) Raman spectral maps of the full width at half-maximum (FWHM) of the 2D band, which clearly indicate that the sandwich configuration enhanced direct growth. (j) and (k) Raman spectrum and corresponding SEM image respectively of sample grown at 6 h of growth period whereas, (l) and (m) Raman and corresponding SEM respectively of sample grown at 8 h of growth period. Similar growth result at both growth periods indicating self-limited growth where no additional graphene layers were observed, even after an extended growth period. Adapted with permission from Ref. [91], © American Chemical Society 2017.



**Figure 16** (a) Channel current ( $I_{ds}$ ) as a function of the gate voltage ( $V_g$ ) of graphene transferred using PMMA- and wax-enabled transfer, where the neutral point voltage corresponds to the Dirac point of graphene where the conduction band minimum (CBM) and the valence band maximum (VBM) meet on the density of states. The neutral point voltage reflects the shift in the Fermi level by charge-carrier doping. For wax-enabled transferred graphene, the neutral point is located at approximately 20 V, whereas, that of PMMA-mediated transferred graphene is located at approximately 50 V, indicating a higher residue content. Adapted with permission from Ref. [45], © Elsevier B.V. 2019. (b) AFM of PMMA-transferred graphene showing wrinkles. Adapted from Ref. [17], © Leong, W. S. et al. 2019. (c) AFM image showing cracks caused by graphene transfer. Adapted with permission from Ref. [21], © Elsevier Ltd. 2015. (d) Schematic of the development of single layer graphene via CVD route directly on dielectric SiON/SiC(0001) substrate. (e) Time-dependent XPS of graphene developed using the self-terminating route (inset demonstrates the ratio of the presence of  $sp^2$  and  $sp^3$  carbon). Adapted with permission from Ref. [90], © American Chemical Society 2019. (f) Graphene-based field-effect transistor that is stable in air and humidity. Adapted with permission from Ref. [65], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2014. (g) Artificial-intelligence-assisted Raman study of graphene. Adapted from Ref. [97], © Leong, W. S. et al. 2020.

Currently, advances in graphene technology have not yet achieved graphene production with the desired quality, yield, and scalability. However, the advances in both experimental and theoretical research, and more importantly the evolution of machine learning algorithms (artificial intelligence), are expected to facilitate the development of graphene technology (Fig. 16(g)). In this manner, upscaling of graphene to fully exploit its unique applications could be achieved, along with automation of the process [32, 72, 97]. Hopefully, graphene technology will soon reach its peak, followed by a distinctive technological revolution in graphene applications.

## Acknowledgments

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