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Removing contaminants from transferred CVD graphene

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ABSTRACT

Chemical vapor deposition (CVD) is among the most utilized techniques to fabricate single-layer graphene on a large substrate. However, the substrate is limited to very few transition metals like copper. On the other hand, many applications involving graphene require technologically relevant substrates like semiconductors and metal oxide, and therefore, a subsequent process is often needed to transfer CVD to the new substrate. As graphene is fragile, a supporting material such as a polymer film, is introduced during the transfer process. This brings unexpected challenges, the biggest of which is the complete removal of this support material without contaminating graphene. Numerous methods have been developed, each having advantages and drawbacks. This review will first introduce the classic transfer method using poly(methyl methacrylate) (PMMA) as the support material. The operating procedure and issues of PMMA residuals will be discussed. Methods to minimize/eliminate contamination will be presented, together with alternative approaches that do not require the use of PMMA.

KEYWORDS

chemical vapor deposition (CVD), graphene, poly(methyl methacrylate) (PMMA), transfer

1 Introduction

Graphene is a single-layer two-dimensional (2D) material, consisting of exclusively sp^2 carbon atoms in a gigantic aromatic structure [1]. Since the successful isolation of monolayer graphene by mechanical exfoliation of highly-oriented pyrolytic graphite (HOPG) using a Scotch tape in 2004 [1], extensive research has been conducted on the preparation, functionalization and applications of this fascinating 2D material [2]. Despite its tremendous potentials, the availability of high quality pristine graphene is still an ongoing challenge [3].

Graphene can be generally prepared by one of the following methods: mechanical exfoliation, liquid exfoliation, chemical exfoliation, thermal decomposition of silicon carbide (SiC), chemical vapor deposition (CVD), and chemical synthesis. The first successful graphene preparation, i.e., mechanical exfoliation using a Scotch tape, has been acknowledged to yield the highest quality graphene, as the starting material HOPG consists of many pristine graphene layers, and the peeling of which can give a single pristine graphene layer without contamination [1, 4]. The challenge, however, is to be able to produce single-layer graphene consistently and reproducibility, as peeling produces mostly multi-layer graphene and single-layer graphene requires multiple rounds of peeling. Additionally, the product is mostly irregular in shape and it is difficult to obtain samples larger than millimeters in size. Liquid exfoliation is another top-down fabrication method which involves reducing the size of graphite by subjecting graphite powders suspended in a solvent by mechanical forces like sonication or blending [5, 6]. This process is the most straightforward but it produces few-layer rather than the single-layer graphene. Also, the quality of the product is poor as mechanical agitation not only breaks the graphite powder into finite pieces (microns) of uneven size and thickness, but also creates many physical defects [3]. One way to make single-layer graphene is chemical exfoliation, which is to oxidize graphite with strong oxidation agents like concentrated H_2SO_4 and $KMnO_4$ under agitation or sonication to give single-layer graphene oxide (GO) in high yield (> 80%) [7]. A subsequent reduction reaction gives reduced GO (rGO). Structurally, rGO is not equivalent to pristine graphene as the oxidized domains in GO disrupt the conjugated structure of graphene, and the continuous sp^2 network cannot be completely restored even after extensive reduction [8–10]. Thermal decomposition of SiC is another approach to graphene fabrication [11]. Under certain conditions, such as 1,650 °C in Ar or 1,150 °C in UHV environment, Si atoms in SiC could sublime while C atoms remain and form graphene eventually [12]. The carbonaceous product obtained through this method is however mostly multi-layer graphite and occasionally single-layer graphene [13]. The high cost of SiC also limits the utility of this method. The CVD technique produces graphene with relatively high quality on a large substrate in a controlled fashion [4, 14, 15]. This process will be discussed in more details in the section below. Recently, there has been increasing efforts to build graphene structure from molecular building blocks by chemical synthesis [16–20]. In principle, this allows the preparation of high quality pristine graphene with well- defined shapes and sizes. Building larger structures is however challenging due to the poor solubility of the products and the difficulty in separating them. As such, functional groups are needed, especially on large structures, to help with the solubility and purification.

2 Transferring CVD graphene

CVD graphene always comes with a transition metal support

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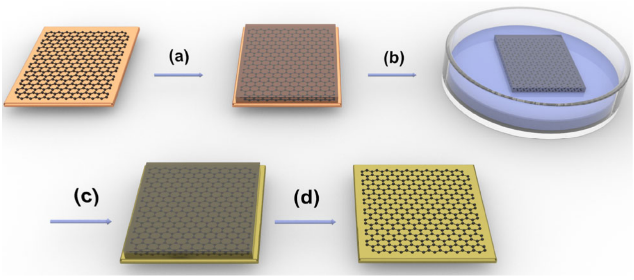
underneath as a result of the fabrication mechanism. For applications that require substrates other than these transition metals, additional operations are needed to transfer CVD graphene to the desired substrate. This is generally accomplished by dissolving the metal substrate via a wet etching process to release graphene. A solid support such as a polymer film is often introduced before removing the metal substrate. The polymer film serves to protect graphene as the free-standing graphene is fragile and breaks easily. The solid support also helps to minimize wrinkles in graphene, which are generated as a result of the differences in the thermal expansion coefficients between the metal substrate and graphene.

The classic CVD graphene transfer uses poly(methyl methacrylate) (PMMA) as the support/protector [13, 21]. PMMA is a widely-used commodity polymer available in different molecular weights and tacticity. It has low toxicity, relatively good stability, and excellent solubility in a number of organic solvents including those with good film forming ability like toluene and that of low toxicity like acetone. As an amorphous thermoplastic, PMMA can cast from the molten neat, or spin-coated from a solution to produce thin film, which are of good mechanical strength and chemical stability towards dilute acids under ambient conditions [22]. Additionally, PMMA thin films are optically transparent, therefore, the integrity of graphene can be observed and monitored during the transfer process.

The classic PMMA-assisted CVD graphene transfer procedure consists of four major steps (Scheme 1) [15]: (a) formation of a PMMA/graphene/Cu triple-layer construct by spin coating a solution of PMMA (M_W 996,000) in chlorobenzene on top of CVD graphene followed by drying in air; (b) removal of the Cu foil substrate by treating the sample with an etchant, e.g., 0.05 g/mL aqueous solution of $Fe(NO_3)_3$, followed by copious rinsing with deionized (DI) water; (c) transfer of PMMA/graphene onto the desired substrate. This is done by placing the new substrate underneath the side of graphene which is submerged in water. Water is then removed by a syringe or by blotting with a tissue paper, and the sample is dried under vacuum followed by heating at 180 °C for > 30 min to flatten the graphene film; (d) removal of PMMA by soaking the sample in an acetone bath, leaving behind graphene on the new substrate after cleaning the sample with fresh acetone and drying. It was observed, by time-of-flight secondary ion mass spectrometry (ToF-SIMS) using deuterated PMMA, that the majority of PMMA was removed by acetone in the first 3 h, and the efficiency levelled off after 5 h [23]. Many different variations of the protocol have been reported, mostly changing the processing parameters such as the concentration of PMMA solution, spin-coating speed and duration which affect the thickness of the PMMA film, heating temperature, the type of etchant and duration of etching.



Scheme 1 Transfer CVD graphene to a new substrate: (a) spin coat PMMA to form PMMA/graphene/Cu triple-layer, (b) remove Cu foil with an etchant, (c) transfer PMMA/graphene onto a new substrate, (d) remove PMMA protective layer by soaking in acetone.

3 Contamination on transferred CVD graphene

The cleanliness of surface is of prime importance in nanomaterials and nanotechnology from the standpoint of both fundamental studies and device fabrication. It is especially critical for 2D materials like graphene where the surface dominates their overall properties. Contaminant-free is thus essential in order to fully realize the extraordinary properties of graphene.

In theory, a clean graphene film should be obtained after the transfer, but this is not the case in practice. In addition to cracks, another major issue is the incomplete removal of PMMA films even after extensive cleaning with the solvent, thus leaving residuals on the transferred graphene (Fig. 1) [10, 14, 15, 23–44]. This residual layer was quantified by Raman scattering and transmission electron microscopy (TEM) to be 1–2 nm thick [45].

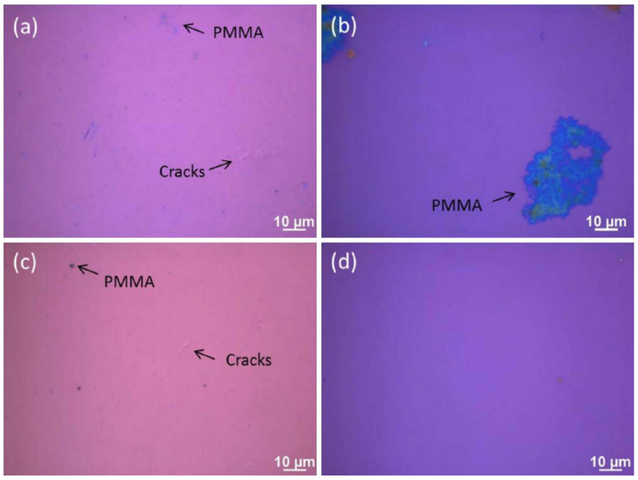


Figure 1 Optical microscopy images of transferred CVD graphene. Cracks and PMMA residuals are indicated with arrows. Reprinted with permission from Ref. [27], © Elsevier Ltd. 2014.

These residuals impact the properties of graphene in multiple ways. Surface contaminants introduce charges and structural deformation causing local doping to the otherwise charge-neutral and zero-gap graphene [46, 47]. This can lead to alteration in charge density and a shift in the Dirac point, hindering the carrier mobility, electron and phonon transport, and impairing the performance of graphene in thermal conductivity [48], electric response [49] as well as in surface-sensitive applications [50–52]. For example, the carrier mobility of as-prepared CVD graphene, 10^3 to 10^4 $cm^2/(V·s)$, decreased to 200–2,500 $cm^2/(V·s)$ after the transfer [53, 54].

The incomplete removal of PMMA was proposed to be due to the interactions of PMMA with graphene resulting from the alignment of polymer chains with the sp^2 carbons of graphene via π–π interactions, and the interaction of the –OH groups at the domain boundary of graphene with the polar groups in PMMA [25, 55]. PMMA was also reported to react with the etchant like $FeCl_3$, producing additional contaminants [56].

The as-prepared graphene is of high surface energy, and thus readily absorbs contaminants from its surroundings. Its high specific surface area also enables multivalent interactions, which further increasing the adhesion of these surface contaminants. All these factors contribute to the adsorption of residuals and contaminants, and their strong interactions with graphene.

A variety of methods have been developed to minimize PMMA residuals on transferred CVD graphene. These methods can be grouped into four main categories (Table 1):

(1) improving the removal efficiency of PMMA; (2) dry transfer using pre-made polymer films; (3) polymer-free transfer; (4) removing amorphous carbons prior to transfer. In the sections below, we will discuss the working principles and operation procedure of each method, and will include specific examples. The current review focuses on minimizing polymer contaminants during CVD graphene transfer. Other topics/issues related to graphene transfer can be found in published reviews elsewhere [57–59].

4 Improving the removal efficiency of PMMA

4.1 Using hot acetone or other solvents

Acetone is the most commonly used solvent in removing the PMMA protecting film. It is a common laboratory solvent, frequently used for cleaning glassware/apparatus due to its excellent dissolution ability for many organic compounds and low toxicity compared to many other organic solvents. Acetone has a Hildebrand solubility parameter of 9.7 $\mathrm{cal^{1/2}\cdot cm^{-3/2}}$, which matches well with PMMA (9.2 $\mathrm{cal^{1/2}\cdot cm^{-3/2}}$) [60]. An obvious way to enhance the dissolution power of a solvent would be to increase the temperature, for example, by using hot acetone vapor to remove PMMA [36, 61–63]. In one setup, the PMMA/graphene/substrate triple-layer construct was hung above the boiling acetone [36]. As the fresh hot acetone droplets condense on the sample surface, the solvent dissolves and removes PMMA as the liquid flows down (Fig. 2). The working principle is similar to that of the Soxhlet extraction used in the purification of materials like polymers, where only the condensed pure solvent is in contact with the product in the thimble and the dissolved impurities remains in the solution. This ensures that the material is always treated with

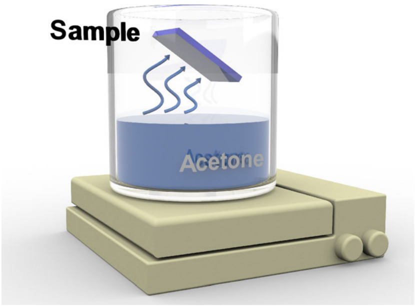


Figure 2 Removing PMMA by acetone vapor.

Table 1 Methods to minimize polymer residuals during transfer of CVD graphene

Strategy	Method		Principle and Features	References
PMMA-assisted transfer	Solvent alone	Acetone vapor	Sample is always in contact with pure solvent. Slow process	[36, 61–63]
		Other solvents (anisole, chlorobenzene, chloroform, glacier acidic acid)	Different solvent modulate solubility Potentially more toxic than acetone	[26, 27, 67, 68]
		Using two layers of PMMA	Second application of hot PMMA re-dissolves and mechanically relaxes polymer. Increased solubility of residuals in solvent	[15, 27]
	Additional treatment	Degradation of PMMA by UV/ion beam/heat	Radiation/heating degrades PMMA. Degraded PMMA has higher solubility in solvent. May oxidize graphene at high radiation doses	[25, 37, 38, 70–72, 78, 79]
		Using low molecular weight PMMA	Higher solubility in solvent Lower mechanical strength	[39]
		Electrolytic cleaning	Gas bubbles exfoliate PMMA residuals. May create defects in graphene	[31]
		Electrostatic force-assisted PMMA removal	Electrostatic attraction removes PMMA residuals. Require careful control of parameters	[40]
Other polymer-assisted transfer		Polystyrene and polycarbonate	Weaker interaction with graphene than PMMA Easier to remove Rigidity/roughness may cause damage to graphene.	[45]
		Polystyrene + plasticizer		[55]
		Polyisobutylene		[56]
Solvent-free transfer		TRT	Pre-formed polymer film is used. No solvent is needed for polymer removal. Require careful operation to avoid damage to graphene	[80]
		PDMS		[15, 81]
		Silicone/PET film		[33]
Non-polymer-assisted transfer		Rosin	Removal can be accomplished by evaporation or sublimation. Small molecules are mechanically weaker than polymer film.	[82, 83]
		cyclohexane		[84]
		Camphor		[85]
		Paraffin		[86, 87]
Reagent-free transfer		Graphene holder	No solvent or polymer is used. Special apparatus is required.	[88]
		Electrostatic force		[24]
Decreasing amorphous carbon on CVD graphene		Treating CVD graphene with CO_2 gas	Reduce contamination by polymer residuals	[89, 90]
		Using $Cu(OAc)_2$ as graphene precursor	Reduce amorphous carbon contamination	[91]

the pure solvent and the removed impurities are not in contact with the purified product. According to the authors, overnight treatment resulted in clean and intact graphene [36].

PMMA also dissolves well in aromatic and chlorinated hydrocarbons. Examples of such solvents used for PMMA removal include anisole [27, 64–66], chlorobenzene [67] and chloroform [68]. Some of these solvents have higher boiling point (e.g., 135 and 132 °C for anisole and chlorobenzene, respectively) than acetone (56 °C), and as such, PMMA removal can be done at higher temperature to increase the dissolution rate. These solvents are nevertheless less used owing to their higher toxicity than acetone, especially in settings that exhaust facilities such as fume hoods are unavailable. Glacier acidic acid has also been used to remove PMMA residuals [26]. Care should however be taken to ensure the complete removal of the acid to avoid the presence of acidic residuals on graphene.

In spite of these developments, it has been acknowledged by many researchers that PMMA residuals cannot be completely removed by a solvent alone [25].

4.2 Using two layers of PMMA

This method was developed with the primary goal of reducing cracks in the transferred graphene [69]. In the PMMA/graphene/substrate triple-layer construct, strains can be generated within graphene by the tension imposed by the polymer film, leading to cracks in graphene after PMMA is removed. To minimize these cracks, Ruoff and coworkers applied a second portion of hot PMMA solution on top of the first PMMA layer to partially or fully re-dissolve it. This operation mechanically relaxed the polymer chains and eased the tension imposed on graphene, resulting in fewer cracks on graphene after the transfer (Fig. 3). An added value of this protocol is that the second application of PMMA facilitated the removal of PMMA by acetone, probably due to the softening of the first PMMA layer by the hot solution. This effectively reduced the PMMA residuals after both layers were removed. This double layer strategy was further investigated by Kong and coworkers, concluding that the quality, cleanliness, uniformity and continuity of the transferred graphene were influenced by the concentration of the two PMMA solutions, the post-heating temperature and time [27]. Their optimized transfer procedure involved two rounds of spin coating and curing (1st: 4.5% PMMA, 80 °C for 5 min; 2nd: 1.35% PMMA, 130 °C for 20 min), an acetone soaking, and a final annealing at 500 °C for 2 h in the presence of hydrogen (700 sccm) and argon (400 sccm).

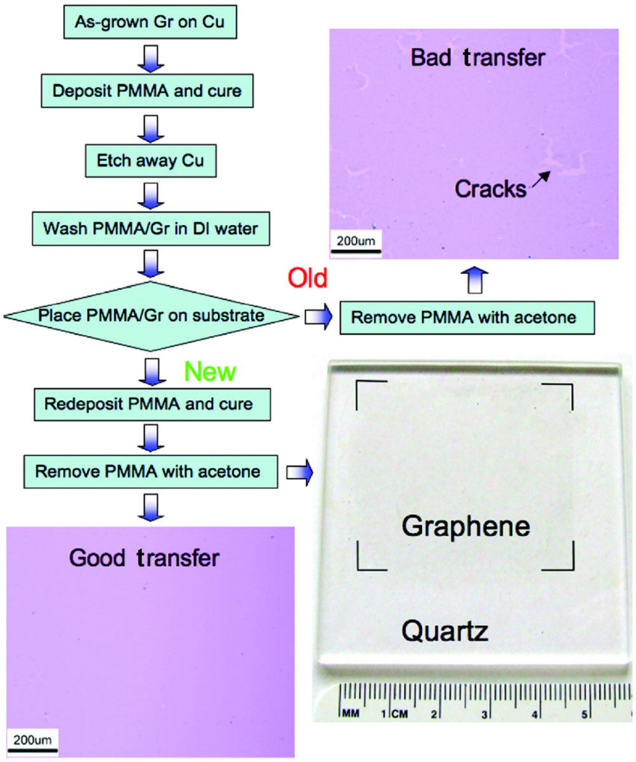


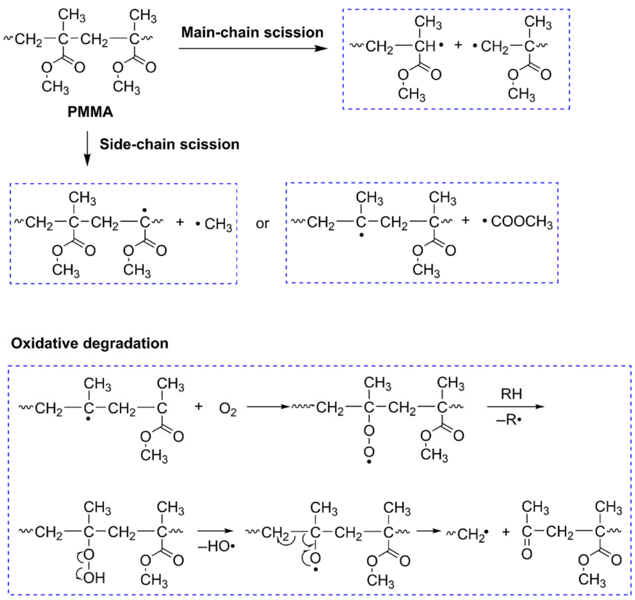
Figure 3 Graphene transfer with double layer PMMA (reprinted with permission from Ref. [69], © American Chemical Society 2009.

4.3 Degradation of PMMA

Since the strong interaction between PMMA and graphene is a major reason for the incomplete removal of PMMA, one way to reduce this interaction is to degrade the polymer into lower molecular weight fragments, which will have higher solubility thus will be easier to remove by the dissolution solvent.

Polymer degradation can be achieved by irradiation with photons, high energy ions, X-ray and electrons [70–72]. The precise molecular mechanisms of PMMA degradation vary slightly depending on the energy source, the intensity and duration of irradiation. Nevertheless, the major events can be summarized in Scheme 2. Upon exposure to irradiation, chain scission reactions occur, resulting in bond breaking at the main chain or the side chains to yield various free radicals. In the presence of oxygen, additional oxidation can take place to yield backbone-oxidized ketone structure and at the same time, and further degrade the polymer into lower molecular weight fragments.

UV treatment at 254 nm, 285 nm [67] or further down to 185 nm [73] was applied to PMMA before subjecting it to the solvent. Indeed, PMMA film after UV treatment was found to be easier to remove by acetone, and additionally, airborne contaminants were less likely to adhere to the graphene surface [74]. In the work of Suhail et al., the samples were exposed to deep-UV (DUV, 254 nm) in air at 180 °C for 20 min before acetone wash [67]. X-ray photoelectron spectroscopy (XPS) analysis on the C1s peak revealed that the carbonyl group (C=O), which belongs to PMMA and was present on transferred graphene without UV treatment (Fig. 4(a)), almost completely disappeared in the transferred sample that was pre-treated with UV/ozone (Fig. 4(b)) [67]. Also improved are the optical transparency, sheet resistance and electron mobility of the resulting graphene. It was reported that the transferred



Scheme 2 Radiation-induced degradation of PMMA.

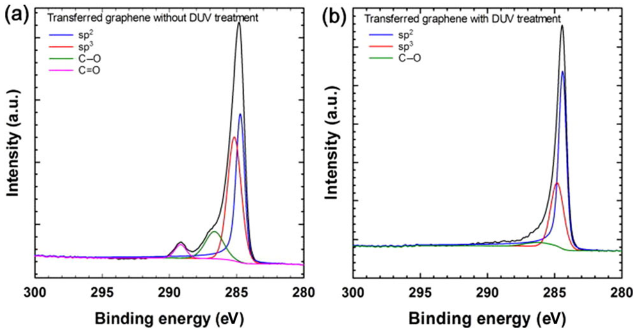


Figure 4 XPS high-resolution C1s spectra of transferred graphene on silicon wafer (a) without and (b) with DUV treatment. The black lines were the measured spectra, which were curve fitted into the sp^2 C from graphene (blue), and sp^3 C (red), C–O (green) and C=O (pink) from PMMA residues. Reprinted with permission from Ref. [67], © AIP Publishing 2017.

graphene with UV pre-treatment was furthermore less affected by the p-doping from the PMMA contamination [73].

Note that UV/ozone treatment could potentially degrade graphene. It was reported that the UV exposure created defects in graphene, and the percent defect increased with the irradiation time (Figs. 5(a) and 5(b)) [73, 75]. It was proposed that under UV exposure, graphene was oxidized by ozone, leading to the conversion of C=C bonds to carbonyl C=O or hydroxyl-bonded sp^3 carbons (C–OH) (Fig. 5(c)) [73, 76]. This was further demonstrated in the water contact angle measurements that the graphene surface became increasingly hydrophilic with UV irradiation time (Fig. 5(d)) [77]. Oxygen plasma treatment also causes damages to graphene by introducing strains and distorting graphene lattice, thus causing both topological and chemical defects [76]. Therefore, care must be taken when carrying out UV/ozone treatment to ensure that graphene structure will not be affected by the exposure.

Ion beam irradiation has also been used to clean the graphene surface. It’s been reported that He^+ beam treatment followed by vacuum annealing could completely remove PMMA residuals [38]. The authors hypothesized that upon He^+ bombardment, PMMA decomposed and reacted with graphene. A subsequent vacuum annealing treatment removed PMMA and also reduced graphene as characterized by dynamic XPS and Raman spectroscopy. In this protocol, the dose of the He^+ beam (ranging from 4×10^{12} to 1.2×10^{13} He^+/cm^2) was the key factor in the successful and effective removal of PMMA residuals. If the dose was higher than 1.2×10^{13} He^+/cm^2, permanent defects were generated in graphene. Subsequent work by the Pollard group showed that a mass-selected argon gas cluster ion beam was also effective in removing PMMA residuals from graphene [37]. This method does not need vacuum annealing thus simplifying the protocol. Similar to He^+, the Bi^{3+} beam can also generate defects in graphene if high doses are used. The authors stated that by optimizing the energy level and dose density of the Bi^{3+} ion beam, one could remove PMMA as well as minimize defects in graphene. In summary, the high-energy He^+ or Bi^{3+} ion beam facilitates the degradation of PMMA and its subsequent removal. As the ion beam could potentially react with almost all organic substances including graphene, the technical challenges in implementing this approach would be to maximize the decomposition of PMMA and minimize the damage to graphene.

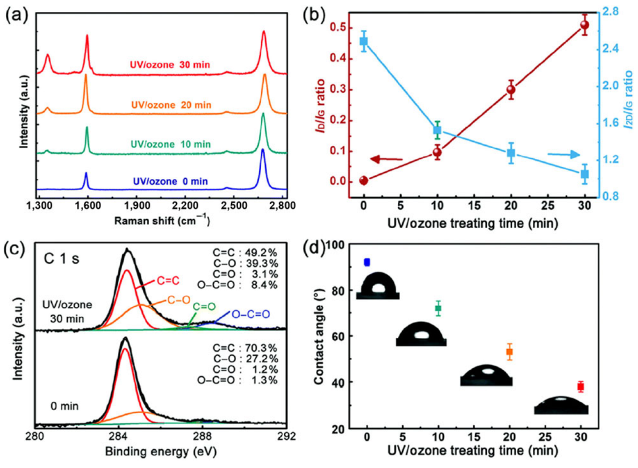
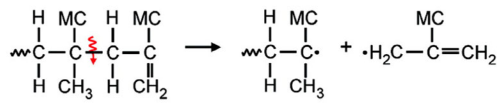


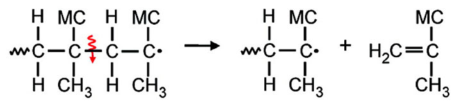
Figure 5 (a) Raman spectra and (b) I_D/I_G and I_{2D}/I_G ratios of graphene vs. UV/ozone treatment time. (c) XPS spectra of graphene before and after UV/ozone treatment. (d) Change in water contact angle on the graphene surface as a function of UV/ozone treatment time. Reprinted with permission Ref. [73], © The Royal Society of Chemistry 2017.

PMMA decomposition can also be initiated thermally. In air, the weight loss of bulk PMMA starts at ~ 275 °C and decomposes completely at ~ 400 °C, following similar chain scission reactions as in the radiation-induced degradation (Scheme 2) [78, 79]. In CVD graphene transfer, procedures have been developed to heat the samples at high temperature before soaking in acetone. This simple method is however acknowledged to be more difficult to achieve practically. It was reported that annealing could not completely remove the polymer residuals, and increasing the temperature had a negligible effect [25]. It was further pointed out that the radicals generated by the chain scission of PMMA would react with graphene thus creating defects on the sample (Fig. 6) [25]. Nevertheless, annealing is straightforward to operate compared to the UV/ozone or ion beam treatment, and as such, more studies have been carried out to investigate the annealing conditions, for example, by changing from heating in air to in vacuum or inert atmosphere [32, 34, 35, 41]. However, no agreement has been reached on the optimal annealing conditions from these studies. For instance, Kim et al. achieved the best PMMA removal and the least damage to graphene by annealing at 300–400 °C under mixed Ar/H_2 atmosphere [41]. The optimized condition presented by Chabal et al. was 500 °C under CO_2 atmosphere [35]. In addition, the Raman peak of graphene in the 1,050–1,550 cm^{-1} region broadened after annealing (Fig. 7), which was proposed to be the result of the dehydrogenation reaction of PMMA leading to the formation of unsaturated double bonds as shown in Fig. 7 [35].

(a) Terminal scission



(b) Random scission



(c) Reaction with graphene

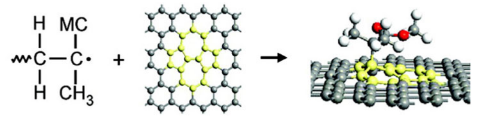


Figure 6 Thermal decomposition of PMMA by (a) terminal or (b) random scissions. (c) Possible reactions between graphene and radicals generated from thermally decomposed PMMA. Reprinted with permission from Ref. [25], © American Chemical Society 2012.

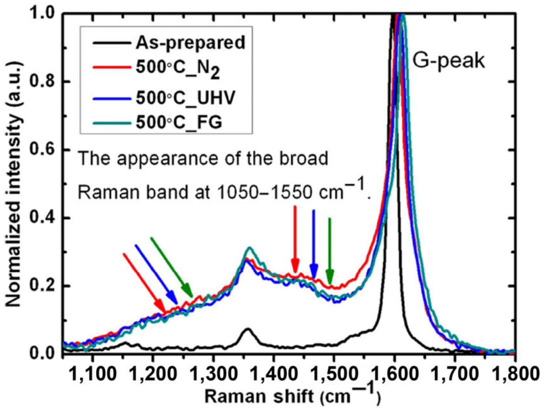


Figure 7 Raman spectra of transferred graphene on silicon wafer before and after annealing at 500 °C in N_2, UHV, or FG (forming gas: 10% H_2/90% Ar, ethylene of 101.3 ppm in N_2). The red, blue and green arrows point to the annealing-induced broadening of the Raman bands. Reprinted with permission from Ref. [35], © American Chemical Society 2013.

4.4 Using low molecular weight PMMA

The molecular weight of the polymer impacts both its mechanical property and solubility. In PMMA-assisted graphene transfer, the molecular weight of PMMA should be as such that it has sufficient mechanical strength to support graphene after the removal of the metal substrate, while at the same time has good solubility in acetone in order to be removed afterwards. Examples discussed above used PMMA of fairly high molecular weight (~ 996,000), which readily forms intra- and/or inter-molecular entanglements among the polymer chains. As a result, the spin-coated film provides the necessary mechanical strength to support graphene during the transfer process. The requirement for PMMA removal is however the opposite. The solubility of the polymer generally increases with decreasing molecular weight due to fewer chain entanglements and weaker inter-chain interactions in lower molecular weight polymers, which makes it easier for the solvent molecules to break. Both UV/ozone treatment and ion beam irradiation as well as thermal annealing aim to degrade PMMA into lower molecular weight fragments to facilitate their dissolution in the solvent. The idea of using lower molecular weight PMMA would be an obvious alternative, provided that the polymer would possess sufficient mechanical strength to support graphene during the transfer process. More importantly, high energy radiation or high temperature thermal treatment is no long needed, which are known to create defects on graphene. In the work of Seo et al., PMMA with molecular weight of 15,000 was used [39]. The results, when compared with those of 35,000, 350,000 and 996,000 PMMA, showed that the lower the molecular weight, the fewer polymer residuals left on graphene, with the cleanest graphene obtained from PMMA having the molecular weight of 15,000.

4.5 Electrolytic cleaning

In electrolytic cleaning, graphene transferred to silicon wafer was used as the working electrode in a three-electrode electrochemical cell configuration (Fig. 8) [31]. Cyclic voltammetry was carried out where hydrogen was generated on the working electrode. The hydrogen bubbles helped removing PMMA residuals from graphene surface by a combined effects of mechanical exfoliation and weakened graphene–PMMA interactions [35]. The resulting graphene sample showed reduced surface roughness and enhanced carrier mobility, judging from the atomic force microscopy (AFM) and transport measurements.

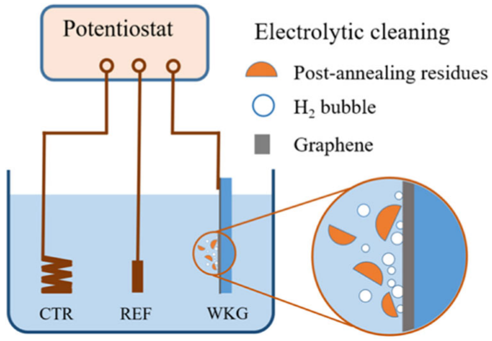


Figure 8 Electrolytic cleaning to remove PMMA residuals. CTR: counter electrode (a platinum wire), REF: reference electrode (Ag/AgCl), WKG: working electrode (graphene on silicon wafer). Electrolyte: 0.5 M sulfuric acid. Reprinted with permission from Ref. [31], © IOP Publishing Ltd 2017.

4.6 Electrostatic force-assisted PMMA removal

Electrostatic force was shown to be helpful in removing PMMA residuals on graphene. In the report by Choi et al., an electrostatically charged rubbing cloth was placed above the surface of PMMA [40]. As the positively-charged cloth approached the sample, it induced negative charges on the sample surface such that the PMMA residuals were removed by the rubbing cloth through electrostatic interactions (Fig. 9(a)). The authors observed effective removal of PMMA residuals after more than 3 cycles of charging. This method used simple materials, and can in principle be operated with unlimited number of cycles (Fig. 9(b)). Obviously, the strength of the electrostatic attracting force dictates the removal efficiency, and is affected by the distance between the rubbing cloth and the sample. A large gap will greatly reduce the electrostatic force, whereas too small of a gap would result in the physical contact of the sample surface with the fibers of the rubbing cloth, creating friction and mechanical scratches on graphene (Fig. 9(c)).

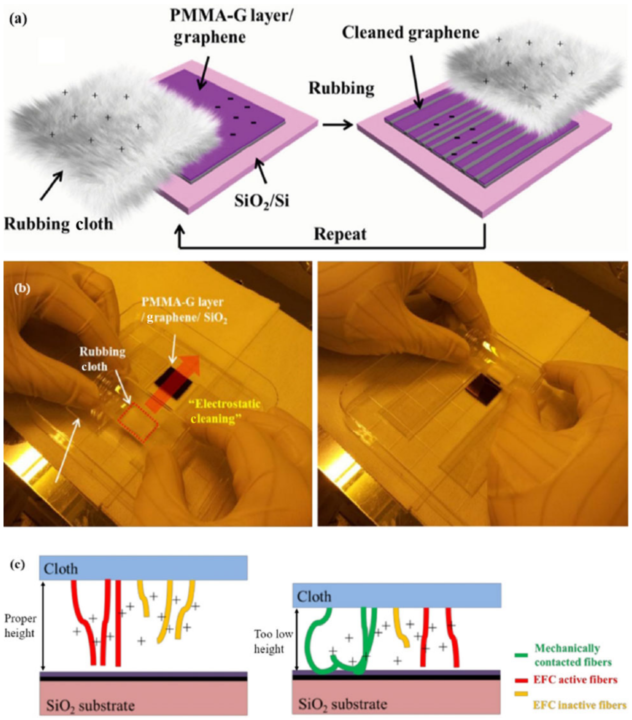


Figure 9 (a) Electrostatic force (rubbing cloth)-assisted removal of PMMA residuals. (b) Photographs of the setup and a cycle of the process. (c) The impact of the distance between the rubbing cloth and graphene on the residual removal efficacy. Reprinted with permission from Ref. [40], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2013.

5 Using polymers other than PMMA

Polymers other than PMMA have also been tested, including polystyrene and polycarbonate (using chloroform as the solvent) [45], as well as polyisobutylene (decane, hexane or squalene as solvent) [56]. The application of these polymers in graphene transfer follows a similar procedure as in the case of PMMA except that the solvent was replaced with the ones indicated above.

Thermoplastic polymers like polystyrene and polycarbonate are more brittle, which restricts their uses in large scale graphene transfer. To circumvent this issue, a plasticizer can be added to the polymer, for example, plasticizer 4,4'-diisopropylbiphenyl (DIPB) in the case of polystyrene [55]. The plasticizer serves to soften the polymer, which facilitates the removal of the polymer residuals by solvent. The plasticizer also decreased the stress built in the polymer film leading to fewer cracks in graphene after transfer [55].

6 Solvent-free transfer

Solvent-free transfer, i.e., dry transfer, refers to methods that do not require the use of any solvent during the removal of the protective support. One such approach is to use a pre-formed polymer film as the support. The transfer of graphene is accomplished by taking advantage of the difference in the adhesion force between the support material and graphene such that graphene can be attached or detached from the support material by changing the processing conditions. Thermal release tape (TRT) [80] and polydimethylsiloxane (PDMS) are two examples of such support materials [15, 81]. Both materials can adhere to the as-prepared CVD graphene/Cu at room temperature. After the metal support is etched away, the graphene/TRT or graphene/PDMS film was then placed on the new substrate, and the TRT or PDMS film was subsequently removed by gently peeling off the TRT or PDMS at 125 and 180 °C, respectively, leaving graphene on the new substrate.

Solvent-free transfer avoids using polymer solutions or solvents altogether to minimize the generation of residuals during polymer dissolution. However, contamination cannot be completely avoided as the pre-formed polymer film may still leave residuals on graphene. The soft silicone could also cause wrinkles and deformations to graphene if not carefully handled. Improvements were made to overcome this issue, for example, by using a double-layer transferring film consisting of a poly(ethylene terephthalate) (PET) film on top of the silicone. The PET layer served as a rigid support to compensate for the soft silicone (Fig. 10) [33]. The low surface tension of silicone allows the transfer to be done at room temperature, and the rigid PET provides the mechanical strength reducing the damage to graphene during the transfer process. The authors reported to have obtained clean and intact graphene film after the transfer.

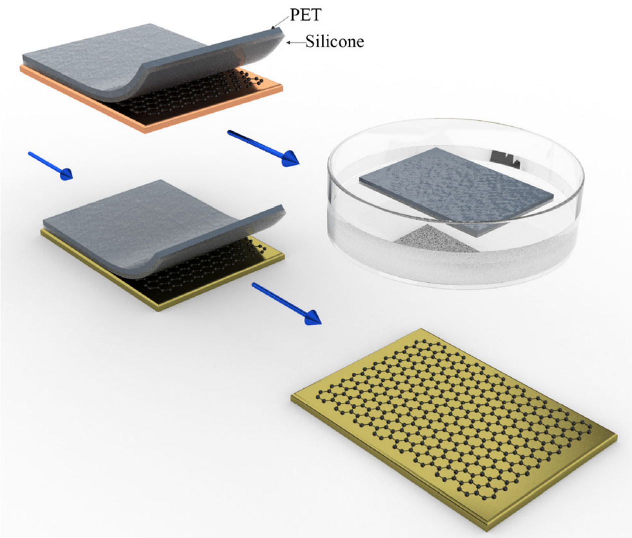


Figure 10 Dry transfer of CVD graphene using PET/silicone [33].

7 Non-polymer material as support

To avoid contamination concerning polymer residuals, methods have been developed without the use of a polymer altogether. For instance, rosin, a semi-transparent natural resin, was used as the transfer agent [82]. Rosin melts at 100–120 °C and solidifies at room temperature. In the reported procedure, rosin was spin-coated on CVD graphene from a 50 wt.% solution in ethyl lactate. The removal was done using acetone followed by banana oil. Prior to this, the sample was annealed at 40 °C for 1 h, followed by at 120 °C for 20 min to evaporate the residual water. This procedure may soften/liquify rosin which facilitated its subsequent removal by the solvents. The authors reported adequate support strength provided by the rosin film, and low surface roughness on the transferred graphene. A drawback of rosin is its acidity as the major components of rosin are resin acids such as abietic acid, which restricts its use, for example, in alkaline conditions. To overcome this limitation, an additional PMMA layer was spin coated on rosin/graphene/Cu film to prevent rosin from delamination in the alkaline electrolyte [83].

Schneider et al. developed a clever way to transfer CVD graphene using cyclohexane, by taking advantage of the temperature-dependent phase change of cyclohexane (Fig. 11(a)) [84]. In their experiment, cyclohexane was added to the CVD graphene/copper sample immersed in the etching solution (Fig. 11(b)). After the copper foil was dissolved, the detached graphene film came into contact with cyclohexane. When the temperature was lowered to 2 °C, water remained as a liquid whereas cyclohexane solidified which acted as the protective support layer to graphene just like the PMMA film. The solid cyclohexane was subsequently removed simply by raising the temperature above its melting point (7 °C) when cyclohexane eventually evaporated. Because the solid support was a solvent that can be removed by evaporation, contamination was greatly reduced. Nevertheless, care should be taken to

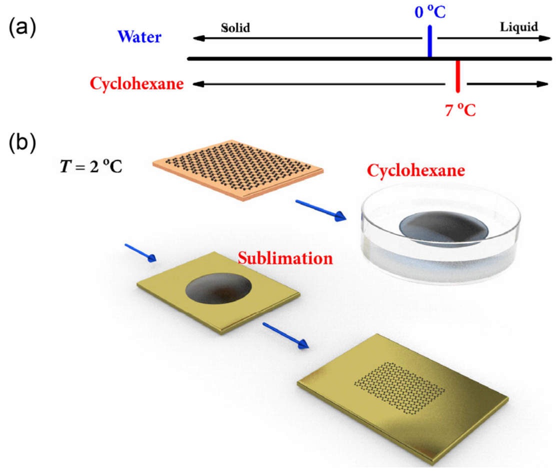


Figure 11 Graphene transfer aided by cyclohexane. (a) Temperature dependent phase changes of cyclohexane and water. (b) Biphasic transfer using cyclohexane. APS, ammonium persulfate, is an etchant for copper [84].

minimize physical damages to the graphene film during the washing and transfer process as the solid cyclohexane is not as mechanically strong as polymer films.

Camphor is another alternative to polymer-based protection. In the camphor-mediated transfer process, solution of camphor in chlorobenzene was coated on CVD graphene followed by etching the Cu foil. Removal of camphor was achieved by sublimation at room temperature for 1 h and at 90 °C for 5 min [85].

Paraffin can also be removed by sublimation, and has thus recently been used as an alternative to PMMA in CVD graphene transfer [86, 87]. Paraffin is a long-chain hydrocarbon with a melting point of ~ 45 °C. To use it as the protective layer, the melt paraffin was coated on CVD graphene, and removal was accomplished by sublimation at 80 °C for 8 h. An additional feature of paraffin is its thermal expansion property. Upon heating, paraffin expands and simultaneously stretches the graphene underneath. This releases the internal strain in graphene, removes wrinkles and flattens the graphene sheet as a result (Fig. 12).

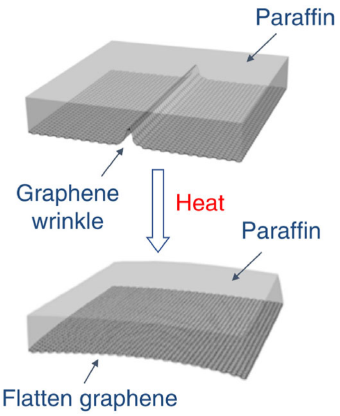


Figure 12 Paraffin as the protect layer in CVD graphene transfer. Thermal expansion of paraffin removes wrinkles and flattens graphene. Reprinted with permission from Ref. [86], © Leong, W. S. et al. 2019.

8 Reagent-free transfer

Methods have also been developed to transfer CVD graphene without the use of any transferring agents. In the example shown in Fig. 13, a sample holder was fabricated to assist the transfer of CVD graphene [88]. The graphene/Cu foil sample was placed within the confinement of the holder so that detached graphene would not float away after the Cu foil was removed. The free-standing graphene was lowered onto the substrate underneath by pumping out the liquid. The transferred graphene was reported to have low defects and residual contamination, as well as high carrier mobility characterized by Raman, XPS, sheet resistance and conductivity measurements. Another reagent-free method takes advantage of electrostatic forces to accomplish the transfer. In the example shown in Fig. 14, the target substrate was charged using an electrostatic generator so that the CVD graphene could adhere to the charged substrate through electrostatic forces [24]. If the attractive force is sufficiently strong, graphene will remain on the new substrate after etching away the Cu foil. Using this method, CVD graphene was successfully transferred onto silicon wafer and PET film, as well as several layers of graphene by repeating the transfer procedure. The target substrates are however limited to semiconductors and insulators as metals cannot be electrostatically charged and may also corrode in the etchant solution.

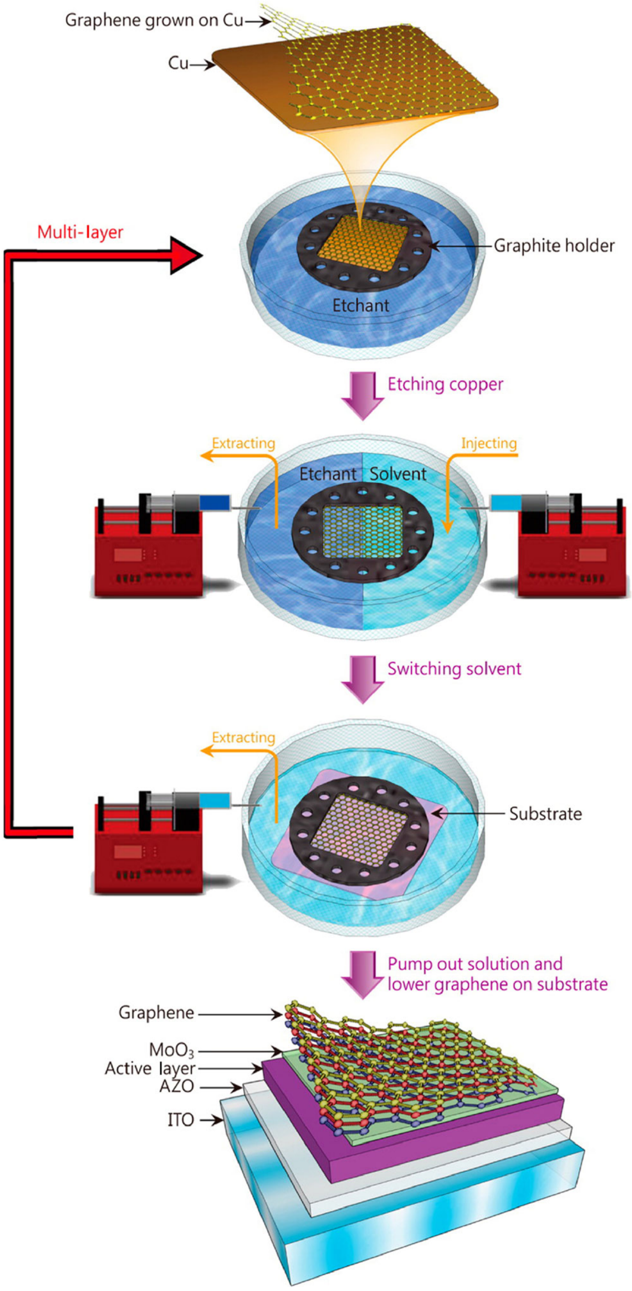


Figure 13 Polymer-free transfer of CVD graphene using a graphite holder (reprinted with permission from Ref. [88], © American Chemical Society 2014).

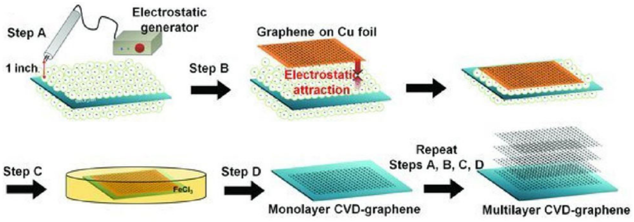


Figure 14 Polymer-free transfer of CVD graphene assisted by electrostatic forces (reprinted with permission from Ref. [24], © WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2013).

9 Removing amorphous carbons on CVD graphene prior to transfer

During CVD graphene growth, carbon species are generated from decomposition of the hydrocarbon precursor, producing graphene as well as the amorphous carbon byproduct on the graphene surface. These amorphous carbons can serve as anchoring sites to attract PMMA residuals and other contaminants, thus affecting the removal of PMMA. It has been shown that CVD graphene having the least amount of amorphous carbons gave the highest quality graphene and the least PMMA residuals after transfer [89]. In a recent report, the Liu group oxidized amorphous carbons with CO_2 by treating freshly-prepared CVD graphene with the CO_2 gas at 500 °C (Fig. 15) [90]. With this operation, the authors were able to remove amorphous carbons, and obtained graphene having minimal PMMA residuals after the transfer.

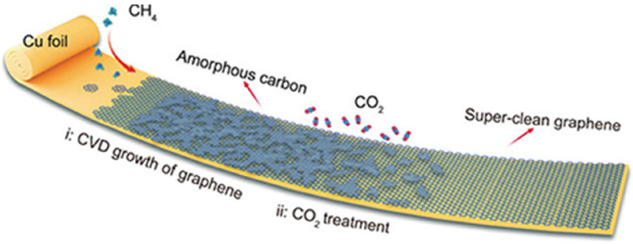


Figure 15 Removing amorphous carbons on CVD graphene with CO_2 prior to transfer (reprinted with permission from Ref. [90], © Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim 2019).

An alternative approach to reducing amorphous carbons was to use $Cu(OAc)_2$ instead of hydrocarbons as the precursor in the fabrication of CVD graphene [91]. $Cu(OAc)_2$ was first decomposed at 220 °C (~ 122 Pa) to generate the carbon source, which then reached the Cu foil surface to produce a clean graphene film (> 99% region) at 1,020 °C. Minimal PMMA residuals were found on this graphene surface after the transfer.

10 Conclusions

The availability of high-quality single-layer pristine graphene continues to be a critical technical challenge. CVD has become a popular technique to prepare graphene of relatively high quality at reasonable cost. However, the requirement of a transition metal catalyst in CVD graphene fabrication limits the scope of the substrate on which graphene is supported. As such, graphene needs to be transferred to a different substrate. The classic CVD graphene process requires a solid material to support the fragile graphene when the metal substrate is removed by wet etching. PMMA has been the material of choice for graphene transfer, providing the needed mechanical strength, resistance to metal etchants, optical transparency, and straightforward removal by a benign solvent like acetone. The procedure is straightforward to perform, carried out by spin coating a PMMA solution to form a thin film that is mechanically robust. Removing the film also seems to be straightforward, done by soaking the film in acetone which is an excellent solvent for PMMA. While this would have been sufficient for many occasions, for graphene however, the requirement is much more stringent as even a minute amount of contaminants would alter the superb properties of this 2D nanoscale material. In addition to its high specific surface area, the freshly prepared graphene is ready to adsorb any molecules or materials especially hydrophobic hydrocarbons in order to lower its high surface energy. As such, the transferred graphene surface is often contaminated with particles consisting of mostly PMMA fragments generated during the dissolution of the PMMA film. These contaminants are impossible to remove completely, causing issues in applications where the purity of graphene cannot be compromised.

The importance of this problem can be seen from the many techniques and methods that are subsequently developed by researchers in order to minimize contamination, and at the same time, to maintain the physical integrity of the sample. Of the methods that still use PMMA, the post heating treatment is the most common and relatively effective in reducing PMMA residuals. Substituting PMMA by other polymers, such as PS, was furthermore aided by the addition of a plasticizer to facilitate the removal of the polymer film. This approach, however, cannot overcome the inherent high surface energy of graphene which tends to absorb impurities regardless of the nature of the support material. Dry transfer uses a pre-prepared polymer film as the support, the adhesion of which should be sufficient to withstand the Cu etchant while at the same time readily to be peeled off afterwards. The challenge again is the complete removal of the polymer film from graphene as well as minimizing the damage to the graphene film during the operation. The use of a non-polymer transferring agent such as cyclohexane, rosin or paraffin faces similar challenges. In addition, as the protective film made of small molecule lacks the flexibility and mechanical strength like a polymer, it introduces additional technical challenges in preventing damages or folding of the graphene film. The reagent-free approach avoids the use of any transferring agents altogether. Whether it relies on electrical, mechanical or electrostatic forces, additional technical skills as well as careful handling are critical to ensure sample cleanliness and integrity.

The need for high-quality pristine graphene will continue to drive the development of new fabrication techniques and methodologies. In the context of transferring CVD graphene to a new substrate, the ultimate goal would be to obtain transferred graphene without introducing chemical contaminants or physical damages to the sample. Current approaches are still limited in the experimental scale and each method has its own advantages and shortcomings. There are needs for improvements and the development of completely new strategies. In this regard, in addition to eliminating contamination and sample damages, the procedures should also be reproducible and straightforward to operate.

Acknowledgements

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