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Direct transfer of graphene onto flexible substrates

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In this paper we explore the direct transfer via lamination of chemical vapor deposition graphene onto different flexible substrates. The transfer method investigated here is fast, simple, and does not require an intermediate transfer membrane, such as polymethylmethacrylate, which needs to be removed afterward. Various substrates of general interest in research and industry were studied in this work, including polytetrafluoroethylene filter membranes, PVC, cellulose nitrate/cellulose acetate filter membranes, polycarbonate, paraffin, polyethylene terephthalate, paper, and cloth. By comparing the properties of these substrates, two critical factors to ensure a successful transfer on bare substrates were identified: the substrate's hydrophobicity and good contact between the substrate and graphene. For substrates that do not satisfy those requirements, polymethylmethacrylate can be used as a surface modifier or glue to ensure successful transfer. Our results can be applied to facilitate current processes and open up directions for applications of chemical vapor deposition graphene on flexible substrates. A broad range of applications can be envisioned, including fabrication of graphene devices for opto/organic electronics, graphene membranes for gas/liquid separation, and ubiquitous electronics with graphene.

CVD graphene | glass transition | sheet resistance

Graphene has been the focus of intense research due to its unique electrical, mechanical, optical, and thermal properties (1–9). So far, most work exploring these properties has been conducted on rigid substrates such as Si/SiO₂ or quartz. This choice is understood to be convenient for electronics applications involving, for example, transistors or photoelectric devices (1, 3–7). Because of graphene's inherent flexibility, it is also advantageous to develop its applications on flexible substrates. These applications include photonics, optoelectronics, and organic electronics such as in solar cells, light-emitting diodes, touch screen technology, photodetector devices, and membranes for molecular separation in gases or liquids (1, 10–13). Nevertheless, at present, there are only limited reports for graphene transferred onto flexible substrates, and most of these transfer graphene onto a substrate using polymethylmethacrylate (PMMA) as an intermediate membrane (14, 15). In this work, we use a simple lamination technique and report on the transfer of graphene onto a variety of flexible substrates. By comparing the characteristics of these substrates, we identified the important factors that are needed to have a successful transfer onto bare substrates. In addition, for the substrates that are not suitable for such a transfer, we have found PMMA can either be used as a surface modifier or as a glue to ensure a successful graphene transfer. Furthermore, we investigate multilayer transfers and demonstrate that these multilayers enable large area conducting sheets to be placed on most substrates investigated in this work.

The most commonly used procedure for transferring chemical vapor deposition (CVD) graphene onto different substrates is to spin-coat PMMA on the graphene/metal surface (16, 17). Afterward, the metal is chemically etched away and the PMMA/graphene membrane is scooped onto the target substrate (17). Finally, the PMMA is removed either via high-temperature annealing (~350–500 °C) or dissolving in acetone (or acetone vapor) (16, 17). This PMMA-based technique has some drawbacks: the complete removal of PMMA residues is challenging (18), and most flexible

substrates either dissolve in acetone or cannot withstand the annealing temperature. Other PMMA-free techniques have been investigated, including using thermal release tape as the transfer membrane (10), directly transferring onto polydimethylsiloxane (PDMS) (12, 19), or using particular functional groups to attach graphene to other flexible substrates (20, 21). Nevertheless, the types of substrates investigated have been limited [polyethylene terephthalate (PET), PDMS, or polystyrene], and such techniques often leave other unwanted residues, which can degrade the quality of the graphene (10, 12, 19, 21).

Fig. 1 shows a schematic illustration of the direct transfer process used in this work, which entails hot/cold lamination followed by chemical etching of the Cu substrate. The hot/cold indicates whether or not heat is applied during the lamination. The lamination provides the pressure necessary to achieve close contact between the graphene/copper interface and the substrate so that the graphene sheet remains attached to the substrate during the etching process.

The target substrates studied in this work were polytetrafluoroethylene (PTFE, commonly referred to as Teflon) filter membrane with a 0.2- μ m pore size, PTFE thread sealant tape, clear rigid polyvinyl chloride (PVC), polished polycarbonate (PC), paraffin, cellulose nitrate/cellulose acetate (CN/CA) filter membrane with a 0.2- μ m pore size, PET films, paper, and cloth (cotton). The substrates were cleaned using isopropanol and blow-dried with a nitrogen gun, except for the paper and cloth, which were just dusted with a nitrogen gun. After the CVD growth, the graphene/copper/graphene (G/Cu/G) stack was cut and pressed against the target substrate to provide initial graphene–substrate contact. A protective sheet of weighing paper was put on top of the substrate/G/Cu/G and this stack was sandwiched between two PET films (Fig. 1A) and put into a 330-

Significance

We investigated a lamination technique for directly transferring graphene onto various flexible substrates, which does not require using polymethylmethacrylate (PMMA) as an intermediate transfer membrane. Our studies reveal that the method is most effective on hydrophobic substrates with low glass transition temperature. For substrates like paper or cloth that do not meet these criteria, a polymer such as PMMA can be used as a surface modifier or as an adhesive to ensure successful transfer. Having graphene on substrates such as paper or cloth will open up wide opportunities for ubiquitous or wearable electronics, and we anticipate our work will have significant impact on the research community.

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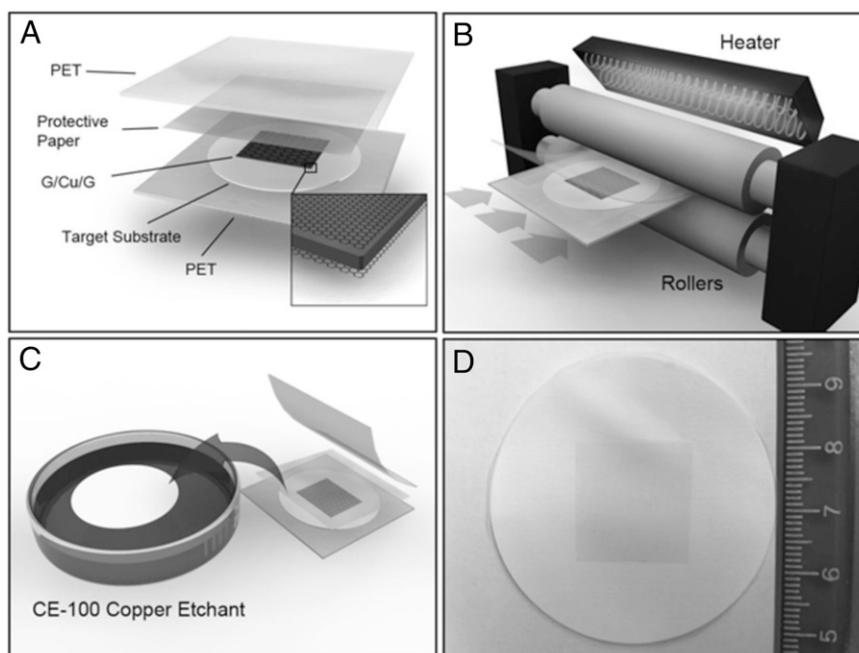


Fig. 1. Schematic diagram of the direct transfer technique via lamination. (A) Copper foil with CVD graphene grown on both sides (G/Cu/G) is placed in between the target substrate and the protective paper. This stack is then put between two PET films. (B) The PET/substrate/(G/Cu/G)/paper/PET sandwich is inserted into the hot/cold lamination machine. (C) The PET films and the protective paper are then removed and the remaining substrate/graphene/copper stack is floated on a copper etchant solution for 15 min. (D) The graphene/substrate is rinsed in DI water and blow-dried with nitrogen. In this picture, graphene is on a Teflon filter. The ruler is scaled in centimeters.

SCL hot/cold laminator machine, as shown in Fig. 1B. In this step, the PET films were used to prevent the copper foil from directly contacting the rollers in the lamination machine and to lend mechanical robustness to the stack. The protective paper was used to prevent the copper foil from adhering to the PET films, which become viscoelastic when the laminator is heated to temperatures above 100 °C. When applicable, the temperature was set to be above the substrate's glass transition temperature (T_g), as shown in Table 1. This laminator machine also provides the pressure necessary to mold the substrate to the morphology of the G/Cu/G.

Paraffin (Parafilm) is soft at room temperature and has a very low melting point. Applying heat during lamination causes the film to melt and stick strongly to the protective weighing paper; thus, room-temperature (commonly called cold) lamination was applied to paraffin. Teflon membrane samples were tested both above the PTFE T_g and at room temperature. After lamination, proper adhesion was verified by visually checking for gaps between the substrate and graphene/copper foil. If gaps were found, the lamination procedure was repeated. After lamination, the substrate/G/Cu/G stack was placed in a copper etchant solution (FeCl₃-based) for 15 min, as shown in Fig. 1C. Finally, the

samples were rinsed in deionized (DI) water and blow-dried with a nitrogen gun. Note that the only chemical necessary is the copper etchant, that most of the materials such as the PET films can be reused, and that the entire process takes less than 30 min.

Interestingly, the graphene sheet can almost always be visually identified after the transfer procedure to the target substrates, as shown in Figs. 1D and 2. One can identify a region of color contrast between the graphene layer and the respective

Table 1. Target substrates used in this work and their respective T_g values

Target substrate	Glass transition temperature (T_g), °C	Target substrate	Glass transition temperature (T_g), °C
Polycarbonate	145	Teflon filter	115
PVC	85	Teflon tape	115
PET	70	Parafilm	Undefined
PET with PMMA	~70	Paper	Undefined
CN/CA	Undefined	Cloth	Undefined

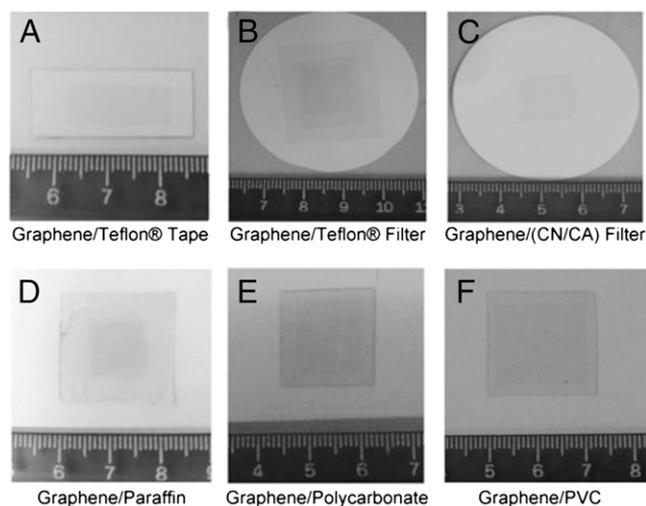


Fig. 2. Photograph of graphene transferred to different flexible substrates. (A) Monolayer graphene transferred to Teflon tape. (B) Multilayer (three layers) graphene on a Teflon filter by transfer three times. (C) Graphene on a CN/CA membrane filter. (D) Multilayer (two layers) graphene on a paraffin film. (E) Graphene on a polycarbonate substrate. (F) Graphene on a PVC substrate. The rulers are scaled in centimeters.

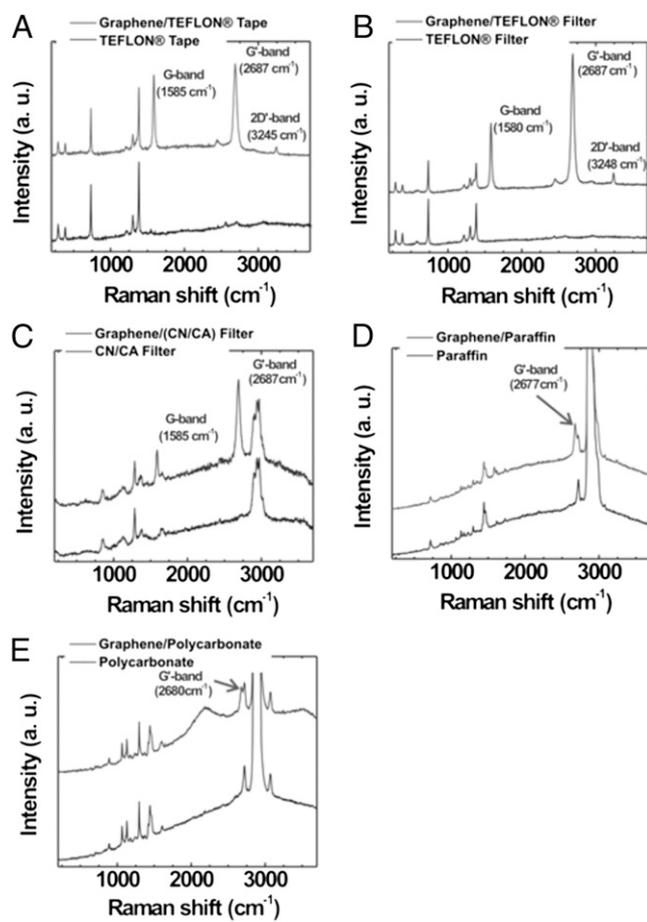


Fig. 3. RRS, comparing the spectra of the target substrates (bottom solid lines) and the spectra of the graphene/substrate system (top solid line) (A–E). The graphene Raman features, as well as their peak frequencies, are accordingly indicated. The G bands in *D* and *E* are very small; please refer to Figs. S1 and S2 for zoomed-in spectra.

substrate, which gives us initial evidence for the transfer's success. For opaque substrates, this color contrast is very pronounced, as shown in Fig. 2*A* and *B* for the graphene/Teflon tape and filter, respectively, and Fig. 2*C* for the graphene/(CN/CA) film. This color contrast is not as evident for the translucent substrates, but a larger region is still distinguishable, as shown in Fig. 2*D–F*.

To obtain multiple layers, one can simply repeat the direct transfer process using the substrate on which graphene has already been transferred. Here, we show a triple transfer on a Teflon filter (Fig. 2*B*) and a double transfer on paraffin (Fig. 2*D*). The differences in gray-scale between the monolayer and multilayer regions suggest that subsequent transfers were successful. Even though only two examples are shown, the procedure worked consistently on all other target substrates.

The direct transfer procedure, as described earlier in the text, worked without any additional steps for five out of the nine different kinds of substrates investigated: Teflon tape (Fig. 2*A*), Teflon filter membrane (Fig. 2*B*), paraffin (Fig. 2*D*), PC (Fig. 2*E*), and PVC (Fig. 2*F*). The basic technique did not work consistently for CN/CA membranes (Fig. 2*C*) and did not work for bare PET, paper, and cloth. Explanations for why the technique is ineffective on these substrates and solutions to the problems will be presented later in this article. In ref. 22 it was reported that graphene can be directly transferred to a PET substrate with a similar lamination procedure as the one discussed here, which contradicts our result. However, PET is an encompassing name for a class of materials with varying physical and chemical properties depending on processing conditions (i.e., what is the filler, what is the surface functionalization, etc.). Thus, it is likely that the PET used in ref. 22 has different properties than the one being used in this work.

To further evaluate and confirm the transfer result, resonant Raman spectroscopy (RRS) was used to characterize the graphene on target substrates. RRS has been shown as an efficient technique to understand the electronic and vibrational properties of carbon and nanocarbon materials (23, 24). In particular, RRS has been extensively used to determine the number of layers of a graphene flake (24), to evaluate its quality as well as to determine if it is doped or not (23, 25). In this work, all of the measurements were performed with a neodymium-doped yttrium aluminum garnet laser that emits at 532 nm (2.33 eV) with an acquisition time varying from 5 to 20 s, depending on the quality of the output signal produced from each sample. In all of the measurements, the laser power was conveniently chosen to avoid damage to the sample or heating effects. To evaluate the overall quality of the transferred graphene films, which present relative large areas (~ 1 cm²), RRS measurements were performed at several different locations on the same sample both at single-layer graphene, multilayer graphene, and also the substrate. Consistent results as shown in Fig. 3 have always been observed. Indeed, the authors have chosen representative spectra from each sample.

By comparing the Raman features of bare substrates and substrates with graphene, the presence of monolayer graphene was verified on the following samples (here, Raman G and G'-band features were used to identify and evaluate graphene): Teflon tape (Fig. 3*A*); Teflon filter (Fig. 3*B*), CN/CA (Fig. 3*C*); paraffin (Fig. 3*D*), and PC (Fig. 3*E*). In the paraffin case (Fig. 3*D*), the Raman measurements were accomplished in both the mono- and the double-graphene layers regions. One might observe that, in the case of the graphene/PC system, although the G-band feature appears as a small perturbation of the substrate spectrum (Fig. S2), the G'-band feature appears quite strong, which satisfactorily guarantees the presence of the graphene sheet. The detailed Raman spectra zoomed in the G and G'-band regions for graphene on paraffin and PC substrates are shown in SI Text. We could not perform Raman measurements on PVC because the high reflectivity of the graphene/PVC film created a strong backscattered signal that saturated the CCD camera.

Sheet resistance measurements were also carried out to evaluate the success of the transfer. Table 2 shows representative sheet resistances values of graphene transferred onto different

Table 2. Sheet resistances of the transferred graphene layers

Target substrate	Sheet resistance, Ω per square	Target substrate	Sheet resistance, Ω per square
Polycarbonate	$1,890 \pm 309$	Teflon tape, transfer one time	Not conductive
PVC	$1,440 \pm 151$	Teflon tape, transfer two times	$1,250 \pm 174$
Teflon filter, transfer one time	Not conductive	Paraffin	$2,920 \pm 191$
Teflon filter, transfer two times	$35,000 \pm 10,500$	PET with PMMA coating	$1,210 \pm 187$
Teflon filter, transfer three times	$3,610 \pm 542$	Cloth with PMMA coating	812 ± 97
Paper with PMMA coating	301 ± 10	CN/CA with PMMA coating	172 ± 18

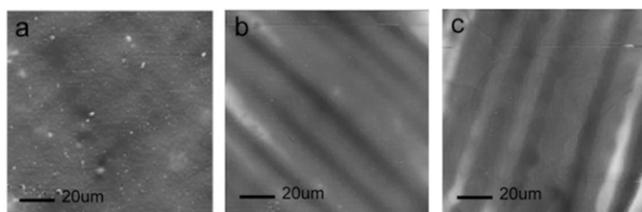


Fig. 4. AFM images of (A) PVC before transfer; (B) PVC after applying the transfer procedure; and (C) graphene/copper foil before transfer. The similarities between B and C provide evidence that the substrate is molded into the morphology of the graphene/copper surface for a good contact.

substrates. On porous substrates, such as Teflon tape and Teflon filter, multiple transfers are required to obtain a measurable sheet resistance. The measurements were performed using a home-built four-point probe station. The resistance values obtained here are several times higher than typical values obtained with rigid substrates (26) or reported by Bae et al. (10). This will be discussed later.

First, we discuss the factors that contribute to a successful transfer on bare substrates. The substrates in this work can be categorized into three different groups: (i) substrates on which a successful and fully reproducible transfer was observed, such as Teflon filter, Teflon tape, paraffin, PC, and PVC; (ii) substrates on which the transfer is inconsistent, such as CN/CA; and (iii) substrates in which the transfer was unsuccessful, such as PET, paper, and cloth. We identified the two most important factors that contribute to a successful transfer on bare substrates and these factors are as noted in the following two sections.

Large Surface Contact Area Between the Substrate and Graphene Achieved by Molding the Substrate to the Graphene/Copper Morphology.

Our observations show that a successful transfer requires close contact between graphene and the substrate, which is consistent with the fact that short-range van der Waal forces are responsible for interactions between them. Therefore, it is necessary to mold the substrate to the graphene/copper morphology through some mechanism. Thermoplastic polymers, such as PVC, PC, and PTFE, can undergo a phenomenon known as glass transition—if these plastics are heated to their glass transition temperature (T_g), they turn into a viscoelastic state and can be easily molded. With this in mind, the lamination technique is effective in maximizing the contact area for thermoplastics because it heats the

substrate past T_g and applies the necessary pressure to mold the substrate to the graphene/copper surface morphology. Comparing the atomic force microscope (AFM) profiles of the copper foil with graphene grown on its surface and the AFM profiles of the substrate after transfer (see Fig. 4, in which PVC is used as an example), it can be seen that the substrate is indeed molded to conform to the surface of the G/Cu/G stack. To exemplify the importance of heating the substrate past T_g , the transfer onto PC was not successful when the lamination machine was heated to only 100 °C, which is less than T_g for PC, but was successful when the temperature was raised to 150 °C, a temperature slightly higher than the T_g for PC. In this work, we were limited by both the maximum temperature of the lamination machine and the rate of heat transfer. For PC, which has a relatively high T_g , it was necessary to feed the stack through the laminator several times because the machine could not apply sufficient heat with just one pass. Hence, for our experimental conditions, relatively low T_g s generally resulted in easier transfer. Consequently, the sheet resistance measured on PC ($T_g = 145$ °C) was higher than that on PVC ($T_g = 85$ °C), as shown in Table 2. Substrates that do not have a well-defined glass transition point, such as CN/CA, were difficult to transfer onto (without the PMMA glue). Paper, cloth, and CN/CA do not have a glass transition temperature, making it hard to mold them to the graphene on copper surface. Paraffin is already very moldable at room temperature so the transfer was successful without any heating.

Substrate's Hydrophobicity. In order for the graphene to be transferred onto the substrate, contact must be maintained throughout the etching process. The particular PET substrate used in this work has a very low T_g of 70 °C and good contact was easily achieved during lamination. However, surface roughness, the type of the filler, or the manufacturer's surface treatment causes it to be quite hydrophilic (Fig. S8). As a result, during the etching process, water molecules can easily permeate between the PET and the G/Cu/G stack, resulting in loss of contact between the graphene and substrate (Fig. 5A). Indeed, most of the recent works in the literature that have succeeded in transferring graphene onto PET used some additional mechanism to improve the graphene/substrate adhesion. For example, Han et al. used ethylene-vinyl acetate as a binder between graphene and substrate (20). To validate the hydrophobicity hypothesis, we spin-coated PMMA, which is hydrophobic, onto PET. Contact angle measurements are shown in Table S1. After coating, transfer was successful using our technique. Note this still avoids the disadvantages

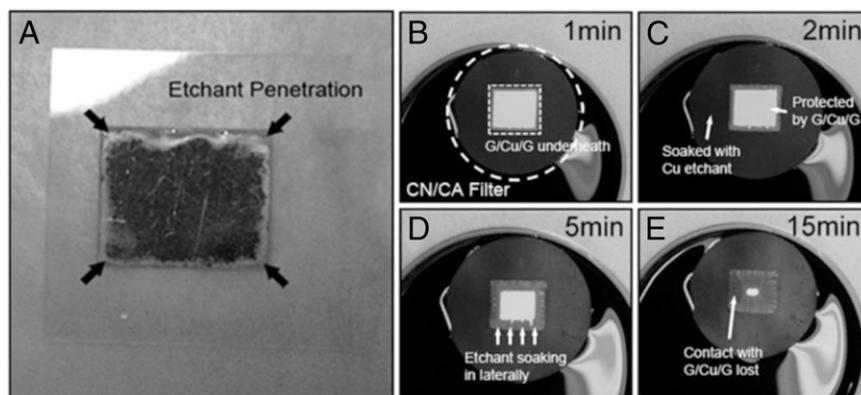


Fig. 5. (A) G/Cu/G on PET after 2 min in FeCl_3 etchant. Because the PET used in this work is hydrophilic, the etchant laterally penetrates (see the bright borders in the figure) between the PET and G/Cu/G, resulting in the loss of contact around the edges. In some cases, the etchant penetrates the entirety of the interface and the G/Cu/G falls away from the target substrate. (B–E) G/Cu/G/CN/CA stack floating on Cu etchant, showing similar lateral penetration. In the center region, the G/Cu/G stack prevents the etchant from soaking the filter from underneath (C). However, etchant still seeps into the dry region from the periphery (D) and contact is eventually lost (E).

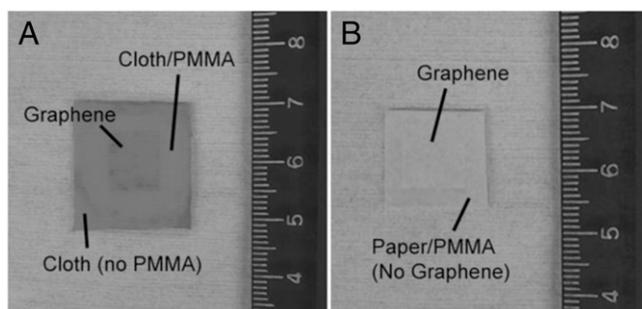


Fig. 6. Photographs of graphene on (A) a piece of cloth and (B) regular A4 paper. A drop of PMMA was placed in the center of the cloth, so the edges soaked up more FeCl_3 etchant than the middle, and is therefore darker. In the case of the paper, the entire surface was uniformly coated with PMMA but the graphene offers some protection from the etchant, resulting in more color contrast.

of the standard PMMA transfer procedure because the exposed side of the graphene is still free of PMMA residue.

A similar technique can be applied to achieve transfer onto paper, CN/CA, and cloth: A drop of PMMA is placed on the substrate before pressing the G/Cu/G stack onto it and, after lamination, the stack is baked at 80°C to allow the PMMA to dry before etching the Cu. A larger drop is needed for paper or cloth because these substrates soak up PMMA, and therefore more PMMA is needed to ensure close contact to the G/Cu/G surface. Furthermore, PMMA has a low glass transition temperature, so coating paper and cloth with the PMMA makes them artificially more moldable. Here, PMMA acts more as glue than as a surface modifier because it is directly responsible for the adhesion between the graphene and the substrate. Fig. 6 shows graphene

transferred onto a piece of cloth and a piece of paper using the aforementioned method. Using this PMMA-aided transfer method, large-area conductivity was obtained on all substrates (Table 2). We note that the sheet resistance varies by orders of magnitudes across the different substrates and layers numbers; this point is discussed in *SI Text* (Table S2).

Moreover, the success in transferring multiple layers relies directly on the fact that graphene is highly hydrophobic (27, 28). After transferring the first layer, the substrate is coated with graphene, making it hydrophobic for subsequent transfers. Thus, we assert that the technique can be extended to an arbitrary number of layers, given that the first transfer works. Another potential application of graphene on flexible substrates is the fabrication of graphene membranes for separation processes such as gas separation or desalination (11, 13, 29). Numerous theoretical works have been presented on this subject, although there are many challenges involved in fabricating a graphene membrane, such as the creation of pores of specific sizes and a high-quality transfer of graphene onto a porous support substrate. The substrate must be porous so it will not offer resistance for the mass flow after permeation through the graphene membrane. Flexible substrates are easier to handle and therefore more suitable for practical applications.

The porous substrates used in this work, such as the Teflon and CN/CA filters, require additional comments. Even though the Raman signals are strong (Fig. 3A, B, and F), SEM images (Fig. 7A and B) show that the transferred graphene layers are highly discontinuous. Although the Teflon filter meets both requirements, being hydrophobic and having a low T_g (115°C), its surface is so porous that contact cannot be achieved at all points. During the copper etching step (with aqueous etchant), and/or during the drying process, the graphene regions that are suspended will likely be broken and collapse due to the surface tension. This explains why a measurable sheet resistance cannot be obtained on

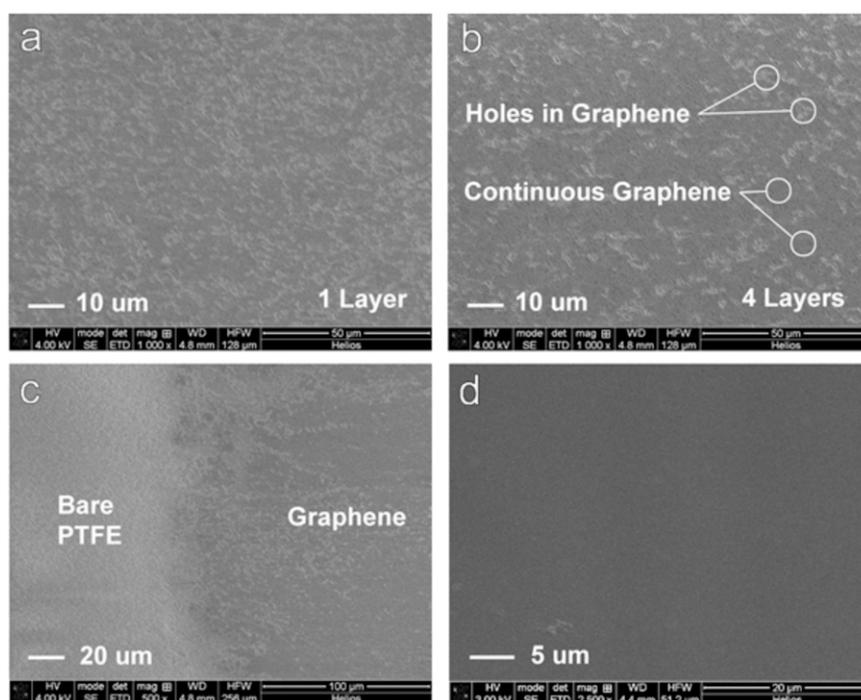


Fig. 7. (A) SEM images of one-layer graphene on a PTFE filter. The film appears to be discontinuous and therefore nonconductive. The blurriness is due to charging. (B) SEM image after transferring four layers of graphene onto a PTFE filter using the aforementioned multiple transfer procedure. The coverage improves, which is consistent with the drastic decrease in sheet resistance. (C) SEM image of the edge between bare PTFE and PTFE with graphene. (D) SEM image of polycarbonate with graphene; it can be seen that polycarbonate has a flat and nonporous surface. The contrast in all SEM images has been artificially increased for better clarity.

Table 3. Summary of results for the various substrates used in this work

Target substrate	Easily moldable	Hydrophobic	Conducting film obtained on bare substrate	Conducting film obtained with PMMA coating
Polycarbonate	Yes	Yes	Yes	N/A
PVC	Yes	Yes	Yes	N/A
PET	Yes	No	No	Yes
Paraffin	Yes	Yes	Yes	N/A
Teflon filter	Yes	Yes	Yes	N/A
Teflon tape	Yes	Yes	Yes	N/A
Paper	No	No	No	Yes
Cloth	No	No	No	Yes
CN/CN	Yes	No	Partial	Yes

these filter substrates with a single transfer. Transferring multiple layers improves the coverage (Fig. 7B) and makes the film conductive macroscopically but there are still many holes present even after four layers. Therefore, to obtain a continuous graphene film for membrane application in the future, special care must be taken in the etching/drying step (for example, supercritical drying should be used instead of simply drying in air) to prevent the suspended graphene regions from breaking and collapsing.

Further SEM examinations were carried out for the other flexible substrates, and it was found that Teflon tape is also porous, similar to Teflon filter (Fig. S7). PVC, PC, paraffin, and PET are nonporous (Fig. 7D and Figs. S3–S5). Thus, porosity of the substrate is also an important consideration if transferring a continuous layer is desirable. The results for the CN/CA filter also merit special discussion. Even though CN/CA is neither hydrophobic nor does it have a well-defined T_g , transfers could be achieved, albeit inconsistently (Fig. S8). We hypothesize that even though the filter does not enter a viscoelastic state, it is soft enough so that the pressure from the lamination machine is sufficient to achieve good contact (similar to paraffin). The observation that good transfer can be achieved on the Teflon filter even with cold lamination supports this conjecture. Even though

CN/CA is hydrophilic, the rate of lateral penetration is quite slow (Fig. 5 B–E). Thus, we often observe that graphene is only transferred onto the center of the filter. Table 3 summarizes our results for the various substrates.

With the studies carried out in this work, it was found that moldability and hydrophobicity are critically important properties that determine whether or not it is possible to transfer graphene onto a bare substrate via lamination. For substrates that do not possess these identified characteristics, like PET, paper, or cloth, surface modification (e.g., coating with PMMA) can be used to improve the success of the transfer. Moreover, large-area conductivity was obtained on all substrates on which transfer was successful. The investigation carried out here brings forward the capabilities to obtain graphene on various flexible substrates, and is anticipated to open opportunities for the applications of graphene.

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