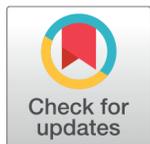


Large-scale Graphene Production and Transfer for Industrial Applications



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 OPEN ACCESS

Received: 02 December 2021

Accepted: 10 January 2022

Published: 30 January 2022

Citation: Avishan N, Hussain N, Nosheen F (2021) Large-scale Graphene Production and Transfer for Industrial Applications. *Materials Innovations* 2 (1), 15-25.

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Published By Hexa Publishers

ISSN

Electronic: 2790-1963

Compared to chemically derived graphene (Gr), chemical vapour deposition (CVD) grown Gr has better crystal quality and hence superior electrical properties, which render it applicable for next-generation electronic and optoelectronic applications including solar cells, photodetectors, imagers, sensors, etc. Though the excellent performance of CVD grown Gr based devices has been demonstrated on the lab scale, Industrial scale production of these devices is limited by reliable large-scale production and transfer of CVD grown Gr. In this review, we will summarize the latest developments on large scale CVD production of Gr and industrially applicable transfer methods.

Keywords: Graphene, Graphene Transfer, Industrial applications, Large-scale CVD growth

INTRODUCTION

Graphene (Gr), a representative of two-dimensional materials, possesses a unique set of properties including high mechanical strength, thermal conductivity, electrical conductivity and surface area.¹⁻⁴ Due to such unique properties, Gr has found application in electronics, optoelectronics, coatings, energy, environment, etc.⁵⁻⁹ Most of the applications of Gr are demonstrated on the lab scale, and industrial-scale production/fabrication of Gr based products is still a dream. The major bottleneck for the industrialization of Gr is its large-scale high-quality production and transfer.¹⁰

Graphene nanoflakes and Graphene oxides can be easily produced on large scale (tonn scale), but poor control over the production process and inherent limi-

tations of the processes used for the production of these materials, lead to a wide range of flake size, thickness, and structural defects, which limit the application of these materials to composites, conductive coating, and batteries.¹¹ For applications, which require extremely high-quality Gr, such as electronics and optoelectronics, chemical vapour deposition (CVD) grown Gr is more suitable as it produces Gr with fewer defects and hence superior electrical properties.¹² CVD grown Gr has been used for various electronic devices such as photodetectors, imagers, sensors, transistors, memory devices, etc.^{8,13-19} Although the record performance of these devices has been demonstrated on the lab scale, their large-scale production remains elusive, mainly due to limitations of large-scale CVD growth of Gr. Moreover, since CVD Gr requires the transfer of Gr from

metal substrate to the desired substrates, the lack of an efficient industrial transfer method for Gr is another major bottleneck. Recently, significant progress has been made regarding industrial-scale production and transfer of CVD Gr. In this review, we will summarize the recent developments in the production and transfer of Gr for industrial applications.

GRAPHENE SYNTHESIS

For commercial applications of Gr, the first step is to synthesize defect-free, cost-effective, and large-scale graphene. Graphene obtained from mechanical exfoliation is defect-free and high quality but cannot be scaled up. Chemically derived graphene oxide (GO) and reduced graphene oxide (rGO) can be cost-effectively produced on ton scales but contain significant structural damages which impede their use for electronic applications. Chemical vapour deposition (CVD) can produce high-quality graphene films (not as good as mechanically exfoliated Gr but better than chemically-derived GO) on a large scale and cost-effectively (chemically-derived GO still holds the advantage in terms of price and scalability), and is potentially more suitable for large scale electronic and optoelectronic applications

In a typical CVD process, a substrate is exposed to volatile carbon precursors, which decompose on (react with) the metal substrate surface to produce graphene layers. CVD graphene on metal substrates can grow either via precipitation or via surface-mediated reaction (Figure 1).^{12,20,21} In precipitation growth, at high temperatures, the carbon source decomposes on the metal to form carbon radicals, which then diffuse into the metal bulk. During the cooling, the dissolved carbon reaches supersaturation and segregates back onto the metal surface to form the graphene. Generally, graphene grown via this mechanism is multilayer and the exact number of layers depend on

the solubility of carbon in the metal and the cooling rate. Another important consideration for the precipitation mechanism is metal carbide formation. If the dissolved carbon makes a stable metal carbide, it is hard for carbon to be released from the carbide during the cooling process to form graphene. Hence, the limited availability of carbon during the segregation process, despite the high solubility of carbon, will form mono-layer graphene. In surface-mediated growth, Once the carbon source decomposes, it nucleates to form graphene islands which then may coalesce with other islands to form continuous graphene film. This type of growth is self-limiting and once the graphene fully covers the metal surface, the growth will stop and thus yield predominantly monolayer graphene.

Which mechanism dominates on a certain metal substrate depends on the solubility of carbon in that particular metal. Metals with low carbon solubility produce Gr (generally multilayer) via surface mediated mechanism while those with relatively high carbon solubility produce Gr (generally monolayer) via precipitation.¹² The solubility of carbon in various metals is given in table 1.

Table 1. Solubility of carbon in different metals

Metal	Carbon solubility at 1000 °C (at.%)
Co (0001)	3.41
Ni (111)	2.03
Cu (111)	0.04
Ru (0001)	1.56
Rh (111)	0.89
Ag (111)	0.01
Pd (111)	5.98
Re (0001)	4.39
Ir (111)	1.35
Pt (111)	1.76
Au (111)	0.01

A lot of progress has been made regarding lab scale synthesis of high-quality CVD graphene, but for integration of graphene with Si for commercial

purposes, large scale industrial production of high-quality Gr is more relevant to this chapter. Hence, here, we only focus on the current status and challenges of mass production of Gr.

Mass CVD production of graphene

Mass production of graphene includes scientific (temperature, pressure, precursors, selection of substrates, reaction time) as well as engineering considerations (macroscopic reaction, heat-transfer, and mass-transfer processes). Both continuous (roll-to-roll (R2R)) and batch processes are widely reported for mass production of graphene. Here, we explain and compare advantages and disadvantages of both of these two processes.

Batch processing of graphene

Bae et al.²² were first to report large scale batch-to-batch synthesis of graphene (30 inch in size) using CVD technique (Figure 2(A)). To avoid the inhomogeneity caused by the temperature gradient, a 7.5-inch quartz tube wrapped with a copper foil was inserted and suspended inside the 8-inch quartz tube. The copper foil was treated at 1000 °C for 30 min in hydrogen atmosphere to increase the grain size of copper from few micrometres to 100 μm to grow better crystal quality Gr. Resultantly, sheet resistance as low as 125 at 97.4% transmittance was achieved. Though this low-pressure CVD approach was shown to be scalable for large area Gr synthesis, continuous feeding of the catalyst foil into a low-pressure reactor, severe evaporation of copper catalyst and the requirement of a vacuum system compatible with flammable precursor gases are major obstacles for large scale industrial growth. To overcome these challenges, Vlasiouk et al.²³ reported an atmospheric pressure CVD growth of large-area (40 inch) graphene.

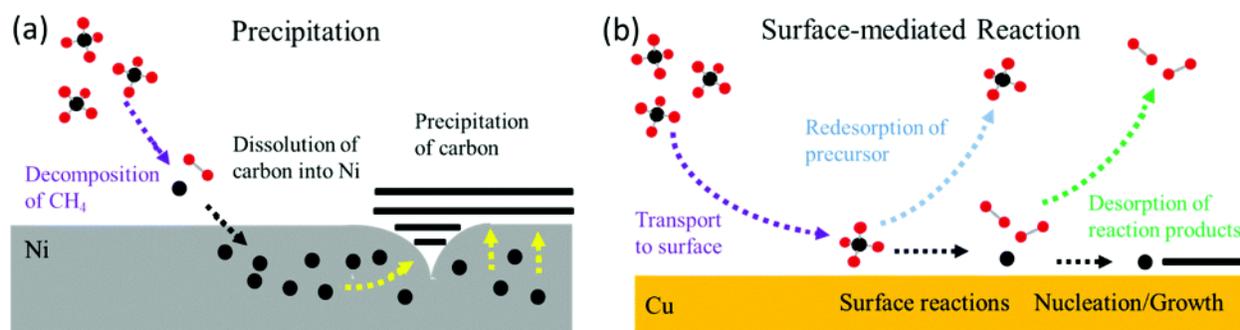


Figure 1. Schematic of the growth mechanism of graphene via (a) precipitation and (b) surface-mediated reaction.²⁰ Reprinted with permission from ref 20. © 2015, Wiley-VCH.

To increase the production rate of Gr, stacks and helices of metal substrates (Ni and Cu) have been used. Stacks and Helices can be packed compactly inside the furnaces and hence we can grow more graphene in a single batch (Figure (2B)).²² While stacked, distance between two stacks is important, as ideally should be greater than the mean free path of the gas to avoid inhomogeneity. It has also been found that due to small distance between the copper stacks allowed a high collision frequency of methane molecules with the Cu catalyst, which greatly enhanced the growth rate of graphene. Since copper foils are flexible, they can be fitted into a glass chamber in various geometries which can allow us to grow more Gr per batch. Four of proposed geometries are presented in the (Figure 2(C&D)).^{12,23}

Continuous processing of graphene

Continuous roll-to-roll (R2R) processing is a common industrial standard for flexible electronics and can also be applied for large scale Gr growth. Comparatively, it is easy to obtain uniform and high quality in static growth conditions of B2B process. R2R growth has its own unique challenges that include continuous and stable rolling, thermal uniformity, softening of Cu foil at high temperature, and tension control of the Cu foil. Hesjedal was the first to report the continuous growth

of graphene films on Cu foil using R2R atmospheric-pressure CVD (Figure 3(a)), where long Cu strips were continuously rolled out into the reaction chamber for heating, graphene growth, and cooling processes.²⁴

However, the quality of Gr was not good due to the atmospheric pressure conditions. Deng et al.²⁷ improved the quality of R2R produced graphene by using low-pressure CVD and reported an optimized rolling speed of $\approx 5 \text{ cm min}^{-1}$ for very high homogeneity of single layers. They also used bubble transfer method, which allows to reuse the copper foils for graphene growth, significantly reducing the process cost. An obvious disadvantage of above reported studies is that these do not allow the annealing of copper foil as copper is directly fed to reaction chamber and the furnaces do not have any separate annealing chambers. Annealing is important as it removes the surface oxides and also increases the grain size of Cu, which is important for high quality Gr growth. Polsen et al.²⁸ made important contribution in this regard by combining the annealing and growth in a continuous rolling process by using concentric tube CVD (CTCVD).

As mentioned above, Cu strips soften at high temperatures, and as a constant tension force is applied to copper for stable continuous rolling, so this tension force cause necking in soft copper foils at higher temperatures. To avoid this necking process either growth temperature needs to be low-

ered (such as in microwave enhanced CVD) or tension need to be optimized at higher temperatures to limit the necking process. Zhong et al.²⁹ reported a vertical CVD chamber where Cu foil was suspended on its own weight which allowed free contraction and expansion of Cu with the temperature changes without causing any significant structural distortions in Cu (Figure 3(b)).

LARGE SCALE GRAPHENE TRANSFER

After the Gr growth, for its subsequent applications, Gr needs to be transferred from the catalytic metal surface (Cu, Ni, etc.) to the desired substrate (e.g., Si, polymers) for its subsequent applications. While significant progress has been made toward large scale and high crystal quality Gr growth, an industrial scale transfer method is still lacking. While the range of lab-scale transfer methods for Gr and other 2D materials has been demonstrated successfully, however, most of these methods cannot be applied on industrial scale. An industrial-scale transfer method should be continuous, clean, cost-effective, stable, easily scalable, and most importantly fully automatic. While principles to obtain a clean Gr transfer on industrial scale are the same as on the lab scale, however, other conditions (cost, stability, automation, etc.) are different from lab-scale and need to be carefully designed for large scale transfer.

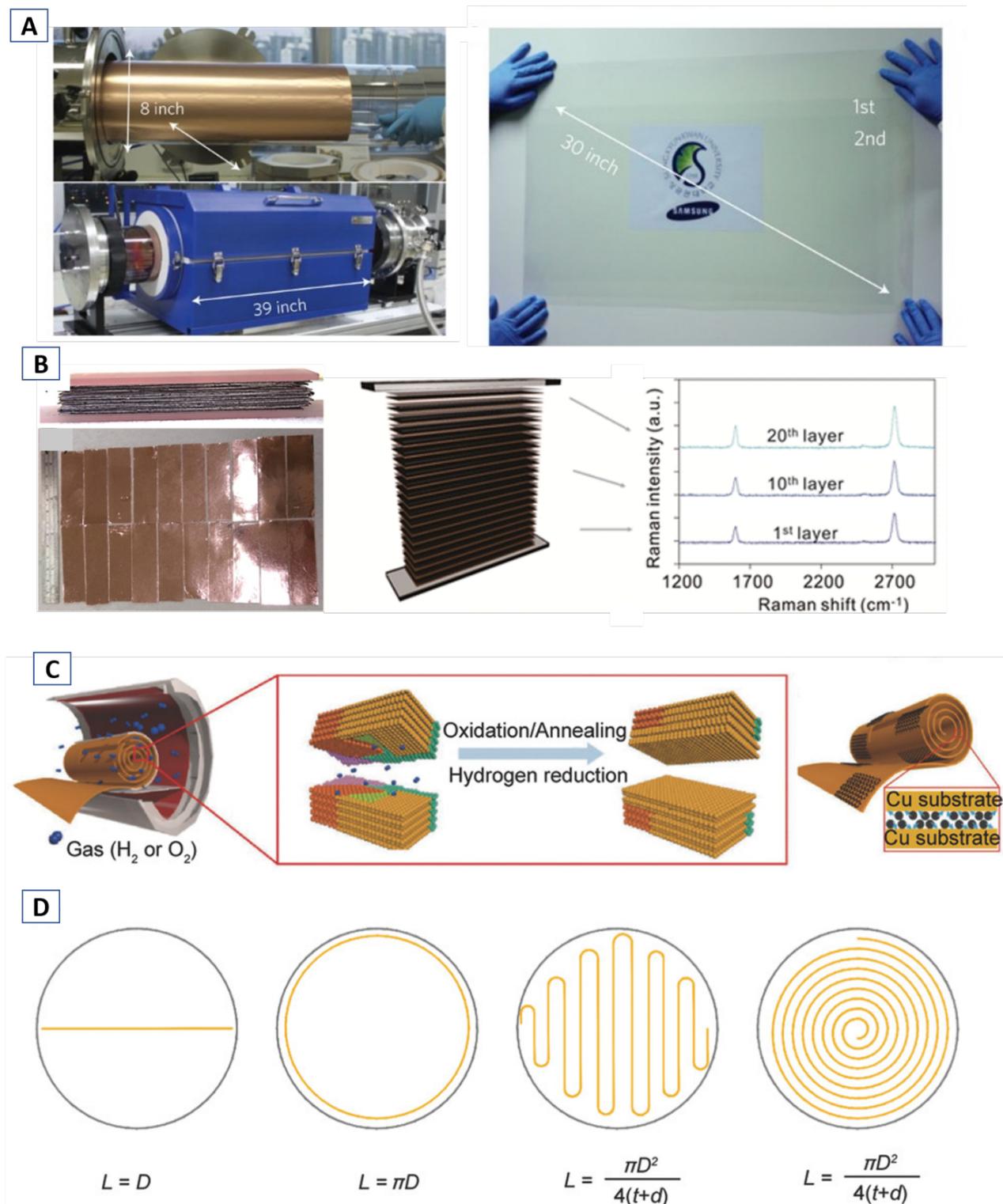


Figure 2. (A) Pictures of a Cu foil wrapped on a quartz tube and a large tube furnace.²² (B) Photograph of a stack of Cu foils and Gr grown on them. Schematics of Cu stack and Raman spectra of selected layers.²⁵ (C) Schematic of a roll of Cu foil inside a tube.²⁶ (D) Schematics of plates, rolls, stacks, and helices structures of Cu foil.¹² (A) Reprinted with permission from ref 22. © 2010, Macmillan Publishers Ltd. (B) Reprinted with permission from ref 25. © 2016, American Chemical Society. (C) Reprinted with permission from ref 26. © 2016, Wiley-VCH. (D) Reprinted with permission from ref 12. © 2019, Wiley-VCH.

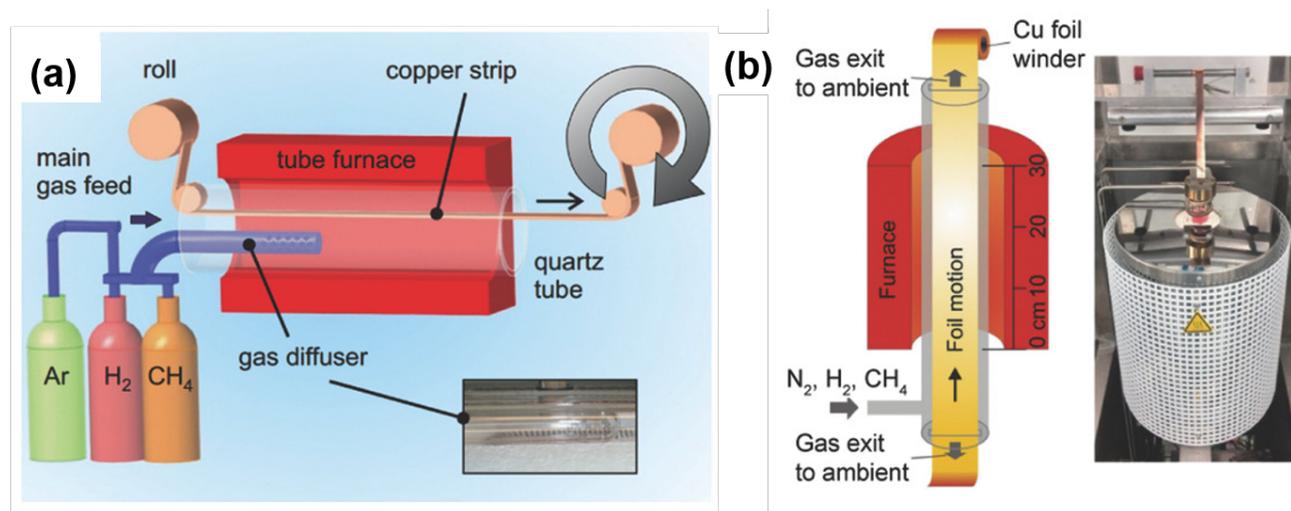


Figure 3. (a) Schematic of the R2R APCVD.²⁴ (b) Schematic and picture of the R2R OPCVD.²⁹ (a) reprinted with permission from ref 24. © 2011, AIP Publishing (b) reprinted with permission from ref 29. © 2016, AIP Publishing.

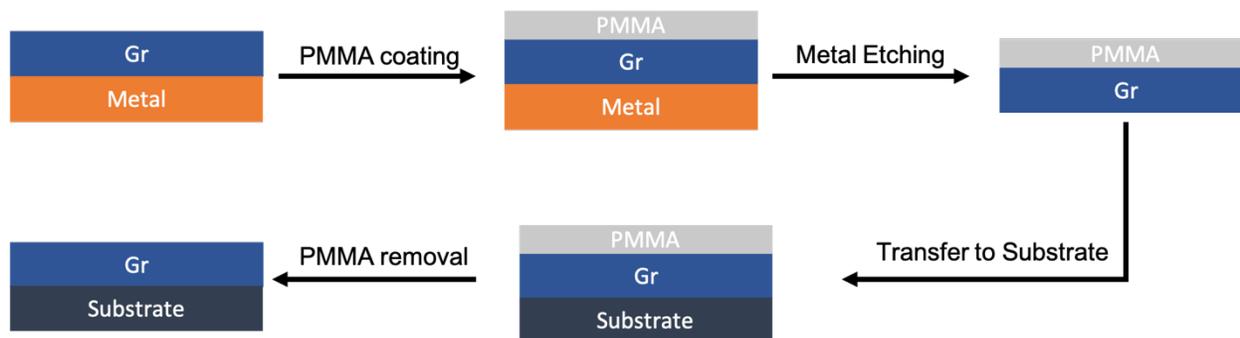


Figure 4. Typical PMMA based graphene transfer method involving PMMA coating, metal etching, transfer to substrate and PMMA removal in the solvent.

Transfer techniques of Gr can be divided into etching based and non-etching-based techniques. We will summarize the principles, advantages and disadvantages of both of these techniques in the following sections.

Etching based transfer techniques

Ryu et al.³¹ has used thermal release tape as a support layer for the R2R etching based transfer method, demonstrating a pilot-scale automated production. Though the method was as quick and clean, this method produced Gr with cracks and wrinkles. To improve the transfer process, X. D. Chen et al.³²

proposed a PET/Silicone support layer. As silicone has low surface energy, so adhesion between silicone and Gr was relatively low, hence delamination process was easier which produced better quality Gr.

PMMA based transfer technique is the most commonly used technique for the transfer of Gr grown on metallic substrates.³³ In a typical method, PMMA as a carrier/support layer is coated on the Gr/metal stack, the metal substrate is etched in an etchant solution, PMMA/Gr stack is transferred to the desired substrate, and PMMA is finally removed in the acetone. The process flow of the transfer is shown in Figure 1.

The process in Figure 4 can be further optimized by changing the support layer, etching solutions and adding rinsing steps to remove the contaminations. Various etchants have including HNO_3 , FeCl_3 , and $(\text{NH}_4)_2\text{S}_2\text{O}_8$ have been employed for etching the metal substrate.³⁴ FeCl_3 is considered a milder etching agent but can dope Gr with metal atoms, which is considered a disadvantage for the CMOS process. HNO_3 is a more reactive etchant but releases of nitrogenous gases is a major drawback. $(\text{NH}_4)_2\text{S}_2\text{O}_8$ is another alternate metal-free etchant, it's relatively slow, and is generally considered a contamination-free etchant. However, some reports suggest that sulfur-based compounds may

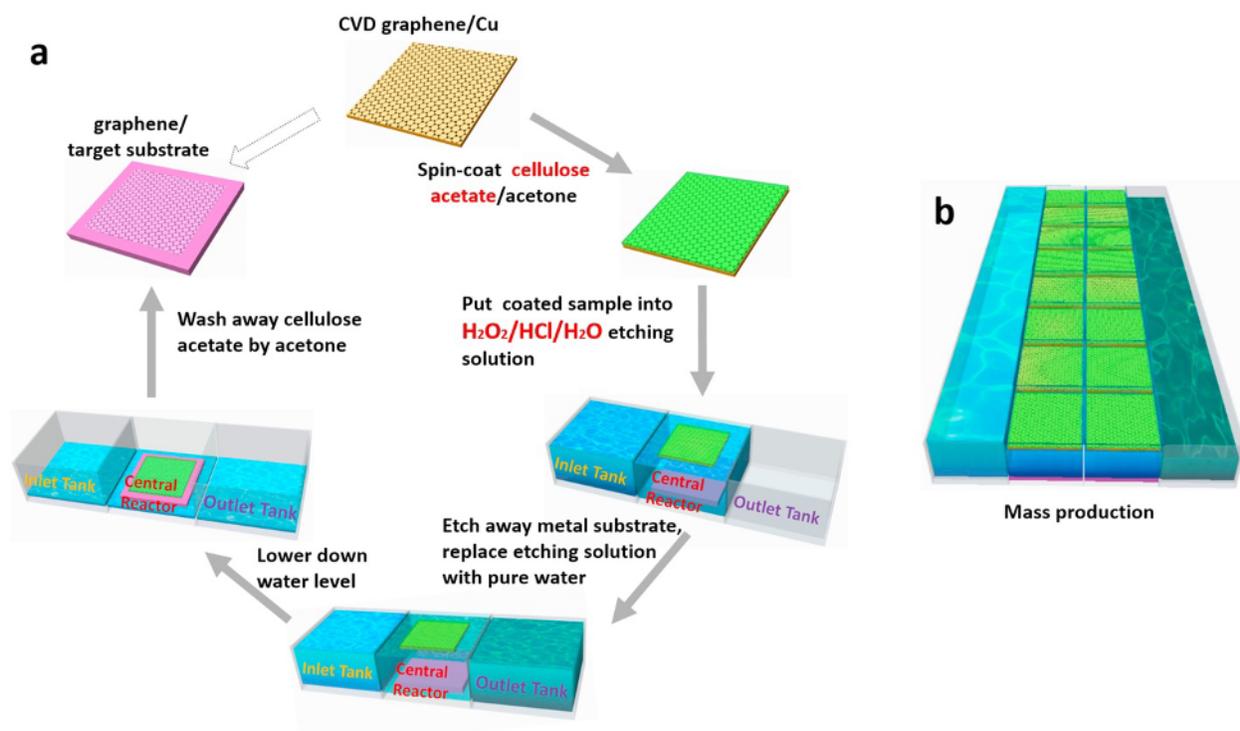


Figure 5. (a) Schematics of the cellulose acetate assisted transfer method of Gr. (b) Schematics of the reactor for transfer of Gr onto multiple substrates at the same time at industrial scale.³⁰ Reprinted with permission from ref 30. © 2016, Elsevier.

dope the Gr. Other etchants with potential for industrial applications include FeCl₃/HCl, CuCl₂ and H₂O₂.^{31,35,36}

Different support layers can also be used for industrial-scale transfer. M. Chen et al.³⁰ have used cellulose acetate as a support layer, which not only helps avoid contaminants associated with PMMA and other support layers but is also cost-effective and environment friendly (see Figure 5). Moreover, cellulose acetate-based transfer is claimed to be wrinkle- and crack-free. The etchant used in this method was H₂O₂/HCl/H₂O, which also helped accelerate the etching process. This method was demonstrated to be applicable on large scale.

Etching based methods have also been demonstrated on large scale for a direct transfer on the substrate, where no support layer was used. In such methods, generally, an intermediate layer is used which need not be removed after the transfer. Finally, the metal substrate is removed through the

etching process. Epoxy is one such intermediate layer, which has been commonly used.³⁷ Figure 7 demonstrate one such process Cu/graphene was bonded to a PET substrate by R2R roller lamination.³⁶ After removing Cu by spraying CuCl₂ etching solution, a 100 m-long graphene/epoxy resin/PET flexible film was obtained. It must be noted that this method is applicable only for a few substrates (mostly for flexible substrates).

Etching free transfer techniques

One big disadvantage with etchant-based transfer techniques is that metal substrate is lost and cannot be recovered/used, which seriously increases the cost of the process. Loss of the metal substrate will become even more serious if the Gr has grown on the noble metal (Pt, Pd) substrates. Hence, there was a need to find transfer methods where the metal substrate can be recovered and can be reused for CVD growth of Gr. The main principle of

etching free method is to weaken the interaction between the metal substrate and the Gr, so that Gr can be peeled off easily. Hot water can accelerate the oxidation of Cu substrate, and oxidized Cu has weak bonding with Gr, hence, Gr will be peeled off conveniently (Figure 8(A)).^{38,39} This method has been successfully demonstrated for continuous R2R transfer of Gr. Another method called the “bubble method” has also been used for etching free transfer where through electrochemical reaction (hydrolysis) Hydrogen gas bubbles are produced between Cu and Gr to strip the Gr off (Figure 8(B)).⁴⁰ A strong bubbling reaction may damage the surface of Gr, hence the reaction rate needs to be controlled.

While hot water and bubble methods produce etching free Gr, however, these methods need extra equipment and procedures. Nong et al.⁴¹ have reported a roll-to-roll (R2R) dry transfer process for large-scale graphene grown by chemical vapour deposi-

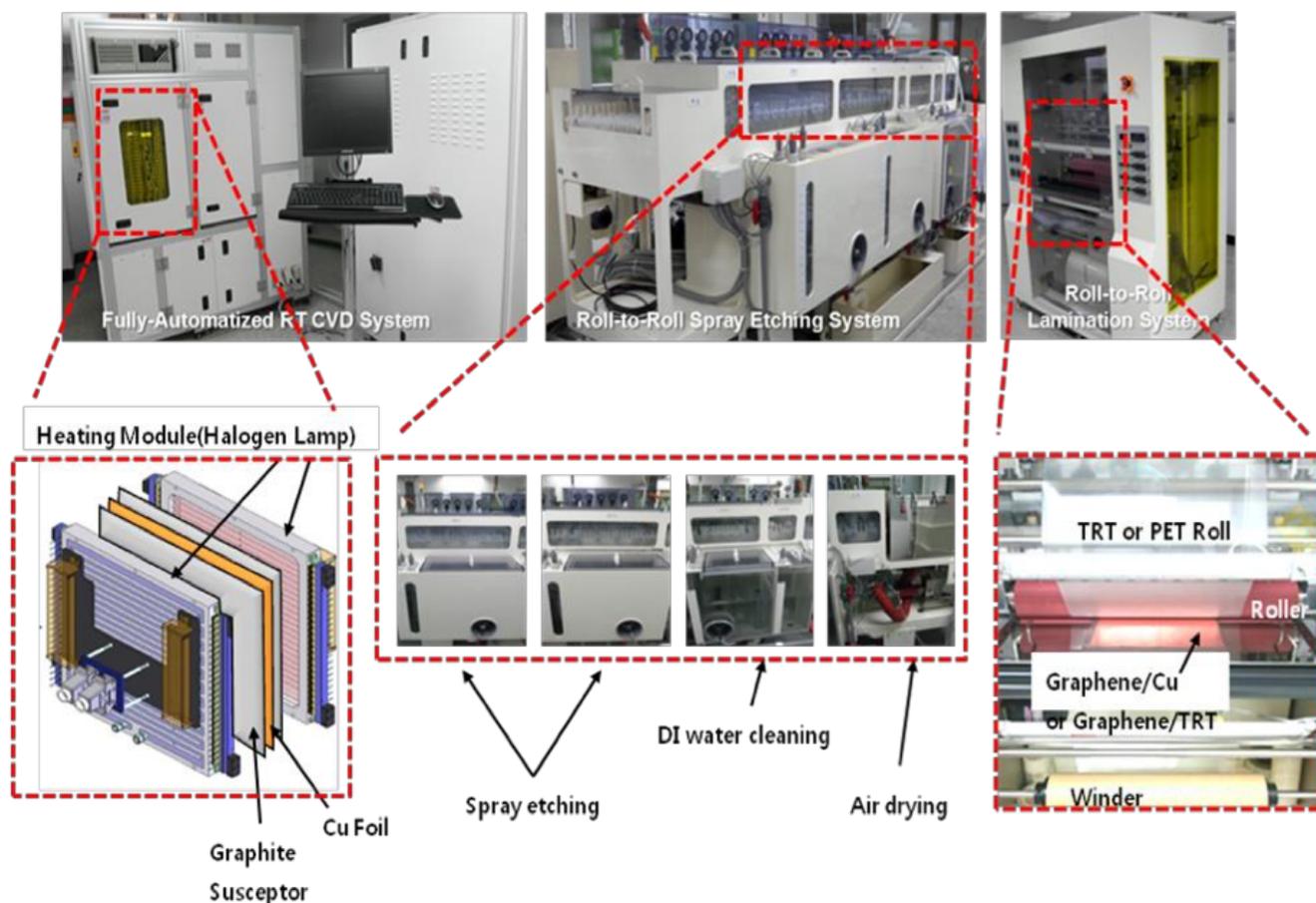


Figure 6. Photographs of pilot-scale RT-CVD, roll-to-roll etching, and lamination systems.³¹ Reprinted with permission from ref 31. © 2014, American Chemical Society.

tion. In this report, CVD-grown monolayer Gr on copper foil was laminated with polyethylene terephthalate/ethylene vinyl acetate (PET/EVA) film. Mechanical Peeling was performed with simultaneous control over peeling tension and speed (Figure 9). Though etching free methods are promising as these methods avoid etching of the substrate, hence certain metallic contaminations, coming from etchant solutions, to Gr can be avoided. However, in most cases, using these methods, Gr can only be transferred to flexible substrates only.

FUTURE OUTLOOK AND CHALLENGES

B2B and R2R are the most commonly used methods for the production of large-scale Gr growth. Both methods have their advantages and disadvantages. The quality of B2B is good but for continuous large-scale production, R2R has better scope and potential. However, the quality of R2R needs to be improved. For further improvements in both B2B and R2R processes, industry scale CVD equipment need to be produced. Moreover, fundamentals of the CVD process including source gases, choice of better substrate, CVD chamber gas pressure, etc also need to be further optimized to grow good quality Gr at a large scale. For integration of Gr with commonly used substrates

(Si, polymers, etc.) in electronics, Gr should be grown directly on these substrates. However, the high temperature can damage the underlying substrate. Hence, to find a suitable low-temperature Gr growth method, which can be easily scaled-up is essential.

For Gr transfer, focus should be on to find transfer free strategies, where Gr can be directly grown on target substrates. However, it is still not favourable to grow good quality Gr on non-metallic substrates. Si is the most commonly used substrate in the electronic industry. Direct growth of Gr on Si is hampered by poor crystal quality and the requirement of high temperature for Gr growth. As mentioned above, high temperatures can significantly change the properties of Si and devices built on it. Hence, so far the

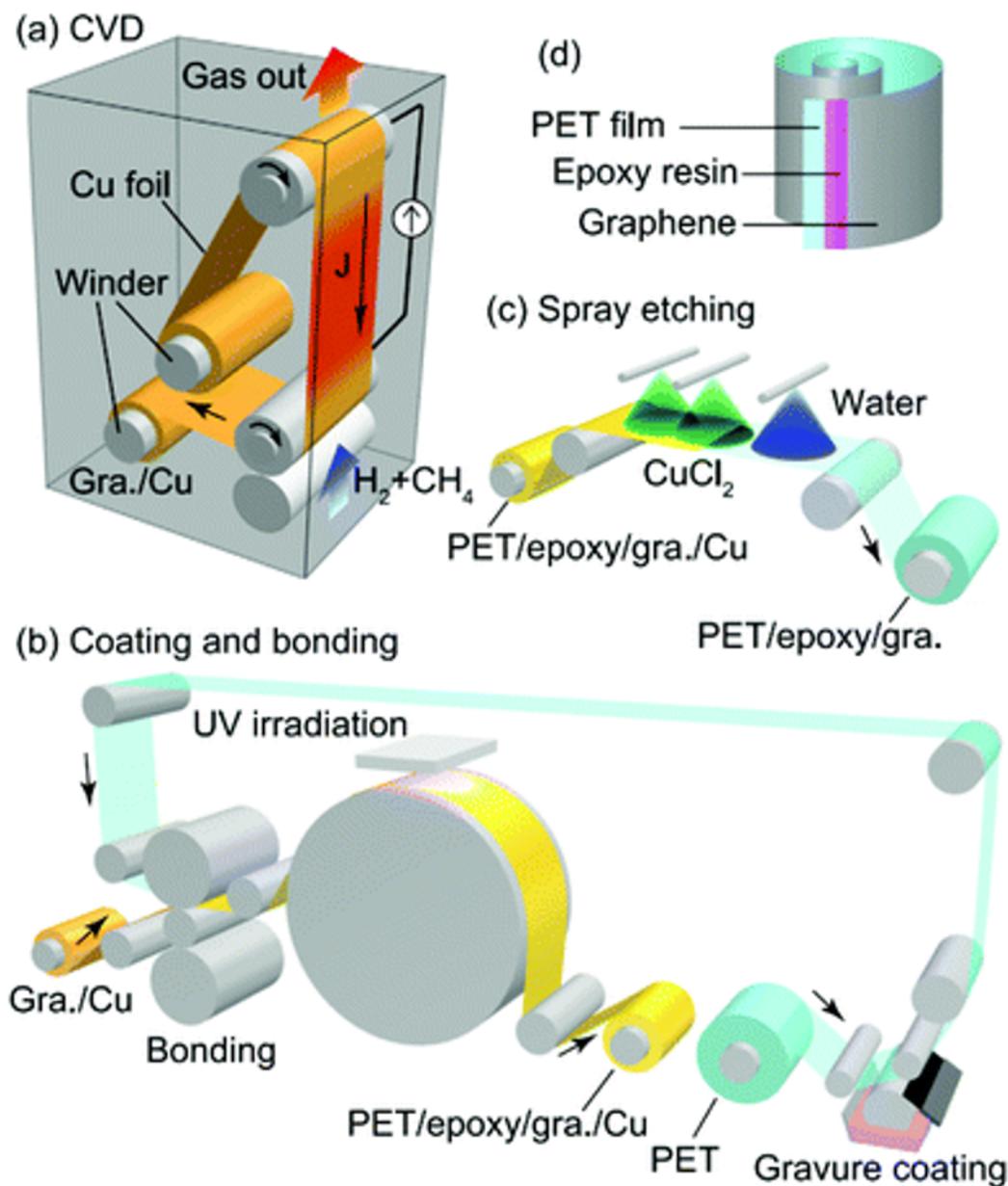


Figure 7. Diagram of (a) Graphene synthesis, (b) R2R Gr Transfer, (c) Cu foil etching and (d) graphene/UV cured epoxy resin/PET structure.³⁶ Reprinted with permission from ref 36. © 2013, AIP Publishing.

best solution is to grow Gr separately on the metallic substrates and transfer it to the Si. For that, we need to improve the current transfer techniques. Current challenges for existing transfer techniques include avoiding contaminants, making the process cost-effective, scaling the processes to industrial-scale, stability of the process, and full automation. Automation is per-

haps the biggest challenge, as existing methods are labour-intensive and quality of transferred Gr vary person to person and lab to lab.

ACKNOWLEDGMENTS

This publication/paper has been produced benefiting from the 2232 International Fellowship for Outstanding

Researchers Program of TÜBİTAK (Project No: 118C214). However, the entire responsibility of the publication/paper belongs to the owner of the publication/paper. The financial support received from TÜBİTAK does not mean that the content of the publication is approved in a scientific sense by TÜBİTAK.

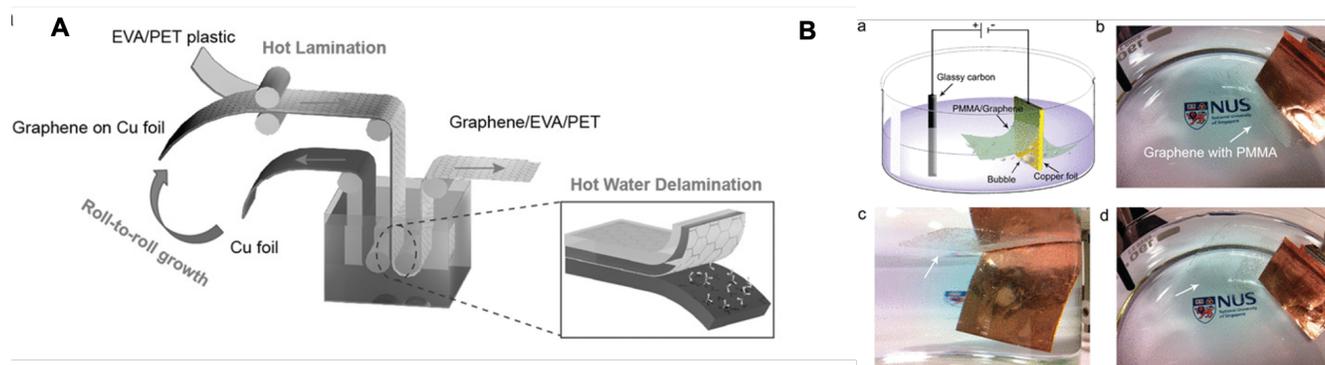


Figure 8. (A) Schematic illustration of the R2R delamination of copper and graphene onto EVA/PET substrate.³⁸ (B) (a) Schematic diagram of electrochemical exfoliation. (b–d) Optical images show the peeling process of the PMMA/Gr stack from the Cu foil.⁴⁰ (A) Reprinted with permission from ref 38. © 2015, Wiley-VCH. (B) Reprinted with permission from ref 40. © 2011, American Chemical Society.

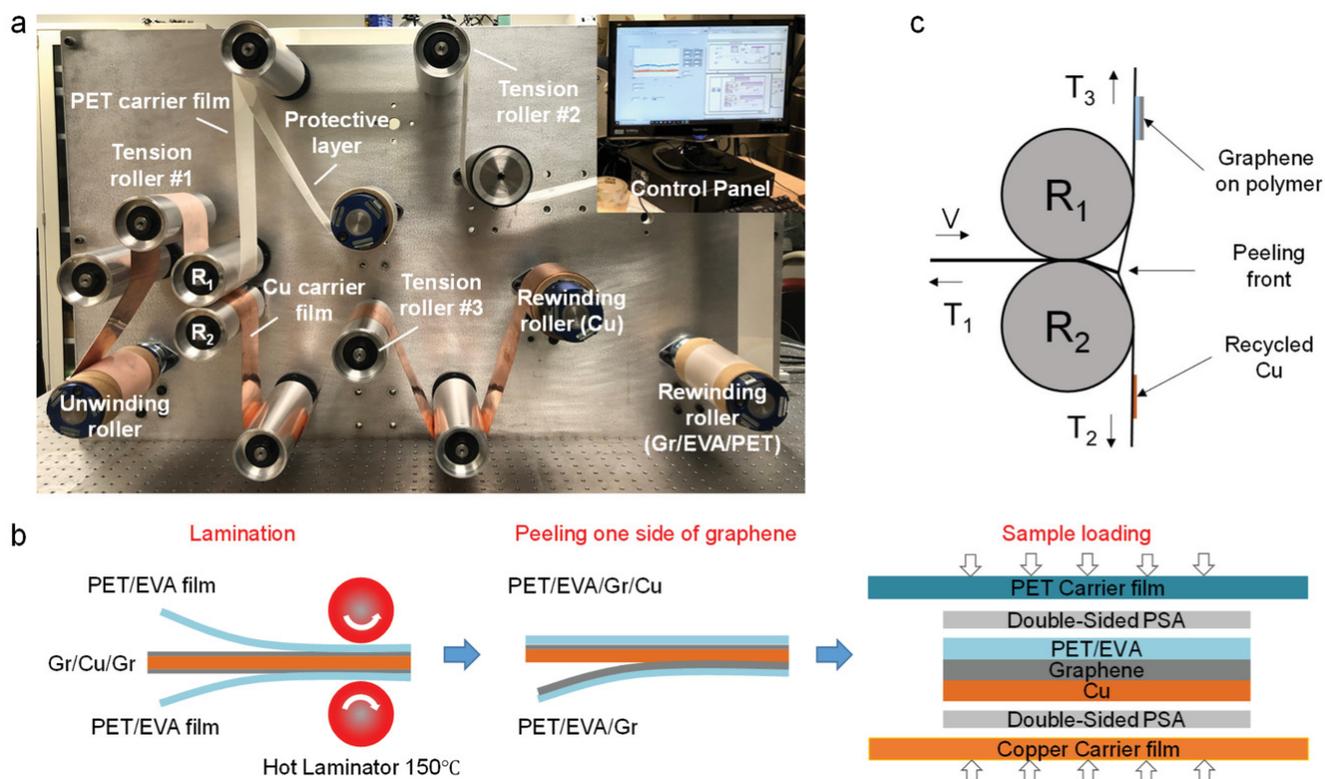


Figure 9. (a) Control panel of R2R Gr transfer system. (b) Sample lamination and loading. (c) Mechanical peeling front, where V is the linear film speed, and T_1 , T_2 , and T_3 are the tension forces on the webs before and after peeling.⁴¹ Reprinted with permission from ref 41. © 2022, Wiley-VCH.

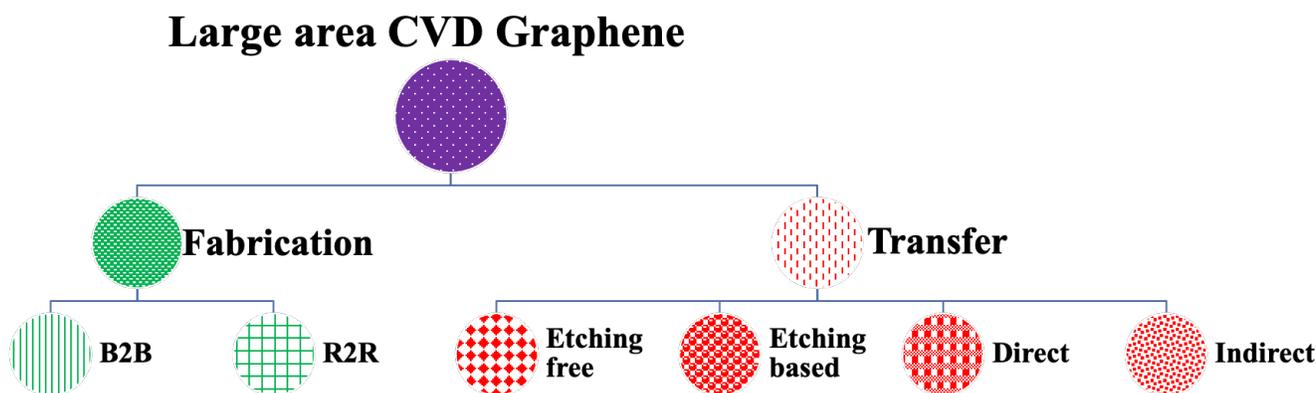


Figure 10. Summary of large-scale Gr fabrication and transfer techniques.

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