Evaporable Glass-State Molecule-Assisted Transfer of Clean and Intact Graphene onto Arbitrary Substrates

Jingyi Qu,† Bao-Wen Li,*‡ Yongtao Shen,*† Shuchun Huo,§⊥ Ying Xu,† Shiyuan Liu,∥ Baokun Song,∥ Hao Wang,§⊥ Chunguang Hu,*§⊥ and Wei Feng*†

†Tianjin Key Laboratory of Composite and Functional Materials, School of Materials Science and Engineering, Tianjin University, Tianjin 300350, P.R China
‡School of Materials Science and Engineering, Wuhan University of Technology, Wuhan 430070, P.R China
§State Key Laboratory of Precision Measuring Technology and Instruments, Tianjin University, Tianjin 300072, P. R China
∥State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong University of Science and Technology, Wuhan 430074, Hubei China
⊥Nanchang Institute for Microtechnology of Tianjin University, Tianjin 300072, P. R China

Supporting Information

ABSTRACT: Graphene and its clean transfer methods have gathered growing interest and concern in recent decades. Here, we develop a novel large-scale intact transferring technology of paraffin wax onto arbitrary substrates. The wax will then be removed by thermal evaporation, avoiding uncontrollable reactions and leaving no residues. For characterizations, we adopt Raman, FT-IR, XPS, and DRS to measure the optical reflection difference on various surfaces and the thickness of graphene accurately. All the results demonstrate transferred surfaces’ cleanliness and our method’s validity. This technique allows for an effective transfer of graphene and enables a wider range of applications in many fields.

KEYWORDS: graphene, clean transfer, wax, evaporable, glass-state, differential reflectance spectroscopy (DRS)

Chemical vapor deposition (CVD) has enabled scaling up of high-quality graphene on metal, thus fueling a wide range of research efforts. However, CVD-grown graphene needs to be transferred to a target substrate for further exploration. For various applications, transferring CVD-grown graphene films to target substrates while preserving their high quality remains to be addressed, especially for applications in electronic devices. Several transfer methods have been widely employed involving different types of polymers, such as PMMA, PDMS, PC, thermal released tap (TRT), and special self-release polymers. Because these polymers are resistant to scratching, they were used as carrier materials to prevent folding or wrinkling of graphene during metal-etching and transferring. Removing polymer layers after transferring the graphene to a target substrate, remains a challenging issue. On this basis, some methods with small molecules such as rosin and pentacene have been proposed to avoid the drawback of polymers. However, there are still inevitable issues leading a negative impact. First, the residues left on the surface of graphene can never be eliminated completely when rinsed by organic solvents. Furthermore, wispy cracks and scrolls would be generated during this process, resulting in degraded performance in graphene-based devices because of triggering charged impurity scattering and unintentional graphene doping.

Further thermal annealing at 300–500 °C has been effective for decomposing the residues, but they cannot be thoroughly removed from graphene because of the characteristic of polymer gasification. The gasification of polymers is in general much more complicated than that of ordinary small
molecules. In the thermal annealing process, polymeric materials were broken up into smaller molecules and underwent more complex uncontrollable reactions. In contrast, the evaporation of small molecule is not accompanied by any chemical reactions, implying the possibility of replacing the polymers.

In this study, we report a novel clean transfer method for large-scale graphene films to arbitrary substrates with evaporable molecule (paraffin wax) as the supporting layer. Wax is an evaporable glass-state small molecular aggregation that characteristically consists of long alkyl chains (22–32 C). They are malleable near the ambient temperature and melted above 58°C by releasing a low viscosity liquid. These features allow for thermal evaporation of small molecules from the graphene surface at low pressure and temperature. First, the liquid wax was spin-coated onto one (upper) side of a graphene/Cu foil as a wax/graphene/Cu complex structure. The wax/graphene/Cu foil was floated on (NH₄)₂S₂O₈ solution to etch away the Cu foil for several hours. Next, the suspended wax/graphene film was rinsed by deionized water and subsequently transferred onto target substrates (Scheme 1 and Figure 1a–c). Finally, the wax was removed directly by thermal evaporation at 140 °C and 0.2 Torr for 5 h. Our approach therefore provides a simple, efficient, and clean route for transferring large-scale CVD-grown graphene films onto arbitrary substrates without solvent treatments and is also a general methodology toward some other 2D materials such as h-BN shown in Figure S1.

The morphology of the PMMA layers is rigid and reverse-templated by the rough-textured Cu surface. The surface morphologies of PMMA and desired substrates do not match, leading to incomplete wetting at the interface and formation of

Figure 1. Wax-assisted transfer of graphene film onto target substrate. (a) Floated wax/graphene film on water. The graphene film was outlined by the dashed lines. (b) Demonstration of a light-emitting diode (LED) connected through the graphene sheet. (c) Wax-assisted transfer of large-area graphene films on 6 × 6 cm² SiO₂ wafer. (d) Optical image of wax-transferred graphene on SiO₂/Si substrate.
ripples and tears after dissolving the PMMA layers. The soft wax tends to mechanically relax the underlying graphene during annealing, accordingly leading to an improved contact with SiO_2/Si. The van der Waals contact area between graphene and the target substrate could be maximized and the formation of ripples and cracks could be minimized during the wax-evaporation process. We observed continuous graphene films over a 6 × 6 cm^2 region (Figure 1c) using an optical microscope, with fewer tears, holes, and visible wax residues on graphene visible to the naked eye than those observed in PMMA-transferred graphene (Figure 1d), indicating optimization of the contact between wax/graphene and target substrate via our method. The clean and undoped graphene surface enabled by the wax-assisted transfer method is expected to be favorable for further electronic applications and applicable to flexible and curved substrates (Figure 1b, inset photos of Se). The light-emitting diode (LED) connected through the graphene sheet was turned on at 6 V, showing that the transferred graphene on the substrate is continuous and uninterrupted even on a curved surface (Figure 1b). In the following report, we assume that graphene is prone to be more easily transferred to SiO_2 because of the comparatively stronger charge-transfer interaction between graphene and an oxygen-rich surface, so we chose SiO_2 wafer for demonstration. In fact, our wax-assisted method could be applied to any other substrates.

SEM images are used for characterizing the surface of graphene samples both grown on the copper foil and transferred onto the substrates in various ways. After transferring, some scrolls and cracks on the surface often observed can be attributed to the inhomogeneity of surface strain in graphene. The edge is the most fragile area of graphene and easily broken during the transfer process. To demonstrate the influence of the transfer method on the edge of graphene and compare the surface strain in different methods, we performed the transfer process using hexagon-shaped graphene. As shown in Figure 2a, single-crystal graphene on Cu foil shows dendritic branches at the corner and edge of the hexagon as reference, indicating that the growth is diffusion-limited. In the wax-assisted transfer method, it almost duplicates the topography of the previous graphene surface even at the nanoscale. Apparently, these dendritic branches remain intact after transferring onto SiO_2 and thermal evaporation (Figure 2b, Figure S2a, b). However, ripples, rolls, and tears at the edge of the hexagon clearly appeared when the transfer was assisted by PMMA (Figure 2c, Figure S2c, d). A stable, equilibrium core size for the scroll of graphene is dominated by the surface strain, which is a net driving force for the graphene to contract. In the PMMA transfer method, there are relatively strong π−π interactions between the PMMA molecules and graphene, which prevented the complete desorption of the PMMA molecules from the graphene surface. Moreover, the dissolution of PMMA with acetone accelerates the surface strain, resulting in the formation of scrolled structures and tears at the fringe of graphene. In contrast, fewer scrolls, ripples, and tears could be ascribed to a gradual transition in the surface strain of graphene because of the rather slow evaporation rate of wax.

Figure 2. Edge of graphene on SiO_2/Si substrate. SEM images of (a) as-grown graphene on Cu foil, (b) wax-transferred graphene on SiO_2 wafer, and (c) PMMA-transferred graphene on SiO_2/Si substrate.

Figure 3. AFM images of graphene on SiO_2 wafer. (a) As-exfoliated graphene, (b, c) graphene after wax was removed by thermal evaporation, and (d) wax-transferred CVD-grown graphene after thermal evaporation.
AFM is one of the most efficient and direct ways to detect the thickness and surface appearance of graphene. As expected, peculiar features including a clean, flat surface were observed in as-exfoliated graphene (Figure 3a). After spin-coating wax onto graphene and subsequent treatment by thermal evaporation, we still observed those features for exfoliated and CVD-grown graphene films (Figure 3b, c), suggesting the complete removal of wax and crack-free on the graphene surface. Figure 3c is a typical AFM image of a wax-transferred graphene film on a SiO2 wafer, where a high density of graphene with heights up to 0.5 nm can be seen. This observation is in marked contrast to a mass of polymer residues appearing in PMMA-transferred graphene film (Figure S3). In addition, high-magnification AFM images and SEM images are shown in Figure S4 to prove fewer residues and tears after the transfer.

Evaluating the Raman spectra of the graphene suspended on TEM grid can avoid substrate reflection of the incident light during measurements and distinguish the multiple reflections and interference of light between the contaminants and graphene. We transferred the wax/graphene film onto a 200-mesh TEM grid, which acted as a scaffold to provide mechanical supports. After removing the wax by low-pressure annealing, graphene is suspended on the micro grid (Figure 4a). The Raman spectrum of position 1 was conducted with an isolated substrate in Figure 4b. To confirm the uniformity, we show spectra of positions 2 and 3 in Figure S5. In this way, three distinctive features of clean surfaces including the relatively low signal-to-noise ratio, absolute Raman intensity, and absence of low-frequency (1100−1600 cm⁻¹) broad background attributed to the existence of amorphous carbon (mixture of sp² and sp³-bonded carbon), which demonstrate the inappreciable residues of the wax-assisted graphene.

Furthermore, the Raman map image presents the effectiveness of our method. Figures 4c, d show the optical image and its corresponding Raman map image of D peak to G peak intensity ratio (I_D/I_G) of wax-assisted transfer graphene in 140 °C observed indicate the typical characteristic of high-quality single-layer graphene. The D peak emerges when the temperature increases to 200 °C, which is attributed to the destruction of wax’s decomposition products. The 2D peak of graphene films transferred by PMMA is obviously blue-shifted (from 2672 to 2697 cm⁻¹), implying doping induced by polymer residues. However, the intensity of D peak increases with higher evaporative...
temperature because of the uncontrollable impurity. FT-IR of PMMA and wax at room temperature and 140 °C (annealed in Ar, 1 atm, 5 h) also support our point as shown in Figure 5b. Thermal decomposition of PMMA is a complex radical chain reaction and generally accepted that the process involves initiation, depropagation, transfer, and termination reactions.\textsuperscript{27} The results show that, as the temperature rises, PMMA tends to be decomposed into some active functional groups such as νC═O (in 1735 cm\(^{-1}\)) and νsC−O− (in 1275−1020 cm\(^{-1}\)). Other polymers proposed before, such as EVA,\textsuperscript{28} are in a similar situation as that demonstrated in Figure S6. In contrast, paraffin wax, as a hybrid saturated alkane, has strong chemical inertness and is of great stability. It is worth noting that a much higher-temperature annealing (>200 °C) for PMMA does not actually yield a much cleaner surface at the risk of structural damages. There is also a critical point when removing wax by

Figure 5. Comparison of graphene transferred by wax and PMMA. (a) Raman spectra and magnified detailed images of graphene films transferred on SiO\(_2\) wafer (excitation wavenumber, 532 nm) after thermal annealing. (b) FT-IR of PMMA and wax in RT and 140 °C. (c) XPS spectra of as-grown graphene on Cu and wax-transferred graphene on SiO\(_2\) after thermal annealing. The peak intensity is normalized for comparison. (d) FT-IR spectra of wax, and PMMA-transferred graphene films on SiO\(_2\). (e) Transmittance spectra of wax-transferred graphene on quartz glass. Insert photo shows graphene transferred on quartz glass and its transparency.
means of low-pressure annealing. It will become less efficient after the appropriate condition is reached, as concluded from our experimental findings.

The cleanness of graphene surface was also verified by XPS (Figure 5c) and FT-IR full spectra (Figure S7). The wax-transferred graphene clearly exhibits inappreciable peak-shift as well as a similar spectral width of the C 1s peak at 284.6 eV as that of graphene on Cu foil, which demonstrates the narrowest spectral width among all cases due to the absence of polymer adsorption on its surface, also showing the cleanness of the transferred graphene surface. Additionally, we can conclude from FT-IR spectra in the hydrocarbon characteristic region (2700–3400 cm$^{-1}$) (Figure 5d) that the result of wax-assisted transfer is far more similar to that on SiO$_2$, whereas that of PMMA-assisted transfer shows the stretching vibration of saturated hydrocarbons obviously exhibiting the existence of PMMA residues. There are only three small peaks at hydrocarbon compound characteristic region. The 2848 cm$^{-1}$ ($\nu$s CH$_2$), 2921 cm$^{-1}$ ($\nu$as CH$_2$), and 2956 cm$^{-1}$ ($\nu$as CH$_3$) peaks can be observed clearly in PMMA-assisted transfer graphene sample and cannot be observed on SiO$_2$ substrate. In

Figure 6. Comparison by DRS signals of graphene transferred by wax and PMMA. (a) Illustration of DRS signal measuring principle. (b) Schematic of homemade microscopic DRS spectrometer. (c) Measured DRS spectrum of graphene by wax and simulated results. (d) Measured DRS map of graphene at 600 nm wavelength corresponding to c. (e) Measured DRS spectrum of graphene by PMMA. (f) Measured DRS map of graphene at 600 nm wavelength corresponding to e.
wax transfer graphene sample, three small peaks can be observed. The single-layer graphene deposited on glass shows a transparency of ca. 97.3% at a wavelength of 550 nm at 200 °C and 97.1% at 140 °C as shown in Figure 5e, which is comparable to the theoretical transmittance of 97.7% for single-layer graphene at that wavelength, indicating the intrinsic optical property of the pristine single-layer graphene.

Some common methodologies for attesting the transfer quality of the graphene are fabrication of FET\textsuperscript{1,4,6,20,26} or some LED devices.\textsuperscript{23} From the perspective of electrical properties including intrinsic carrier density,\textsuperscript{4} distribution of Dirac Point,\textsuperscript{6} sheet resistance,\textsuperscript{10} field-effect mobilities,\textsuperscript{20} type doping,\textsuperscript{26} etc. Herein we utilized differential reflectance spectroscopy (DRS) to demonstrate the validity of our wax-assisted method directly in the aspect of photometric characteristics.

DRS is used to measure the optical reflection difference on various surfaces\textsuperscript{29} and has been applied to the thickness measurement of two-dimensional materials.\textsuperscript{30} Differential reflection signal $\Delta R$ is expressed as

$$\Delta R = \frac{R_a - R_t}{R_0} \tag{1}$$

The $R_t$ represents the reflectance of the reflected light passing through graphene/SiO$_2$/Si, and $R_0$ represents the reflectance of the reflected light passing through SiO$_2$/Si, as shown in Figure 6a. The system is the homemade microscopic DRS measuring system (Figure 6b). The light source is program-controlled monochromatic output, and the multichromatic DRS measurement is realized in the form of multifold wavelength scanning. In this study, the reference sample and the tested sample are SiO$_2$/Si substrate and Graphene/SiO$_2$/Si, respectively. In the process of measurement, the reflected light map of $R_t$ and $R_0$ are collected to calculate the DRS map by the time-sharing switch control of the electric shutter. The DRS is composed of the mean values of the central region of the DRS maps at all wavelengths.

Figure 6c shows DRS of graphene transferred by wax. The results are in good agreement with the simulated graphene thickness of 0.5 nm. Meanwhile, we characterized the DRS map at 600 nm wavelength because of its highest sensitivity to the thickness (Figure S8). As shown in Figure 6d, the graphene transferred by this method is in high quality, smooth surface and little residue. Figure 6e shows the DRS of the specimen transferred by PMMA. Apparently, the DRS signal here exhibits a significant difference with monolayer/bilayer/multilayer graphene due to the PMMA residues, so that the spectrum does not fit the characteristics of pure graphene model very well. From the DRS map in Figure 6f, there are obvious residues and carbon blocks in some areas transferred by PMMA. The black region is the more obvious DRS signal caused by the residue, which is consistent with the spectrum analysis from Figure 6e mentioned above. As a result, the wax-transfer method is superior to the PMMA-transfer one in terms of transferred film quality and residual situation.

In summary, we demonstrate a simple, reliable, cost-effective, and easily scalable procedure for transferring monolayer graphene grown on Cu surface by controlling adhesion of paraffin wax. Compared with the traditional polymer-assisted transfer approach, the methodology with evaporable glass state molecular aggregation paraffin wax proposed here is beneficial to manage the boiling point of wax by tuning the pressure given its heat of vaporization and vapor pressure at a certain temperature, thereby maintaining good crystalline integrity and large-area continuity without defects on the edge or remnants on the surface. The analyses of our results on transferred graphene indicate less damage or contamination especially at the fringe of graphene films resulting from our transfer technique, which allows more applications regardless of other 2D materials or target substrate. In the foreseeable future, better effects are also expected by means of lower-melting point glass state small molecular under lower pressure.

**ASSOCIATED CONTENT**

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.8b21946.

Experimental materials, methods, characterization, effect of reductive atmosphere (with hydrogen) and evaporation environment, fabrication and introduction of DRS, SEM, AFM, Raman, FT-IR, ATR-FTIR (PDF)

**AUTHOR INFORMATION**

**Corresponding Authors**

*Email: bwli@whut.edu.cn.
*Email: shenyt@tju.edu.cn.
*Email: cghu@tju.edu.cn.
*Email: weifeng@tju.edu.cn.

**ORCID**

Yongtao Shen: 0000-0002-4463-6436
Chunguang Hu: 0000-0001-6485-904X
Wei Feng: 0000-0002-5816-7343

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Natural Science Foundation of China (NSFC) (Grants 2016YFB1102203, 2017YFF0107003).

**REFERENCES**


**Author Information**

**Corresponding Authors**

*Email: bwli@whut.edu.cn.
*Email: shenyt@tju.edu.cn.
*Email: cghu@tju.edu.cn.
*Email: weifeng@tju.edu.cn.

**ORCID**

Yongtao Shen: 0000-0002-4463-6436
Chunguang Hu: 0000-0001-6485-904X
Wei Feng: 0000-0002-5816-7343

**Notes**

The authors declare no competing financial interest.

**ACKNOWLEDGMENTS**

This work was supported by the National Natural Science Foundation of China (NSFC) (Grants 2016YFB1102203, 2017YFF0107003).

**REFERENCES**


Supporting Information

Evaporable Glass-state Molecules-assisted Transfer of Clean and Intact Graphene onto Arbitrary Substrates

Jingyi Qu¹, Bao-Wen Li²*, Yongtao Shen¹*, Shuchun Huo³,⁵, Ying Xu¹, Shiyuan Liu¹,
Baokun Song⁴, Hao Wang³,⁵, Chunguang Hu³,⁵*, Wei Feng¹*

1 School of Materials Science and Engineering, Tianjin University, Tianjin Key Laboratory
of Composite and Functional Materials, Tianjin 300350, P.R China.

2 School of Materials Science and Engineering, Wuhan University of Technology, Wuhan
430070, P.R China.

3 State Key Laboratory of Precision Measuring Technology and Instruments, Tianjin
University, Tianjin 300072, P. R China.

4 State Key Laboratory of Digital Manufacturing Equipment and Technology, Huazhong
University of Science and Technology, Wuhan 430074, Hubei, China.

5 Nanchang Institute for microtechnology of Tianjin University, Tianjin 300072, P. R
China.

Corresponding Authors

* Email: bwli@whut.edu.cn

* Email: shenyt@tju.edu.cn
Section A. Materials and Methods

Materials.
Continuous large-area monolayer graphene with few-layer particles was synthesized according to the reported literature\textsuperscript{1}. Hexagonal single-crystal graphene was synthesized according to the reported literature\textsuperscript{2}. Monolayer h-BN was purchased in SixCarbon Technology Co.

Graphene and h-BN Transfer. The graphene on one side of Cu foil was first etched upon exposure to an O\textsubscript{2} plasma. The paraffin wax (Aldrich, 58-62 °C (ASTM D 87)) was heated at 70°C and spin-coated on the graphene. Then the graphene/wax film was floated on aqueous (NH\textsubscript{4})\textsubscript{2}S\textsubscript{2}O\textsubscript{8} solution to etch the Cu foil away. The suspended film was rinsed using deionized water and subsequently transferred onto the target substrate. After drying in the ambient condition, the wax layer was removed by annealing at certain temperatures (140 - 200 °C) and pressure (below 0.2 torr) for 5h with the gas flow of hydrogen (20 sccm) and argon (20 sccm).

The PMMA-based transfer method was carried out in similar procedures. After transferring the PMMA/graphene film to the target substrate, the PMMA layer was removed by acetone.

Monolayer h-BN was transferred by wax with the same method as graphene.

Characterization. Optical images were collected with a ZEISS optical microscope (AxioCam MRc5). The microstructures and morphologies were characterized with Scanning Electron Microscopy (SEM, Hitachi S4800, Japan). AFM images were carried out with Bruker Dimension Icon AFM. Raman spectroscopy was performed with a WITec GmbH using 514 nm laser at 1 mW. The chemical compositions were characterized by Fourier-transform infrared spectroscopy (FT-IR, BRUKER AXS GMBH, FTIR-650). X-ray photoelectron spectra were collected using a monochromated Al K\textalpha\ line (Thermo Fisher, spot size, 900 μm). The transparency of graphene on glass and FET film was investigated with Cary Series UV-Vis-NIR Spectrophotometer (Agilent Technologies). The electronic properties were measured with a 4200-SCS semiconductor characterization system (Keithley). TEM grid (200-mesh, without carbon coated, Beijing Xinxingbairui Technology Co., Ltd).

Effect of reductive atmosphere (with hydrogen). Low-pressure is given preference as the atmospheric pressure inside the furnace tube can be adjusted by gas flow and provides gradient to the incoming gases. And hydrogen, as a typical reductant gas, is extensively used by many great
predecessors. Therefore, the density of wax species becomes lower in the furnace tube and evaporation rate remains stable. It is obvious that the high vacuum in the vicinity of melting point temperature of wax intensifies its sublimation from the surface of graphene at such a low-pressure condition. This high degree of evaporation of wax promotes the surface self-diffusion and hence its stepping motion. Additionally, because the experimental conditions cannot reach absolute vacuum in the actual situation, supplementing hydrogen can effectively prevent graphene from being oxidized in the process of paraffin wax evaporation.

**Effect of evaporation environment on wax removal.** In terms of Clausius–Clapeyron equation, the gasification (boiling point) of small molecule corresponds to the temperature at which the vapor pressure of the liquid equals the surrounding environmental pressure.

\[
T_B = \left( \frac{1}{T_0} - \frac{R \ln\left(\frac{P}{P_0}\right)}{\Delta H_{vap}} \right)^{-1}
\]  

where:

- \(T_B\) is the boiling point at the pressure of interest (in K).
- \(R\) is the ideal gas constant, \(8.314 \text{ J} \cdot \text{K}^{-1} \cdot \text{mol}^{-1}\).
- \(P\) is the vapor pressure of the liquid at the pressure of interest, either atm or kPa depending on the standard pressure used.
- \(P_0\) is some pressure where the corresponding \(T_0\) is known, (usually data available at 1atm or 100 kPa).
- \(\Delta H_{vap}\) is the heat of vaporization of the liquid, \(\text{J} \cdot \text{mol}^{-1}\) at \(P_0\).
- \(T_0\) is the boiling temperature (in K).

**Fabrication of DRS.** The experimental sample with graphene film (G/SiO\(_2\)/Si) and the reference sample without graphene (SiO\(_2\)/Si) were placed at the appropriate position; the \(R_t\) image was captured from the experimental sample; the \(R_0\) image was captured from the reference sample. The light source output stable broad-spectrum white light with high stability xenon lamp L2174 (Hamamatsu) and power supply module. The monochromatic optical imaging was collected with SP2155 (Princeton Instruments). Other components of our homemade DRS device include a microscope objective lens (Nikon, 5-fold) and a research-grade CMOS camera (PCO PANDA 4.2). The optical path can be switched by controlling the electronic shutter so that the time-sharing image measurement of the experimental sample and the reference sample can be carried out.
Section B. Supporting Figures

Figure S1. (a) Monolayer h-BN transferred by wax. (b) the SEM image and (c) optical image of monolayer h-BN.

Figure S2. SEM images of Wax- (a, b) and PMMA- (c, d) transferred graphene films on SiO₂.
Figure S3. (a) and (b) Different magnification AFM images of PMMA-transferred graphene films on SiO$_2$.

Figure S4. High magnification (a) AFM and (b) SEM images of wax-assisted transfer of graphene onto the SiO$_2$/Si wafer.
Figure S5. Raman spectra of graphene marked at (a) position 2 and (b) position 3 in Figure 4a.

Figure S6. FT-IR of (a) EVA and (b) wax in RT and 140°C.
Figure S7. (a) ATR-FTIR spectra of Wax, and PMMA-transferred graphene films on SiO$_2$ in the and (b) hydrocarbon characteristic region marked by a red square shown in (a).
I. Measuring principle:
The DR signal is defined as:
\[ \Delta R = \frac{R_0 - R_t}{R_0} \]

The \( R_t \) and \( R_0 \) correspond to the reflectivity of whether there are thin films on the substrate or not. In terms of the measurements for the multilayer-film structure in this case, the reflectivity of the stacked nano-film structure can be modeled mathematically based on Fresnel's law as follows. \( R_t \) corresponds to \( R_{0123} \) and \( R_0 \) corresponds to \( R_{023} \).

\[ R_{0123} = \left( \frac{r_{01} + r_{12}e^{-j\beta_1}}{1 + r_{01}r_{12}e^{-j\beta_2}} \right) + \left( \frac{r_{12}r_{23}e^{-j\beta_2}}{1 + r_{12}r_{23}e^{-j\beta_3}} \right) \\
R_{023} = \frac{r_{23}e^{-j\beta_3}}{1 + r_2r_3e^{-j2\beta_3}} \]

\( r \) represents the reflection coefficient at the interface between two different materials; \( \beta \) represents the optical thickness of the layer; subscript 0, 1, 2, 3 represents the environmental medium (air), film layer 1 (graphene), film layer 2 (SiO\(_2\)), substrate (Si), respectively; \( j \) represents the imaginary unit and the E exponential is the abbreviated form of Euler formula. The parameters are calculated as follows.

\[ \beta_1 = \frac{2\pi d_1}{\lambda} n_1, \quad \beta_2 = \frac{2\pi d_2}{\lambda} n_2, \]

\[ r_{01} = \frac{n_0 - n_1}{n_0 + n_1}, \quad r_{12} = \frac{n_1 - n_2}{n_1 + n_2}, \quad r_{23} = \frac{n_2 - n_3}{n_2 + n_3} \]

\( d \) is the geometric thickness of the layer, and \( N \) is the refractive index corresponding to the measurement wavelength.

Figure S8. Simulated DRS of one to six layers of graphene on silicon substrates with a 300nm-thick SiO\(_2\) layer.
Figure S8 shows the numerical simulation results of the various DR spectrum for G of increasing number of layers. The substrate is 300 nm thick SiO$_2$ on Si, and here the thickness of single layer graphene is set to 0.34 nm. The DR signal near 600nm in visible band shows a monotonous increase with graphene’s thickness. In addition, it also has the characteristics of high signal sensitivity, high precision and relatively low requirement for measuring instruments. Near 270 nm and 370 nm, the sensitivity of DR signal is also quite high, but it requires much higher measuring instruments and is feasible to achieve high precision.

## II. Measuring devices and processes

The light source output stable broad-spectrum white light with high stability xenon lamp L2174 (Hamamatsu) and power supply module. The monochromatic optical imaging was collected with SP2155 (Princeton Instruments). Other components of our homemade DRS device include a microscope objective lens (Nikon, 5-fold) and a research-grade CMOS camera (PCO PANDA 4.2). The optical path can be switched by controlling the electronic shutter so that the time-sharing image measurement of the experimental sample and the reference sample can be carried out.

The measurement process is showed as follows: the experimental sample with graphene film (G/SiO$_2$/Si) and the reference sample without graphene (SiO$_2$/Si) are placed at the appropriate place; the $R_t$ image is captured from the experimental sample; the $R_0$ image is image captured from the reference sample. And the DR image within this wavelength is calculated by formula $\Delta R = (R_0 - R_t)/R_0$. 
References
