

Camphor mediated Graphene Transfer without Washing in Organic Solvent.

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Abstract:

Transfer of a monolayer of chemical-vapor-deposition (CVD) grown graphene from one substrate to another normally requires a transfer agent. This transfer agent will subsequently be washed away with an organic solvent in a process that can potentially destroy the structural integrity of a graphene film, particularly, a graphene film occupying a large area. To bypass this washing step, we have successfully used camphor for transferring a monolayer of graphene to a target dielectric substrate over an area in excess of 10 mm². A layer of camphor was first deposited either by spin coating or drop coating onto a graphene layer that had been grown onto a copper surface by CVD. The copper substrate was then etched away, whilst the remaining camphor/graphene bilayer was placed onto a SiO₂/Si substrate. Finally, the camphor remaining on the camphor/graphene/SiO₂/Si was sublimed into a vapor. The graphene/SiO₂ stack was then examined by microscopic characterization, spectral characterization and electrical characterization. The results of our examination suggest that the proposed method can guarantee a clean and damage-free graphene transfer. The graphene film fabricated on a SiO₂/Si using the proposed method is superior in structural quality to the graphene obtained via other polymer mediated methods. In the case of a large area graphene, an average sheet resistance of approximately 360-1000 Ohm per square was observed.

Keywords: Camphor, sublimation, Graphene, Transfer, Chemical vapor deposition

1. Introduction

Graphene is a two dimensional structure with an excellent electrical conductivity, a high transparency, a high flexibility, an extremely high mechanical strength and a good chemical stability[1]. Because of these features, it is increasingly being seen as a candidate for implementing the next-

generation flexible thin-film electronics devices[2], including organic photovoltaic cells[3] and organic transistors[4]. To integrate a graphene film into these electronics devices, a layer of graphene is first grown onto a metal substrate (which can be copper, nickel or platinum) by chemical vapor deposition (CVD)[5-10]. The graphene film will eventually be transferred from the metal substrate to another device-specific substrate [11, 12], such as SiO₂/Si and polyethylene terephthalate (PET). Since graphene is atomically thin and highly transparent, the transfer process cannot be carried out without a support layer which protects the graphene film from cracking. In recent years, many materials have been reportedly attempted as a support layer for graphene transfer but little progress has been made. These materials include small organic molecules [13] and macromolecular polymers [14, 15]. Macromolecular polymers are often used as a support layer for graphene transfer because they offer sufficient support to a graphene film without cracking [16]. However, due to their low solubility in any known solvent and their strong interaction with graphene, most of the known macromolecular polymers cannot be completely washed away without leaving polymeric residues on the surface of the graphene film after the process of graphene transfer [10]. Polymethylmethacrylate (PMMA) is one of the most commonly used transfer agent with such a problem [17-20]. Following a graphene transfer, it is not uncommon for a large amount of PMMA residues to be left along with many other defects on the surface of a graphene film [21]. Although rigorous rinsing in acetone followed by thermal annealing may help remove some of the PMMA residues, the process of rinsing not only destroys the structural integrity of the graphene film but also induces inevitable roughness on the graphene surface [22]. This roughness not only degrades the optical quality of graphene, but also decreases the mobility of charge carriers, which in turn increases the overall sheet resistance, limiting the applications of graphene in optoelectronics [21, 23]. Because of this reason, conventional graphene transfer approaches involving a macromolecular polymeric transfer agent are not appropriate for integration of a large area graphene film into electronics devices [13]. In addition to the macomolecular polymers, small organic molecules such as rosin [13], pentacene (C₂₂H₁₄)[24] and 2-(diphenylphosphory) spirofluorene (C₃₇H₂₅OP, SPPOI)[25] can be used as an alternative transfer agent to substitute macromolecular polymers. Although these small organic molecules in general have a higher solubility, they are too brittle to support the graphene film without cracking. Some of these small organic molecular transfer agents even form pi-pi bonds with graphene, rendering it impossible to guarantee a clean and defect-free graphene transfer.

Conventional wisdom dictates that removal of the transfer agent by rinsing the graphene loaded wafer in an organic solvent is necessary after a successful graphene transfer to a target dielectric substrate [13, 15]. However, this rinsing step has been proven to be problematic and counter-

productive, particularly when fabricating polymeric flexible electronics or desalination membranes. For the first time, we show that, instead of going through a violent rinse in a solvent, a support layer made with small organic molecules agent can be spontaneously removed by sublimation with virtually no trace of residues left on the graphene surface. In this work, camphor is chosen as a transfer agent. Camphor is a biodegradable medicinal substance that has been used by India households for catering for centuries. Unlike other commonly used transfer agents, camphor has a high solubility in organic solvents and a weak interaction with the graphene surface which ultimately guarantees a clean and damage-free transfer. Unlike other macromolecular polymeric transfer agents, which require to be removed by washing in acetone or any other known solvents after a graphene transfer onto target substrates, camphor does not require to be washed. Instead, camphor is naturally sublimed into a vapor when exposed to a dry atmosphere or an elevated temperature. We have successfully applied the proposed method to fabricate a monolayer of graphene on three different dielectric substrates such as SiO₂/Si, glass and plastics. The results of our experiments suggest that the transferred monolayer graphene films have a low surface roughness with a maximum thickness of about 15 nm and a uniform sheet resistance between 360-10000 ohm per square over a SiO₂/Si covering an area in excess of 10mm². Together with the medicinal and biodegradable properties of camphor, the methodology of such a clean and damage-free graphene transfer enables graphene to be applied in more diverse applications in future, including biological applications and electronic applications.

2. Results and Discussion:

~~HOW ABOUT USE SUBHEADINGS???~~ Why Camphor has been selected for Graphene Transfer

Unlike macromolecular polymers with a low molecular weight, the use of a subliminal substance as supporting materials for graphene transfer can bypass the step of washing in an organic solvent. Camphor is such a material which is not only weakly adhesive with graphene but also easily sublimed to a vapor at a very low temperature. Computation by Discrete Fourier Transform (DFT) shows that the camphor adsorption energy is zero at temperature above 40°C, while camphor – graphene adsorption energy is 0.09 eV, which is one of the lowest adsorption energy found amongst all the known supporting transfer agents (Fig 1a). In this work, we found that the layer of camphor together with a graphene is sufficiently strong to support on its own after copper etching.

Unlike polymer mediated graphene transfer process, which requires a perfectly continuous and flexible supporting backbone to carry out, camphor mediated graphene transfer process has no such a property. >>>>>> The previous statement does not have anything to do with this statement. Instead^[1], after the copper etching step, the presence of small camphor molecules could help to locate the surface of a one-atom thick monolayer graphene under an optical microscope.

The process of transferring a CVD grown graphene film from a copper foil onto a SiO₂/Si substrate involves the following steps, as illustrated in Figure 1b; Step i) depositing a thin film supporting layer onto the CVD grown graphene on copper by spin coating or drop deposition to form the camphor/graphene/copper stack. Drop coating (Figure 1c; right side) will result in formation of a thicker camphor film, whilst spin coating tends to yield a thin camphor film on the copper/graphene stack (Figure 1c, left side). Step ii) Etching the copper substrate by immersing the camphor/graphene/copper stack into a ammonium persulphate solution. Step iii) Rinse the camphor/graphene stack with distilled water many times. Step iv) Scooping the graphene/camphor stack onto a target dielectric substrate such as SiO₂/Si, glass and plastics, where the graphene monolayer directly sticks to the target substrates by Van der Waals force. In our case, the target dielectric substrate is a layer of SiO₂ with thickness being 285 nm. Step iv) Expose the substrate/graphene/camphor wafer to a dry atmosphere for 1 hour and then heat the wafer at 100°C for 5 minutes.

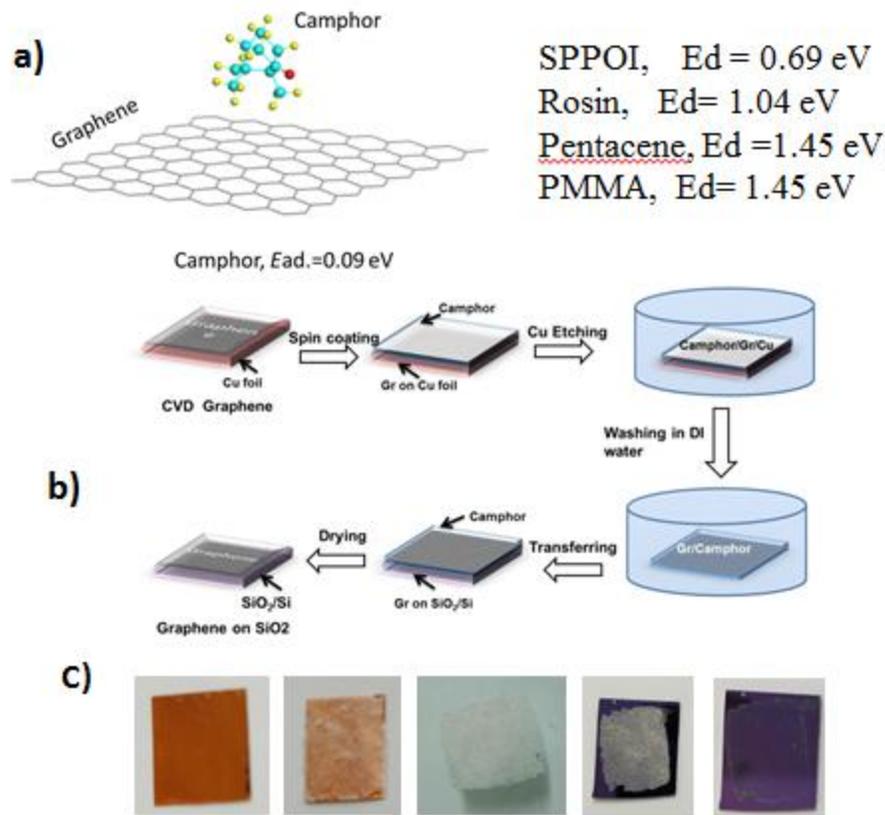


Figure 1: Graphene Transfer without washing in an organic solvent: (a) DFT calculation showing that graphene and camphor molecule tends to have a lower adsorption energy with graphene as compared with other small molecules such as SPPOI, Rosin, Pentacene or PMMA. (b) Schematic illustration of the proposed camphor transfer procedure. (c) Photographs showing the process of transferring a monolayer graphene from a Cu foil on to a SiO₂/Si.

In general, camphor has a waxy nature which has contributed to a rather weak binding with the graphene surface at room temperature. During the early stage of our experiment Upon spin coating, white patches were found in some areas of the camphor coating a thin layer of camphor attached on the graphene/copper stack. These white patches were believed to be formed by camphor residues which remain after rinsing. These white patches attached camphor molecules disappeared at a temperature at or above 90°C. The absence of white patches is an indication that no camphor film has been left on the graphene layer although there remains a negligible interaction between camphor – graphene of $E_{ad} = 0.09$ eV. Supporting video 1 illustrates how the camphor solution is drop-cast onto the graphene surface, dehydrated at 80°C and finally sublimed into a vapor at above 90°C. Although camphor is not a polymer, it can be adhered to the graphene surface very well (see supporting

information video 2). Figure 1c/d shows a photograph of the copper/graphene/camphor stack held with a pair of tweezers). The adhesion between camphor and graphene is one of the important properties that justify the use of camphor as a graphene transfer agent.

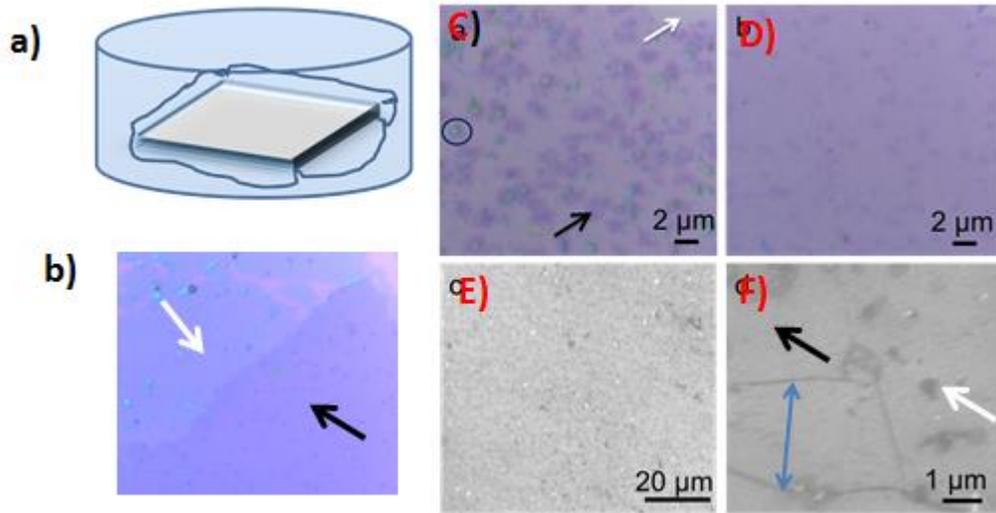


Figure 2: Microscopic characterization of a graphene film transferred onto a SiO_2/Si substrate using the oil boundary assisted method: (a) Schematic showing the camphor oil filled boundary surrounding the edges of a graphene/camphor stack after copper etching; (b) Two distinct regions were observed in the graphene film transferred onto the SiO_2/Si substrate, with the white arrow pointing to a region with the thickened camphor oil attached to the edge of the graphene film, and with the black arrow pointing to the region with a continuous spread of graphene; (c) Optical microscopic image showing the graphene/Camphor transferred onto SiO_2/Si before heat treatment; (d) Optical microscopic image showing the graphene/Camphor/ SiO_2/Si after the camphor support layer was sacrificed at 100°C and rinsed with alcohol; (e) SEM image of Figure 2d (graphene/ SiO_2/Si) at a low magnification and (f) SEM image at high magnification revealing the continuity of graphene without pinholes.

Boundary assistance method of Graphene transfer:

In general, the proposed method of graphene transfer is similar to the conventional method, with an exception that the proposed method bypasses the step of washing in an organic solvent. Similar to the frame used for a PMMA mediated graphene transfer [26], the oil filled boundary in the camphor mediated approach acts as a frame protecting the polycrystalline graphene/camphor thin film from breakage during the process of rinsing in DI water (Figure 2a- schematic). The camphor used for coating

the graphene layer contains 96% camphor and the remaining 4% camphor oil by volume. After spin-coating, some of camphor residues remaining on the backside of the copper substrate were suspended in the etching solution and then re-attached to the edges of the camphor/graphene stack in ways to further thicken the camphor oil filled boundary. However, the central region of the camphor layer remained thin and intact.

After the copper substrate was removed by etching, the outward pulling effect of the edges of the camphor layer has in effect fastened the graphene layer into a flat membrane. Prior to the lift off of the graphene/camphor film, the small oil flakes (i.e. the oversized camphor residues) suspended in the aqueous solution were manually removed. What follows describes in detail the results of our characterizations, including the microscopy characterization, the spectral characterization as well as the electrical characterization. The optical microscope in Figure 2b shows that the oil filled boundary, as pointed to by the white arrow, appears on the edges of graphene after being transferred onto the SiO₂/Si substrate. As a result of the strength of this solidified oil-filled boundary, this fastening effect not only renders the graphene layer self-supporting without creating any fragment in the aqueous solution, but also minimizes all the surface roughness during the entire process of graphene transfer. The appearance of camphor molecules on monolayer graphene (marked in white circles in Figure S1) becomes increasingly obvious shortly after the graphene/camphor stack was placed onto the SiO₂/Si substrate.

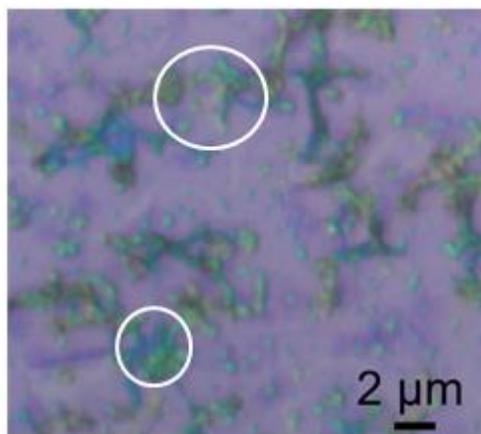


Figure S1: A graphene/camphor stack after being transferred onto the SiO₂ substrate without going through any heat treatment. The white circles highlight the residues of camphor.

As^[Dr. BNC2] shown in the optical microscopic image in figure 2c, no oil filled pattern has been spread to or across the central region of the graphene film. The green dot enclosed by the black circle^[13] in Fig. 2c illustrates an oil flake which failed to be removed after the rinsing step. As shown in Fig. 2d, very few tiny oil flakes were observed on the graphene surface after the graphene/camphor/SiO₂/Si stack was treated at 100°C for 5 minutes.

It is not uncommon for pinholes to be formed over a larger area of graphene due to many other reasons, including the presence of copper wrinkles, the polycrystallinity of the copper/graphene stack and the brittle nature of the coated camphor layer. As shown in Fig. 2e, the graphene layer fabricated using the proposed method appears to be continuous without noticeable pinholes when the microscope is zoomed into an extremely small area.

The^[Dr. BNC4] white arrow in Fig 2c highlights a corner of the SiO₂/Si wafer without any graphene, while the black arrow highlights the area of the bilayer graphene patches spread on the monolayer graphene^[15] (Figure 2c). The amount of camphor residues in the figure 2c was further reduced after being treated with an ultra-centrifugation at 5000 rpm for 30 minutes and soaked in an alcohol for ten minutes (Figure 2d). The lowly magnified SEM image in Fig. 2e shows the monolayer graphene film has appeared continuously intact although we have occasionally observed some regions with multilayers of graphene piling up.

In Fig. 2f, the continuous and smooth region of the monolayer graphene is highlighted by the black arrow whilst the dark contrast, as pointed to by the white arrow, is an indication of multiple layers of graphene stacking up together. On the other hand, the double blue arrow in Fig. 2f highlights the grain boundary which is one of the characteristics of a monolayer polycrystalline graphene. The SEM images in Figure 2 have sufficiently proven that the proposed camphor-mediated graphene transfer approach is readily applicable for production of a large area graphene on dielectric substrates.

Surface Characterisation of Graphene on SiO₂/Si.

In addition to our optical microscopic image characterization, a surface roughness characterization was conducted using atomic force microscope (see Fig.3).

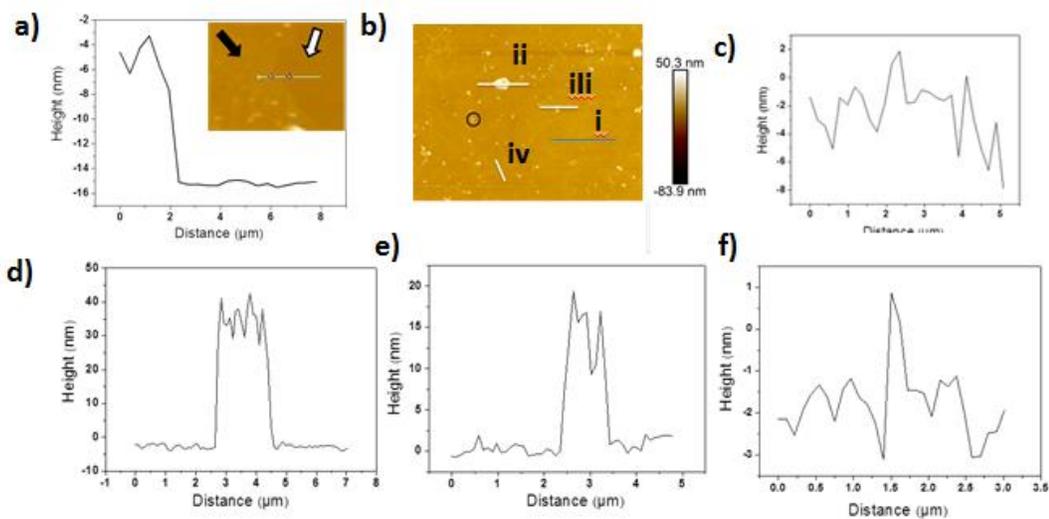


Figure: 3 Surface roughness characterization of a graphene film transferred onto the SiO_2 substrate using the proposed approach: (a) AFM line section plot of the graphene on SiO_2 illustrating the cross-section of a wrinkle. The inset figure in Fig. 3a is the optical microscopic image used to distinguish between the perfect region of graphene (as pointed to by the black solid arrow) and the region with SiO_2/Si only (as pointed to by the hollow arrow). (b) AFM image showing five different regions for cross-sectional height profile analysis, with the black circle highlighting the camphor oil residues on the graphene film, marker i highlighting the spread of a pure monolayer graphene, marker ii highlighting a region with a large amount of camphor oil residues, marker iii highlighting a region with a smaller amount of camphor oil residues, and marker iv highlighting grain boundary. ~~(c) The height-profile of region i (c).~~ ~~(d) The height profile of region ii (d).~~ ~~(e) The height profile of region iii (e).~~ ~~(f) The height profile of region iv (f).~~

The wrinkles on the graphene layer were in part due to the imperfection on the copper surface. The proposed graphene transfer approach also has caused a slight increase in the amount of wrinkles, which are believed to be caused by the difference in thermal expansion coefficients between graphene and the underlying substrate during the cooling process after the high temperature growth. Unlike the PMMA mediated graphene transfer, which necessitates washing in an organic solvent, the proposed transfer method minimizes the possibility of roughness/wrinkles or corrugations through the self-sacrifice mechanism of the camphor layer. Since there is weak interaction between the graphene film and the transfer agent, polycrystallinity of graphene, and random motion of the camphor shear occasionally shrinks certain areas of the graphene film. As shown in Figure 3a, the AFM measurement suggests that the contact height of graphene on SiO_2/Si which is about 8 nm. Due to the free standing nature of the graphene film, and due to the interaction of monolayer graphene with aqueous medium, scooping graphene onto a dielectric substrate is a challenging task. On the other hand, the angle at

which the graphene film is lifted onto a target substrate determines the flatness of the graphene spread on the target substrate. Our camphor-mediated graphene transfer approach yields a small root mean square (RMS) roughness of 1.5 nm, which is believed to be contributed by the wrinkles due to the surface imperfection on the copper surface and due to the fragile support of camphor oil-filled boundary. On a fabricated graphene/SiO₂ stack, 10 regions of 50 μm² in area were randomly selected for measurement of the surface roughness.

The AFM image as shown in Fig. 3b shows five different regions chosen by us for cross-sectional height profile analysis. Fig. 3c, which shows the cross-sectional height profile along the line section marked by marker i in Fig. 3b, suggests the maximum height (R_{max}) of a camphor oil flake on the graphene film is about 15 nm. The RMS value and the R_{max} value are respectively 5 times and 10 times smaller than those of the graphene/SiO₂/Si stack obtained using PMMA-mediated method.

As can be seen in Fig. 3d, the cross-sectional height profile of an area with large oil residue (as pointed to by line ii in Fig. 3b) has an R_{max} of 40 nm. In Fig. 3e, the cross-sectional height profile for line iii in Fig. 3b, which highlights an area with a smaller patch of oil residue, suggests an R_{max} of 15 nm. Finally, the height profile as shown in Fig. 3f, which highlights the region with a grain boundary as pointed to by marker iv in Fig. 3b, suggests that the surface smoothness is virtually unaffected by any breakage between grain boundaries.

For further smoothing of the graphene surface, and for further improvement of the graphene quality, more research efforts should be devoted to minimization of wrinkles over a large area of graphene. The outcomes of our ongoing investigation will hopefully contribute to the progress of this or other fields.

The most important cause leading to creation of the pin holes on the graphene film is due to the failure of the oil boundary to provide adequate mechanical support to avoid damages in the process of rinsing in DI water. As is illustrated in Figure S2, a more detailed study has revealed that the oil boundary has played a highly important role in upholding the quality of the graphene transferred onto the SiO₂/Si substrate. Due to the turbulence of the flowing DI water, the polycrystalline graphene without an adequate mechanical support from the oil boundary tends to tangle randomly in the standing solution, rolling some regions of the graphene film into wrinkles (see the SEM images in Figures S2b and S2c). Since the graphene layer has not been detached from the camphor layer, the rolling of the graphene film indirectly deforms the camphor layer and introduces certain extents of surface roughness. In

addition to the strength of the oil-filled boundary, how intact the final graphene film also depends many other factors, including the weak interaction between the graphene film and the camphor layer, the polycrystallinity of CVD grown graphene, the intrinsic roughness of supporting copper, the extent of the camphor oil filled boundary surrounding the graphene/camphor film withstanding the turbulence of the flowing DI water.

Since camphor can easily be sublimed into a vapor, there is no need to remove the camphor from graphene either by washing in an organic solvent or by going through a thermal annealing process. Camphor film can easily be removed by sublimation at an elevated temperature or in a sufficiently dry atmosphere. To confirm the absence of thick camphor residues left on graphene after the camphor removal process, several SEM images and Raman spectra have been taken (see Fig S2 and Fig S5).

Fig. S2 shows the results of the proposed methodology of graphene transfer in the absence of a camphor oil-filled boundary. The SEM images show that there are still pin holes (as pointed to by the black arrow of Fig. S2b) and wrinkles (as pointed to by the white arrows) on the graphene/SiO₂/Si stack as a result of the weak interaction of polycrystalline graphene. The higher resolution image of Fig. S2b is shown in Fig. S2c. In Fig. S2c, no pinhole was visibly observed. But at the same time, many pinholes that exist elsewhere are difficult to avoid due to the turbulence of flowing DI water. Many studies have reported the same amount of pin-hole patterns following a PMMA-mediated graphene transfer [ref]. The images in Figs b-e display virtually no mark on the graphene film transferred in the absence of any camphor oil filled boundary. While the proposed method appears to be promising, more studies are recommended to further optimize the process to overcome the pinholes and wrinkles aggregation along with the CVD grown strategies.

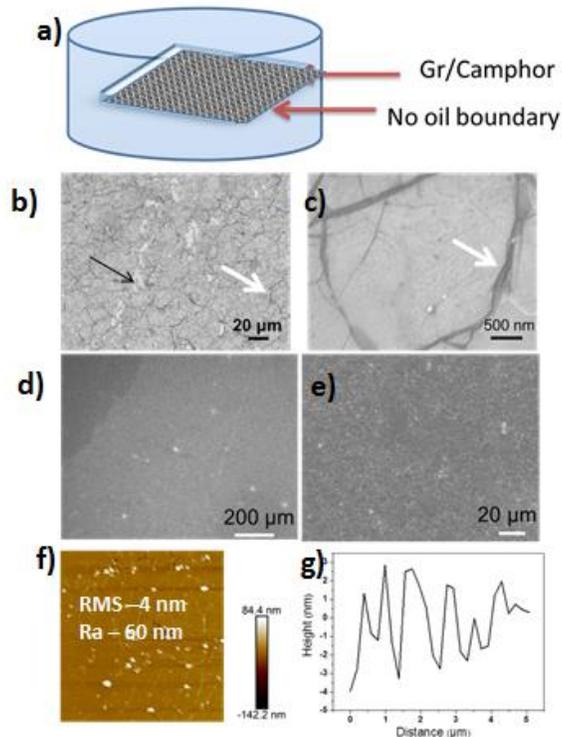


Figure S2: Morphology characterization of a graphene/stack transferred without the support of an oil-filled boundary: (a) Schematic diagram showing a graphene layer without the support of camphor oil boundary. (b) SEM image of the graphene/SiO₂/Si stack at a low magnification, with the black arrow pointing to the pin holes and with the white arrow pointing to the folded or shrunk areas. and (c) SEM image of the graphene/SiO₂/Si stack at a high magnification, with the black arrow pointing to the pin holes and with the white arrow pointing to the folded or shrunk areas. (d) SEM image of a graphene/polyamide stack at a low magnification. ~~(e) SEM image of graphene on polyimide at a high magnification~~(e). (f) AFM image of the graphene/SiO₂/Si stack after sublimation of camphor. (g) Surface roughness of the line section as shown in Fig. S2f.

The graphene layer is a complementary thin film weakly adhered to the camphor film which is formed either by spin-coating or by drop casting. The oil boundary as a result of either deposition approach was sucked out through injection process. As a result, the folded areas of the graphene film tend to be wrapped into a ribbon kind and adhered to the monolayer graphene (Figure S2c; white arrow),

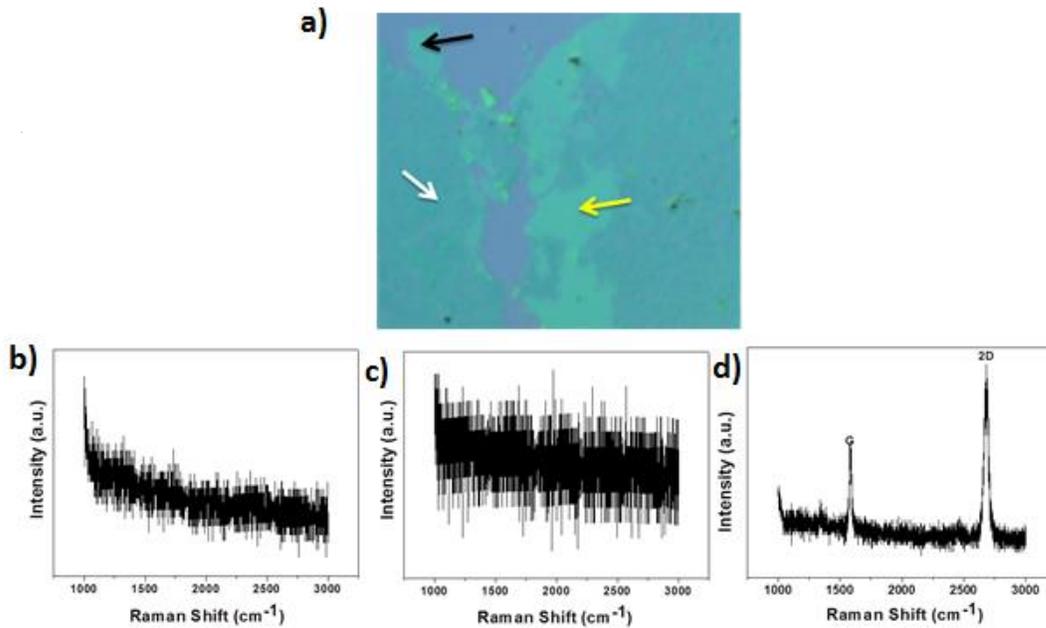


Figure S3: (a) Optical microscopic image of a graphene/camphor stack transferred onto a SiO₂/Si substrate using a camphor oil filled boundary, with the regions selected for Raman Spectra Analysis highlighted by arrows; (b) Evolution of Raman spectra of a camphor oil flake on SiO₂/Si. (c) Raman spectra of a camphor flake artificially added onto the graphene surface; and (d) graphene on SiO₂/Si without any camphor oil flake.

After a thorough rinse of camphor/graphene layer in DI water, the graphene film is placed onto a desired dielectric substrate, which is not limited to Si/SiO₂. Although the proposed method of graphene transfer is applicable to wide variety of other dielectric substrates including plastics and glasses (Figure S4d), SiO₂/Si substrates appears to be the best in terms of quality. Since the camphor/graphene stack is very thin, there exists a stronger adhesion between the graphene surface and the hydrophobic substrates. It should be noted that, due to the presence of strong Van der Waals force between graphene and the target substrate, the camphor/graphene stack already adhered to the surface of a target substrate cannot to be removed or re-transferred to another substrate again. , as was possibly done in a PMMA mediated transfer.

In absence of a thin oil filled boundary surrounding the edges of the graphene/camphor membrane, which acts as a shield protecting the membrane from corrugation in the final graphene film, its surface roughness increases and R_{max} were found to be 60 nm and 4nm, respectively. The surface roughness was almost three times of the roughness obtained in the presence of an oil boundary (See^[16] Fig S2f).

4.2 Spectral Characterization:

Raman spectrum shows that the graphene transferred onto the SiO₂/Si using the proposed method and that using the PMMA mediated method [15] or rosin[13] are equal in qualitative terms. Three contrasting graphene related Raman peaks corresponding to the D(~1350cm⁻¹), G (~1595 cm⁻¹) and the 2D (~2700 cm⁻¹) bands were observed in Figure 4a. Upon careful examination of the process of washing with DI water, we have found some oily residues surrounding graphene impurities on the Si/SiO₂ substrate. To understand this phenomenon further, we have intentionally transferred some artificial oil flakes onto graphene/SiO₂ (see Fig S3a) and used Raman spectrometry (Fig. S3b to S3c) to analyze whether these oil flakes on graphene yields a similar Raman spectrum. After focusing a laser on the oil flakes, no characteristic peak was observed. The result of this phenomenon double confirms the fact that there exists no residue on the graphene/SiO₂ stack. To evaluate the uniformity of the transferred graphene film using the proposed camphor mediated approach, a region over 10 μm² with a large pin hole was selected and captured in the optical microscopic image (see Figure 4b). The colors associated with different optical images were observed and captured for D peak (see Figure 4c), G Peak (Figures 4d) and 2D peak (Figure 4e). In addition, a large pin hole spotted at Figure 4b was also visibly displayed in the optical image in Figs 4c to 4e.

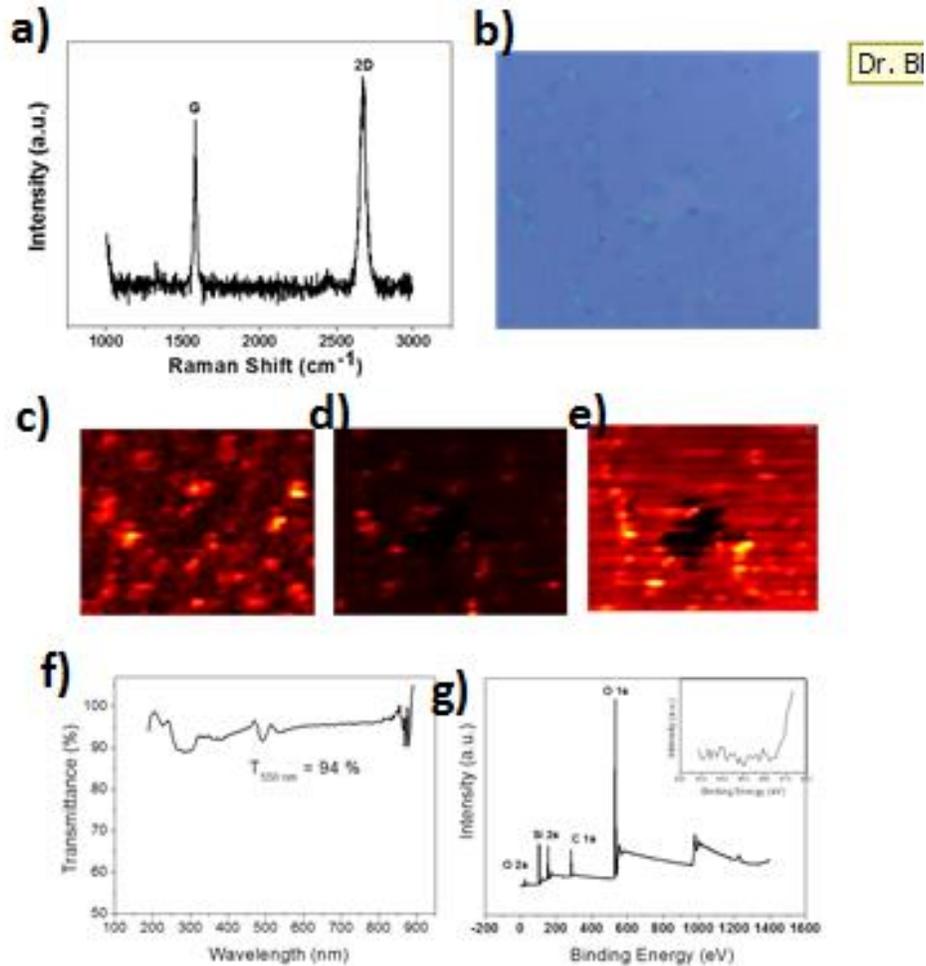


Figure 4: Quality evaluation with spectral characterization: (a) Raman spectra of the region on graphene film containing a pin hole. (b) Optical microscopic image of the graphene/SiO₂/Si stack with a hole displayed in the center. (c) contrasting image corresponding to D peak, (d) contrasting image corresponding to G peak. (e) contrasting image corresponding to 2D peaks, respectively. (f) UV-Visible spectra of the graphene film transferred onto a quartz substrate (e) Convoluted XPS spectra of the graphene film on SiO₂/Si, with the inset graph showing the absence of copper peak following the post treatment of the camphor assisted graphene transfer.

The graphene film transferred in the absence of oil boundary displays too many wrinkles and ribbons, according to the SEM images (see supplementary Figure S2c). These wrinkles or ribbons were not caused by the presence of camphor residues, according to the results of our Raman analysis. With the

laser being intensely focused onto the black ribbons only, the Raman spectra displays three characteristic peaks which can be used to characterize the monolayer graphene. Of these characteristic peaks, the D peak represents the extent of defects on the graphene layer, while the ratio of the 2D peak to the G peak (i.e. 2D/G) corresponds to the number of layers in the multi-layered graphene formed as a result of rolling of the graphene surface (Fig S4a). In Fig S4b, which shows the Raman spectra of suspended ribbon graphene on the SiO₂/Si substrate, the ratio of 2D/G was found to be maximum, confirming the fact that the black dots contain a cascade of multiple layers of graphene. This finding also rules out any possibility of camphor residues encapsulating the graphene layer(s) or any possibility of camphor residues being entangled within ribbon graphene.

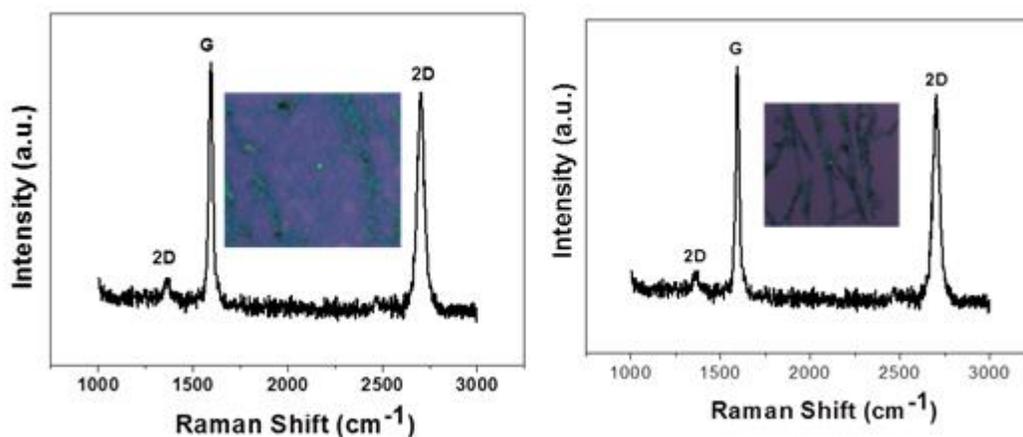


Figure S4: Raman spectra of the Graphene/SiO₂/Si stack using the camphor mediated method. (a) the Raman spectra taken when the laser was spotted on a graphene ribbon. Note, the prominent ratio of the G peak to the 2D peak suggests that black ribbon is due to rolling of monolayer graphene (b) Raman spectra obtained when the laser is spotted on ribbon structure suspended on SiO₂/Si. The G/2D ratio suggests that the graphene ribbon is a structure multi-layered graphene films folding together.

The graphene film transferred using the drop coating option tends to be covered with a thick camphor layer along with a large amount of camphor residues. Very often, this option leads to an inefficient graphene transfer (See Fig S5). Fig. S5 clearly shows that the thickness of camphor on graphene is also

an important factor affecting the efficiency of the graphene transfer process. Overcoming the problems caused by washing is one of the research directions to be taken strategically in much the same manner as the frame approach being optimized for the PMMA mediated graphene transfer. Some greyish contrast observed under the optical microscope are believed to due to the oil patches. These oil patches could be easily eliminated by washing or by pipetting off the small oil flakes before scooping graphene onto the dielectric substrate.

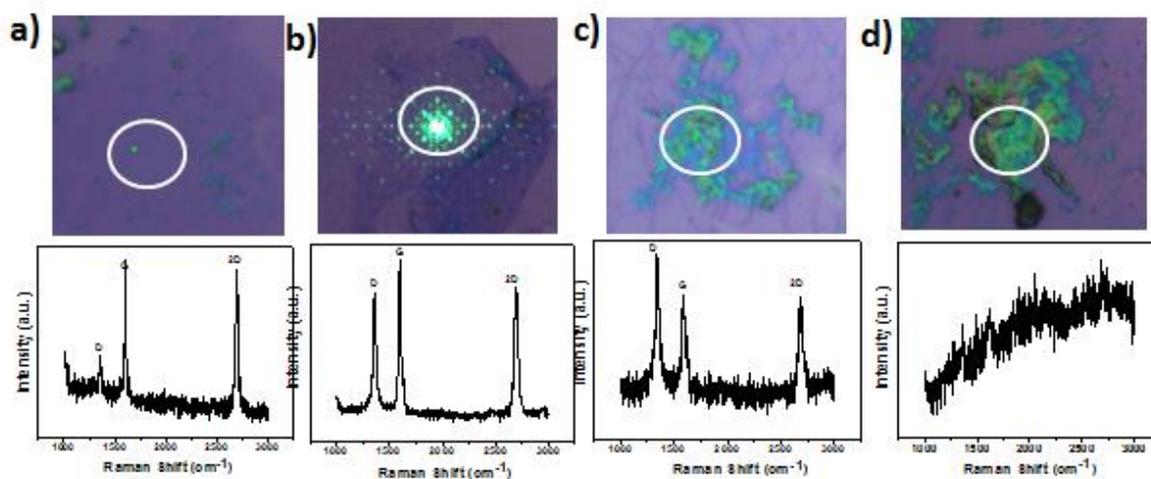


Figure S5: Top row: OM marked with white circle for Raman spectra (Bottom rows) of graphene transferred with the thick camphor deposition method showing different contrasting spots (marked in white circle) after being transferred onto SiO₂/Si. (a) laser spotted on monolayer graphene free from any residues showing characteristics raman peak as of in the case of Fig4a. (b) laser spot on the disoriented or folded graphene showing high intense of D peak. (c) laser upon graphene wrapped with some camphor impurities showing high intensity of D peak, where 2D and G peak is less intense. (d) laser spotted only onto the bright green spot on SiO₂/Si showing no peak which confirms that the green spot is corresponds only to camphor residues.

We have also investigated the UV/Visible transmittance for 2x2 cm graphene transferred onto a quartz using camphor mediated graphene transfer approach. Figure 4f shows the transmittance of graphene at 550 nm is found to be 94%, which is attributed to that graphene (wrinkles) as described in figure S2c.

In addition to Raman spectrometry, XPS spectrometry has also been conducted to examine the chemical integrity of the fabricated graphene on SiO₂/Si. XPS is surface sensitive quantitative analysis method that can be used to measure the elemental composition of a surface in parts per thousand range. It can be shown by deconvoluted XPS spectra (Fig. 4g) that there is no trace of copper left. This proves the fact that the copper has been completely removed by etching before the post treatment step of the graphene transfer. Since the graphene has been placed on SiO₂/Si, the intense peak of O₂ appears as a result of the oxide substrate effect was observed. However, there are no carbon peaks related to the camphor. Instead, the XPS peak corresponds to the carbon 1s peak at 285 eV due to the presence of carbon atoms in the graphene film (Fig S6). This extra spectra is almost identical to the spectra representing the carbon atom in the graphene film obtained from a PMMA mediated approach.

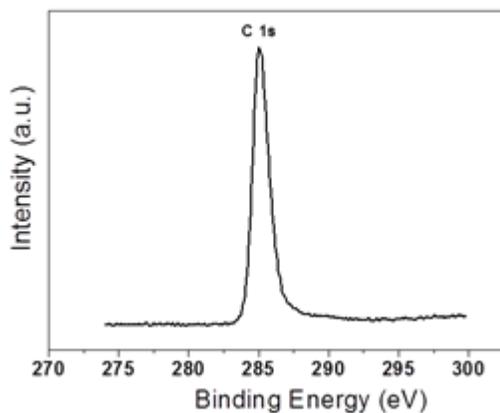


Figure S6: XPS peak of graphene on SiO₂ after the camphor is removed by heating at 120°C. This graph does not display any other peak corresponding to the presence of oxygen atoms or any other interference caused before or after the graphene transfer

4.3 Electrical Characterization:

The surface continuity of the graphene on SiO₂/Si has been evaluated by electrical characterization using a four probe electrical work station. It has been shown in the previous section that the

graphene/camphor stack has been fastened by the oil boundary. This fastening effect has significantly reduced the amount of pin holes which would otherwise increase the sheet resistance. On the other hand, mechanical weakening of the oil boundary will encourage formation of pin holes and ribbons on the graphene film (Fig. S4). **By our measurement, the average sheet resistance was found to be 360-1000 ohm per square.** This sheet resistance is more or less equal to that of the graphene film obtained using the conventional PMMA mediated method. The sheet resistance is slightly higher than the expected, in part because the outward pulling effect of the oil boundary is not strong enough to minimize the presence of wrinkles and residues on the graphene film. **The average sheet resistance has increased to approximately 1000-10000 ohm per square when the area of the fabricated graphene film became larger.** A larger area of graphene was supposed to be fastened by a much stronger oil filled boundary in order to minimize the wrinkles and pin holes. Unfortunately, this was not in the case, where the oil-filled boundary as a result of spin-coating was simply too thin. The weakened oil-filled boundary inevitably encourages formation of wrinkles (Fig S2b) and pin holes, which in effect decreases the overall mobility of charge carriers on the graphene surface. The end result is an increase in the sheet resistance. In addition, the carbon atoms along the wrinkles are found to be less stable due to the curvature effect [14], which is also responsible for the increase in the sheet resistance. This phenomena are commonly observed in almost all other conventional graphene transfer approaches. The large surface roughness often results in a high leakage current[25]

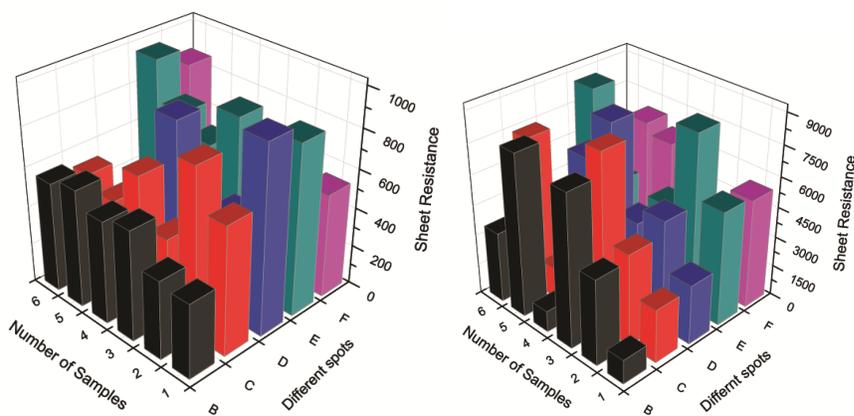


Figure 7 : Electrical measurements showing the sheet resistance measurements (a) with oil assistance and (b) without oil assistance

Although the proposed approach of graphene transfer does not involve any solvent washing step, there remain an excessive number of impurities or patches on the graphene film that ultimately decreases the overall mobility of electrons. Overall speaking, the sheet resistance obtained from the proposed graphene technique is in the same order as that of the graphene film transferred to a plastic substrate using conventional EVA mediated approaches. Multi-layered graphene stack can be fabricated as to further decrease the sheet resistance [13]. The quality of the proposed approach graphene transfer with or without the oil filled boundary can be further controlled or optimized by changing the process parameters such as doping with by HNO_3 or AuCl_3 . [27, 28] On the other hand, since the camphor is a well-known medicinal substance, we expect that the proposed approach can applied in biomedical research or in areas where the surface conductivity is not critically important. Undoubtedly, this study has defied the commonly held belief that graphene transfer without a polymeric transfer agent is never possible.

Conclusion:

In conclusion, we have demonstrated the use of camphor to facilitate a clean and damage-free graphene transfer from copper to a SiO_2/Si substrate. In the proposed method of graphene transfer, a layer of camphor was first formed directly onto a graphene on copper stack by either spin-coating or drop deposition. The copper substrate was then removed by etching, whilst the remaining camphor/graphene stack was placed onto a SiO_2/Si substrate. Unlike other polymer mediated graphene transfer method, in which the polymeric transfer agent has to be eventually washed away in an organic solvent, the camphor remaining on the graphene was sublimed on its own into a vapor at an elevated temperature or in a dry atmosphere. The efficiency of the proposed transfer method efficiency is comparable to that of PMMA mediated approach. The results of our examination suggest the amount of pin holes or wrinkles is positively associated with the strength of the oil boundary. In the case of a small area graphene with oil boundary assisted method yields an average sheet resistance of approximately 300-1000 kohm per square. The method of graphene transfer proposed in this work, opens up new possibilities in industrial graphene-based device applications both in energy and biological application upon thorough future investigation.

Experimental:

Graphene synthesis: CVD monolayer graphene was first grown on 25 μm thick copper foils (99%, Alfa Aesar) using an LPCVD method []. Prior to growing, the copper foils were treated with electrochemical polishing to remove impurities so that a continuous monolayer graphene can be grown. After the pre-cleaning process of the copper foil using DI water and alcohol, a dried copper foil is placed onto the flat quartz plate to ensure an ultraflat support for the copper/graphene stack. Under low pressure, at 1000 °C the copper foil was annealed in a gas flow of 50 sccm of H_2 for 60 minutes. To initiate the graphene growth, 20 sccm of CH_4 is added into the chamber for 30 minutes.

Camphor assisted method of graphene transfer: After graphene growth, the backside of the graphene/copper stack was etched away with O_2 plasma for 60 seconds at a plasma power of XXXXXXXX Watts. 100% camphor/chlorobenzene solution was either spin coated onto the top side of the copper/graphene sample at 2500 rpm for 30 seconds. The wafer is then dried on a hot plate at 80 °C and placed in the Cu etching solution. After complete removal of Cu from Graphene/Camphor, without disturbing the graphene/Camphor, the etchant was replaced with DI water for several times to ensure graphene/camphor is free from residual content of the etching solution.

Characterization: The morphology was characterized by optical microscopy (Olympus BX51), scanning electron microscopy (ZEISS-Merlin) and atomic force microscopy (Bruker). The quality of the CVD grown graphene transferred onto Si/SiO₂ was evaluated using a Raman spectroscope (Horiba, LabRAM HR Evolution) with a laser excitation wavelength of 532 nm. Monochromatic Al X-ray (Physical Electronics 56000 multitechnique system) was used to analyze the existence of any metal residue which has remained after graphene being transferred onto Si/SiO₂. The transmittance measurement was examined using UV-Vis-NIR spectrophotometer (Perkin Elmer, Lambda 750s, 190-3300 nm). The transport measurements are carried out using the standard lock-in technique (SR 830 as the current/voltage meter and DS 360 as the voltage source) in a vacuum system at T=300 K. The DC gate voltages are provided by a DC power supply (PHL 120) together with a home-made Arduino-based inverter.

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