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Sublimation-assisted graphene transfer technique based on small polyaromatic hydrocarbons

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Abstract

Advances in the chemical vapor deposition (CVD) growth of graphene have made this material a very attractive candidate for a number of applications including transparent conductors, electronics, optoeletronics, biomedical devices and energy storage. The CVD method requires transfer of graphene on a desired substrate and this is most commonly accomplished with polymers. The removal of polymer carriers is achieved with organic solvents or thermal treatment which makes this approach inappropriate for application to plastic thin films such as polyethylene terephthalate substrates. An ultraclean graphene transfer method under mild conditions is highly desired. In this article, we report a naphthalene-assisted graphene transfer technique which provides a reliable route to residue-free transfer of graphene to both hard and flexible substrates. The quality of the transferred graphene was characterized with atomic force microscopy, scanning electron microscopy, and Raman spectroscopy. Field effect transistors, based on the naphthalene-transfered graphene, were fabricated and characterized. This work has the potential to broaden the applications of CVD graphene in fields where ultraclean graphene and mild graphene transfer conditions are required.

Keywords: graphene transfer, small polyaromatic hydrocarbons, sublimation

(Some figures may appear in colour only in the online journal)

Introduction

Graphene is a 2D material composed of sp^2 hybridized carbon atoms with unique optical, mechanical, thermal and electronic properties. These properties determine the growing interest in the application of the material in optics [1], electronics [2–5], spintronics [6], energy storage [7–10], composites [11] and biomedicine [12]. Chemical vapor deposition (CVD) grown graphene has developed to be one of the most competitive candidates for graphene synthesis [13]. Researchers have made encouraging progress to produce large scale, large domain continuous single layer graphene [14, 15]. The CVD process utilizes a metal substrate (copper or nickel) for the graphene growth, which requires transfer of the graphene film onto a desired substrate and this is usually accomplished using polymers. In these transfer methods a polymer is used as the supporting layer to protect graphene from the surface tension of the etching solution after the metal substrate is etched away. After transfer to a target substrate, the carrier polymer is removed using a variety of methods including chemical washing, mechanical force, and thermal annealing. However, despite the variety of techniques employed, complete removal of polymer

residues without degrading the quality of graphene is quite difficult. Conventional wet transfer method utilizes poly(methyl methacrylate), PMMA, as the carrier, and the complete removal of PMMA residue has never been achieved without damaging graphene regardless of various post-transfer cleaning processes [16, 17]. Thermal release tape assisted roll-to-roll method [18] has been reported to leave adhesive residues on the surface of graphene [19], while PDMS stamp based transfer method [20] is known to leave oligmers on the surface of graphene which require annealing in vacuum at high temperature (400 °C) in order to be completely removed [21]. Furthermore, these techniques are often incompatible with sensitive substrates which cannot tolerate harsh organic chemical washing or high temperature annealing, such as polyethylene terephthalate (PET).

An ideal carrier would satisfy three conditions: (1) easy to apply onto the Cu/Ni-graphene substrate (2) has strong adhesion to graphene (3) easy to remove under mild conditions once the graphene has been placed on the target substrate. Generally, polymer materials satisfy the first two conditions, but condition 3 remains a challenge. In our previous work we developed a graphene transfer method based on cellulose acetate [22], which produces ultraclean graphene, however, it cannot be applied to plastic substrates because the processes involve the use of organic solvents (acetone).

In this article we discuss a new method to transfer graphene based on the small polycyclic hydrocarbon naphthalene in place of much larger polymers. By replacing large polymers, such as PMMA, with a small molecule, such as naphthalene, the graphene transfer can be performed without leaving behind contaminants that affect the properties of graphene. Naphthalene is an ideal candidate as a graphene transfer material because it satisfies all three criteria: (1) it can easily be spin-coated or melted onto CVD graphene (2) it adheres strongly to the graphene surface due to π–π interactions (3) it is easy to remove since naphthalene sublimes under atmospheric pressure or optionally it can be fully dissolved in most organic solvents.

We demonstrate that the naphthalene-assisted transfer (NAT) of graphene is a simple and facile technique, which produces high quality clean graphene that can be transferred onto arbitrary substrates. The naphthalene is easy to remove by sublimation and it does not affect the electronic properties of graphene, making this technique suitable for preparation of electronic devices. The transferred graphene is characterized with Raman spectroscopy, atomic force microscopy (AFM) and scanning electron microscopy (SEM). The transfered graphene was also used for the fabrication of field effect transistors (FETs) with carrier mobilities above 700 $cm^2 V^{-1} s^{-1}$ at 300 K.

Experimental section

Naphthalene assisted transfer of graphene

CVD graphene grown on copper foil was purchased from Nanjing Mknano Tech. Because CVD growth produces graphene on both sides of the copper foil, one side of the as-grown monolayer CVD graphene was first removed by oxygen plasma (Oxford Plasmalab 100/180 model; forward power 30 W; ICP power 300 W, etch time 30 s). Naphthalene crystals (Sigma Aldrich) were placed into a small beaker and melted on a preheated hotplate at 100 °C. The melted liquid naphthalene was drop cast onto the surface of graphene on copper, followed by immediate pressing with a glass slide to squeeze out extra naphthalene and leave a thin film on top of the graphene. To prevent adhesion of the naphthalene to the glass surface, the slide was covered with a Kapton tape (McMaster, model #7361811). The pressing slide is then removed after the naphthalene has cooled (5–10 s). To remove the copper, an aqueous solution of H_2O_2 and HCl was prepared by mixing equal volumes of 2 M HCl and 1 M H_2O_2; the solution etched away the Cu substrate (25 μm) underneath the CVD graphene within 10 min. The graphene sample supported by the naphthalene film was thoroughly cleaned by replacing the etching solution with distilled water multiple times. The graphene was then lifted with the target substrate, placed in a vacuum oven and kept at 60 °C for 1 h to sublime the naphthalene supporting layer. The graphene can be further cleaned by immersing it into hot (60 °C) ethanol for 15 min to remove any remaining adsorbed naphthalene molecules on the surface of graphene; this step however is not required for successful transfer of clean graphene.

Thermogravimetic analysis (TGA)

The TGA measurements were performed at a heating rate of 1 °C min^{-1} in air with a Pyris 1 thermo-gravimetric analyzer (Perkin Elmer).

Raman spectroscopy and mapping

Raman spectra and maps were recorded with a Nicolet Almega XR Dispersive Raman microscope using 532 nm laser excitation and 25% power source. The laser spot size is around 1 μm. The Raman mapping area for all samples is 10 μm × 10 μm, with a step size of 1 μm in both x and y directions.

Atomic force microscopy (AFM)

AFM images of graphene films transferred on SiO_2/Si substrate were collected in a tapping mode with Digital Instruments Nanoscope IIIA. High resolution silicon AFM Probes NSG01 (cantilever length 125 μm, cantilever width 30 μm, cantilever thickness 1.5–2.5 μm, resonant frequency 87–230 kHz, force constant 1.45–15.1 N m^{-1}, NT-MDT Spectrum Instruments) were used.

Scanning electron microscopy (SEM)

SEM images were collected with a Leo XB1540 Focused Ion Beam Milling system in the cleanroom of the University of California, Riverside.

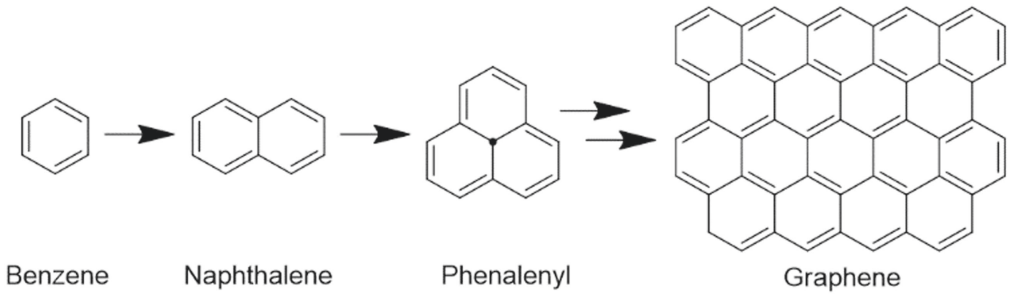

Figure 1. Schematic illustration of the structural similarity between naphthalene and graphene: from left to right benzene (monomer), naphthalene (dimer), phenalenyl (trimer) and graphene (polymer).

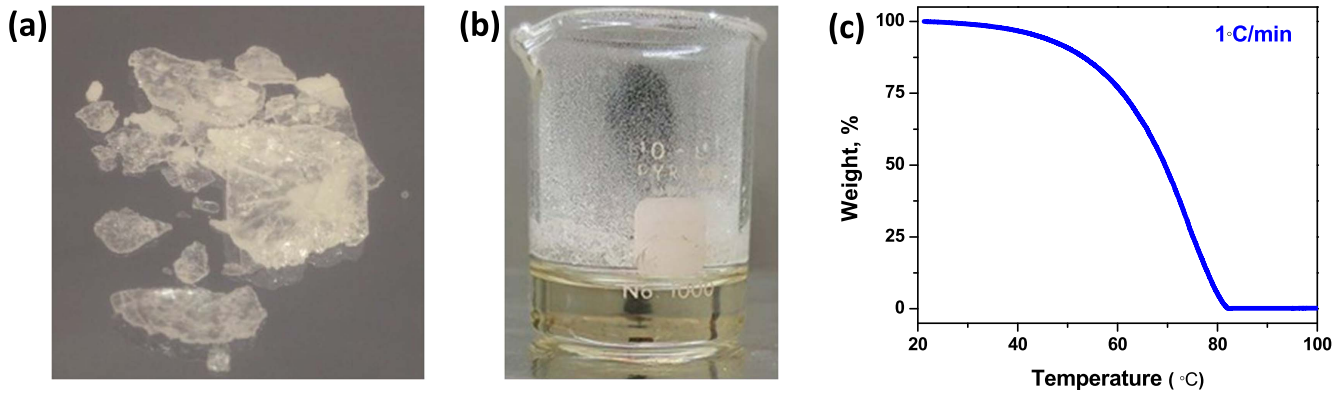

Figure 2. Crystalline (a) and melted (b) naphthalene. (c) Thermogravimetric analysis of naphthalene crystals in air at a heating rate of 1 °C min^{-1}; the weight is normalized to the initial material weight.

Fabrication of field effect transistors (FETs)

For the FETs, the drain and source electrodes (10 nm Cr/100 nm Au) were evaporated by e-beam (Temescal BJD 1800) onto 300 nm SiO_2/Si substrates following photolithography processes. Next the as-grown monolayer CVD graphene was transferred onto the pre-patterned substrates. The channel dimensions of the FET graphene device are 6 μm (length) and 2 μm (width). The devices were thermally annealed at 200 °C in vacuum (5×10^{-7} Torr) prior to measurements to remove atmospheric dopants and bring the Dirac point in the vicinity of 0 V.

Results and discussion

In this work we replace high molecular weight polymers with the small molecule naphthalene as the holding layer in graphene transfer. Naphthalene is the smallest polycyclic aromatic hydrocarbon (PAH) and it is essentially a dimer of benzene [23]. Much like graphene, naphthalene shares the same building block—the benzenoid aromatic ring (figure 1), and this structural similarity has stimulated theoretical and experimental interest in the adsorption of naphthalene on pristine graphene.

Calculations have predicted a strong adsorption of the small PAH molecule on the honeycomb lattice of graphene due to π–π interactions with a binding energy of 763 meV [24], which is comparable to the experimental values obtained for graphite [25]. The adsorbed naphthalene molecule adapts an approximately planar geometry with a preferential AB stacking configuration [26] making this small PAH a good candidate for a supporting layer during graphene transfer. Furthermore, band structure calculations suggest that the adsorbed naphthalene molecule does not induce a charge transfer preserving the electronic structure of graphene [26], which is important for applications in electronics and optoelectronics.

Other attractive features of the naphthalene as a supporting layer are its good casting properties and sublimation at room temperature under atmospheric pressure [27]. In fact, naphthalene is most known as being used in moth balls as it repels unwanted pests upon sublimation. Naphthalene is soluble in most organic solvents and it can be easily spin-coated on top of graphene. Most transfer technique utilize spin-coating for the formation of a carrier layer and in our first experiments we spin-coated an ethanol solution of naphthalene on top of the CVD graphene. However, we also found that the process can be further simplified by coating the graphene films with molten naphthalene, because this small PAH melts at relatively low temperature (melting point 80 °C). This step allows the formation of a supporting film without the use of any solvent. Figure 2 illustrates pictures of naphthalene in crystalline and melted form, and a TGA graph showing the weight loss of the material at low temperature (from room temperature to 100 °C).

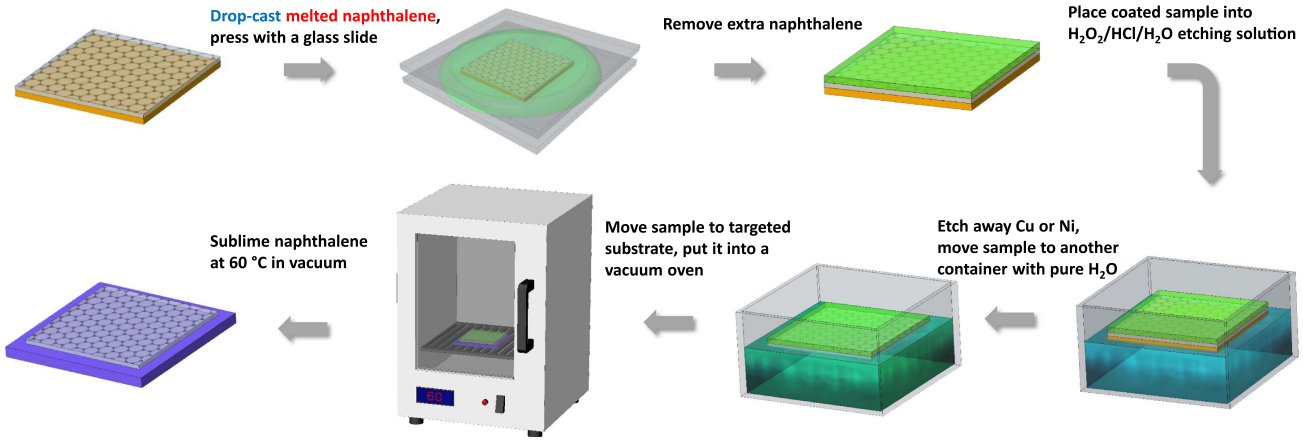

Figure 3. Schematic illustration of the naphthalene assisted transfer of graphene.

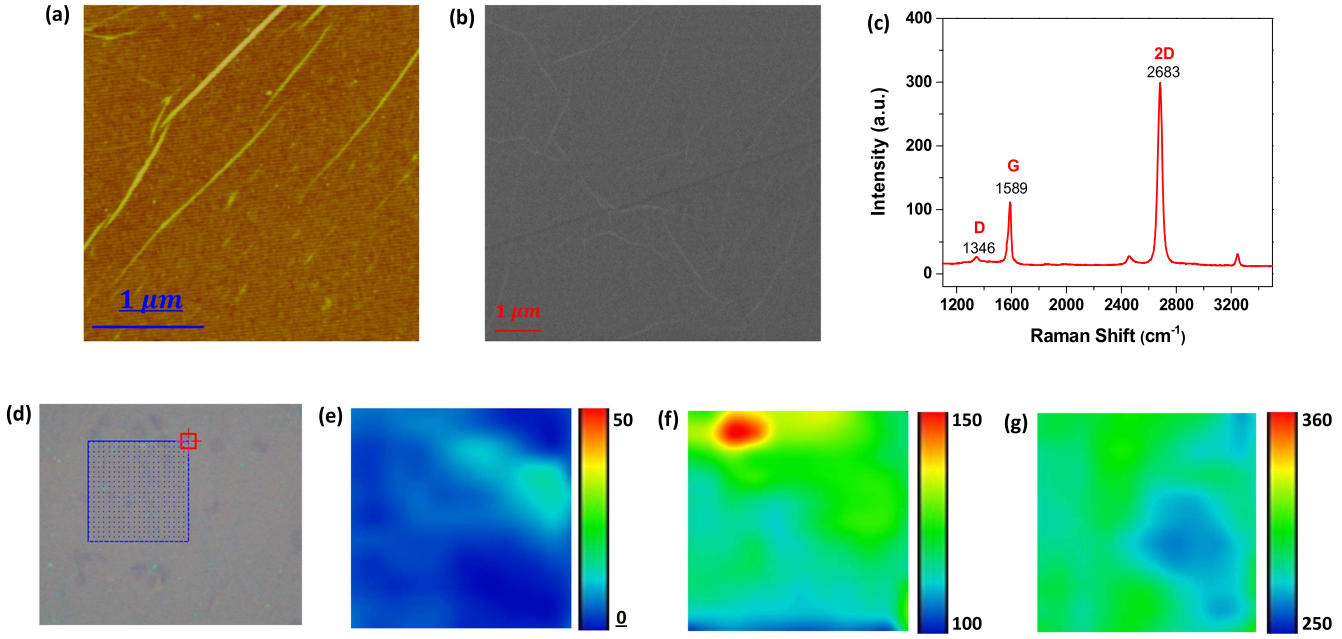

Figure 4. Characterization of the transferred graphene. (a) AFM and (b) SEM images after transfer of graphene on SiO_2/Si substrate; (c) Raman spectrum of a single layer CVD graphene transferred by NAT method. (d) Optical image of transferred graphene on SiO_2/Si substrate, Raman mapping was performed on the 10 μm × 10 μm (blue square). (e)–(g) Raman intensity maps of D, G, and 2D peaks, respectively.

In a typical experiment the naphthalene is melted in a beaker (figure 2) and drop cast onto the surface of the CVD-grown graphene, then pressed with a glass slide covered with Kapton tape to ensure good continuous contact. Once the naphthalene cools into a wax-like solid, the substrate is placed into the water-based etching solution until the copper foil, supporting the graphene, is dissolved. The naphthalene film provides a good mechanical support for the graphene through this step because of the naphthalene's low solubility in water, due to its nonpolar character. In the next step, the naphthalene-supported graphene is placed onto the target substrate and it is sublimed in air (or vacuum) leaving a clean graphene film. The transfer process is schematically illustrated in figure 3.

The cleanliness of the transferred graphene was evaluated by AFM and SEM and representative images are shown in figure 4. Both characterization techniques reveal a very clean graphene surface which is associated with the clean removal of the supporting naphthalene layer by sublimation. This is an important advantage of the sublimation-assisted transfer method over the conventional polymer-assisted transfer techniques, which require tedious cleaning steps to remove the polymer. In fact obtaining residue-free graphene with these conventional techniques remains problematic. Chiu *et al* reported that the PMMA residue cannot be totally removed in a two-step annealing process with air and H_2/Ar without damaging the graphene, because the decomposition temperature of some PMMA residues is higher than the susceptible temperature of graphene [16]. Laser [28] and electrolyte [29] cleaning methods were also employed to reduce the PMMA residues, however none of these methods can fully remove the

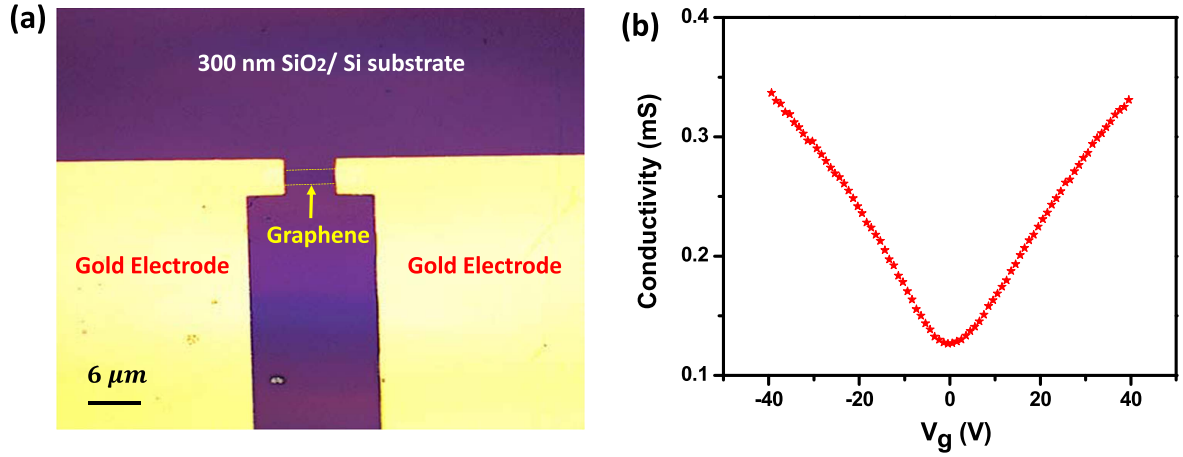

Figure 5. Electrical properties of a NAT-graphene FET on 300 nm SiO_2/Si. (a) Optical image of a typical FET graphene device. (b) Conductivity versus gate voltage recorded at drain–source voltage of 0.01 V.

residues. A combination of washing with a solvent (acetone) followed by vacuum annealing has also been suggested as a cleaning procedure of the PMMA-transferred graphene [30].

The low temperature solvent free removal of the supporting layer makes the naphthalene-assisted graphene transfer technique suitable for transfer on virtually any substrate, especially flexible plastic films that are widely used for transparent electrodes or flexible electronics.

The transferred graphene was further characterized with Raman spectroscopy. This analytical technique is routinely used for evaluation of graphene quality [31, 32]. The characterization typically involves analysis of several distinct peaks: the G peak corresponding to the high-frequency E_{2g} phonon at the Brillouin zone center, the D peak related to the breathing modes of the six-atom rings which becomes Raman active in the presence of defects, and the 2D peak (overtone of D-peak) that appears as a single sharp peak with much higher intensity than the G peak and does not require defects for activation. Doping of graphene is known to shift the position of G and 2D peaks and to significantly decrease the ratio of 2D to G peak intensities [32].

Typical Raman spectrum and Raman maps of the D, G and 2D peaks are shown in figures 4(e)–(g). The Raman spectra showed a small or no D peak, which confirms the good quality of the transferred graphene film. The G peak was observed at 1589 cm^{-1}, indicating absence of doping. Because charge transfer or doping changes the Fermi level of graphene, doping results in shift of the G peak position and it has been reported to upshift the peak for both electron and hole doping [33]. The fact that naphthalene preserves the pristine state of graphene is also manifested in the strong 2D peak at 2683 cm^{-1} observed in the Raman maps of 10 μm × 10 μm areas (figure 4(g)). It is known that both the intensity and the position of the 2D peak are downshifted for high electron doping [34, 35].

To determine the electronic properties of the NAT graphene, FETs were fabricated and tested. The optical image of a typical NAT-graphene FET device with dimensions of 6 μm (length) and 2 μm (width) is shown in figure 5(a). Figure 5(b) illustrates the corresponding conductivity versus gate voltage after thermal annealing. The curve shows symmetric transport characteristics with the Dirac point at 0 V. The extracted values of hole and electron mobilities are in the range of 700 $cm^2\ V^{-1}\ s^{-1}$ with an on-off ratio of 2.3 at 30 V.

Conclusions

In conclusion, we have developed a new single molecule-based transfer method for graphene. This new method is simple and avoids the use of difficult to remove polymers. By replacing high molecular weight polymers with low molecular weight small molecules, high quality graphene films can be easily obtained. The ability of naphthalene to sublime at room temperature is one of the most attractive features for transfer of graphene on substrates that have chemical incompatibility with organic solvents or thermal restrictions.

The transferred graphene films were characterized with Raman spectroscopy, SEM and AFM. Because adsorption of naphthalene does not affect the electronic properties of graphene and it is easily removed, the graphene transferred by this technique is suitable for fabrication of electronic devices and we demonstrate graphene FETs with carrier mobilities above 700 $cm^2\ V^{-1}\ s^{-1}$. The naphthalene transfer method has the potential to expand the uses of CVD graphene by providing a cheap and simple transfer method without the problem of polymer residues. The availability of clean graphene films is crucial not only for device fabrication, but also for understanding the chemical reactivity of this extended pi-conjugated carbon system such as in the formation of organometalic hexahapto bonds with transition metals [36–38].

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