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To cite this article before publication: Jiye Fu *et al* 2019 *Nanotechnology* in press https://doi.org/10.1088/1361-6528/ab0cab

Advanced transferring of large-area freestanding graphene film by using fullerenes

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ABSTRACT

Freestanding graphene films are desired to be widely applied in biosensor fabrication for their distinctive physical properties and improved performance. Chemical vapor deposition has been developed to efficiently fabricate large-area graphene. However, some of the fabricated graphene films might break or be contaminated in the current transferring step using polymers. A stable and high-quality transfer method is expected. Herein, we report an advanced transfer method of large-area graphene film which uses fullerene as supporting substrate. Unlike polymers, which were commonly eliminated by dissolving in organic solution, fullerene can be easily removed by evaporating in vacuum because its different heat stability than does graphene. By using the improved transferring method, the percentage of integrated freestanding films after transferring was increased from 60.7% to 93.4%. Vacuum ought to be benefit for keeping the brittle freestanding films intact. Graphene film transferred by using fullerene showed an advanced flatness and a simplicial elementary composition in comparison to those transferred by using polymers. Even through there is trace residue, this stable allotrope of graphene is considered to be almost no impact on biomolecules sensing. These advantages make fullerene transferring method an attractive candidate for fabricating large-area freestanding graphene films, especially using in the field of biochemistry analysis and biosensors.

KEYWORDS: fullerene; graphene; freestanding film.

Graphene, a crystalline allotrope of carbon with 2-dimensional properties, has caught more and more attention in research due to its fascinating characters.[1] Owing to its strong mechanical properties and high electron and light transmission, graphene is considered as a better freestanding membrane in comparison with other materials such as silicon nitride.[2] Nowadays, the freestanding graphene films are mainly used in the field of nanoporous sensing. For their ultrathin characteristics, freestanding graphene films show a great potential in improving the spatial resolution of nanopores. That would be of great help to promote the accuracy of DNA sequencing and protein detection.[3, 4] Freestanding graphene films could also be used to fabricate liquid cells in transmission electron microscope (TEM) observation.[5-7] The low contrast of graphene improves the imaging of low atomic number material, such as biomolecules and organic molecules. Therefore, controllable production of freestanding graphene films is benefit for the advancement of these fields.

Freestanding graphene films require high structure integrity to maintain their suspended state, so that the graphene films used as freestanding membranes are often fabricated by nanomechanical cleavage of graphite or chemical vapor deposition (CVD).[8, 9] Before CVD method was widely used, some groups used targeted substrates to lift graphite-cleaved graphene films directly from the surface of water .[10] This method should be carried out with great care since the graphene films break easily without efficient protection of the support layer. To decrease the operation difficulty, many other groups used polymer membranes to transfer the cleaved graphene.[11-13] With the aid of optical platform, these methods could be used to transfer graphene films to specific freestanding positions. But when transferring large area graphene films, the instability of these strategies impacts the result obviously.[14, 15] The application of CVD on graphene film preparation provided a good solution to generate small or irregular graphene films. To date the standard transfer method for CVD fabricated graphene films is using PMMA as the supporting layer, which had been a mature method in transferring and aligning carbon nanotube arrays.[16] With the comparable characteristics of simple operation and low cost, some other similar polymer films were also applied in graphene transferring.[13, 17-20] However, these methods have some hidden drawbacks for transferring the freestanding graphene films. On one hand, these methods usually used organic solution to remove the polymer layer and clean the substrate which inevitably introduce some organic

contaminants. As PMMA for example, acetone was often used to remove the PMMA layer, and isopropanol was used for cleaning subsequently.[19] The residue of these reagents will interfere the sensing of biological macromolecules. On the other hand, if the motion between targeted substrates and organic solvent was not gentle, the freestanding graphene films are prone to break. Meanwhile, the tension produced by the volatilization of organic solvent would also influence the integrity of the suspended part of the graphene films to some extent.[21]

To overcome the obstacles above, we developed an advanced freestanding graphene film transferring method by using fullerene as support layer. In our method, fullerene was deposited on the grown graphene film and supported it in transferring to the targeted substrate with pores. We followed the standard PMMA transfer method as a comparison. The use of fullerene films achieved a more reliable transfer performance and a simplicial elementary composition of the transferred freestanding graphene films.

Figure 1 shows the schematic illustration of the improved method and the traditional PMMA method. In the traditional method, graphene films were infiltrated in the liquid environment twice: firstly in the grown layer etching buffer ($FeCl_3$ solution) and secondly in the PMMA dissolving buffer (acetone). With the support of coated PMMA, the integrality of graphene was not influenced by the volatilization of etching buffer. However, after removing of PMMA, there was no support to protect the freestanding area of the fragile graphene film. What's more, to dissolve PMMA layer entirely, the whole PMMA/graphene complex should be immersed into the organic solution before being cleaned by isopropanol. As a result, the graphene film was so brittle at the freestanding areas under the tension from both sides. And the resistance caused by the liquid might break the freestanding areas and even the thin areas of targeted substrate. Meanwhile, tiny amount of acetone and isopropanol will reside on the graphene film inevitably. To avoid damage caused by removing transferring layer and organic contaminant introduced in this step, we used fullerene as support layer instead. Due to the different heat stability of fullerene and graphene, fullerene could be evaporated and removed while graphene keeps intact under appropriate temperature. [22-24] Apart from the key improvement above, the general technical route of our method is similar to the traditional PMMA transfer method. We firstly evaporated 50 nm

thick fullerene film at 600 °C in a vacuum thermal evaporator. Then the Cu foil was etched and the combined graphene film with the support of fullerene film was transferred to targeted substrate. At last, the transferred film and targeted substrate were put into the vacuum chamber again and the fullerene film would be "back-evaporated" under the same condition in the first step. Since the fullerene films were obtained by thermal evaporation, adjacent C60 molecules of the fullerene films are bound incompactly by van der Waals forces.[25] So the stability and mechanical properties are relatively poor and the fullerene films are easily broken and evaporated.

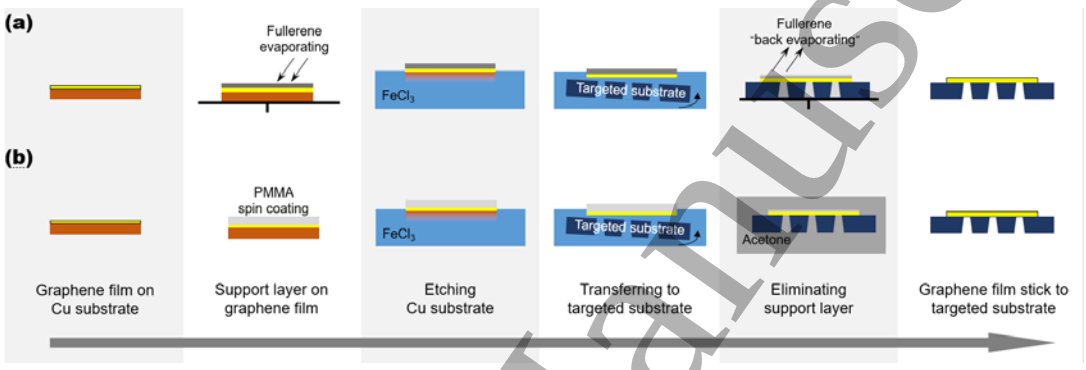

Figure 1. Two different processes for transfer of graphene films. (a). Large-area graphene film was grown on Cu foil. Fullerene was evaporated and deposited on the graphene film as supported layer at 600 °C. After Cu substrate etched, graphene film supported by fullerene film was lifted by the targeted substrate with pores. Fullerene was removed by evaporating at 600 °C to 900 °C. (b). PMMA was spin-coated on graphene film and eliminated by immersing in acetone after transferring. Targeted substrate with freestanding graphene film was lifted from acetone and cleaned in isopropanol.

To compare the success rate, parallel experiments were done by using the improved method and the traditional method. Custom designed silicon nitride chips as the targeted layer were purchased from Suzhou In-situ Chip Technology Co., Ltd. The chip is based on a 200 μm thick, 3×3 mm silicon wafer with a 50 nm thick silicon nitride attached. There are 9 corrosion windows of about 100×100 μm on each chip, making the silicon nitride film suspended. In each suspended area of silicon nitride film, there are several types of micron pore arrays with a diameter of 2.8 μm, and the number of pores in each array is designed to be 4 to 9 variously. The suspended areas were observed under scanning electron microscopy (SEM) after transferring (**Figure 2**), the intactness of graphene in the suspended areas was calculated (**Table 1**). Briefly, by using fullerenes as support layer, 93.4% of the freestanding graphene films were intact, while using PMMA, the intactness rate is only 60.7%. By using PMMA, the 50 nm

thick silicon nitride membranes were also broken in some cases, which is shown in Figure 2a. This phenomenon exhibits that without the support of PMMA, the freestanding graphene films, and even the suspend silicon nitride membranes, were brittle in acetone and isopropanol.

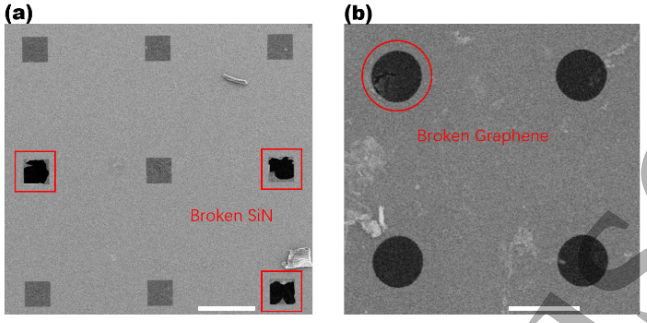

Figure 2. Typical SEM images after graphene films transferring. (a) Array of freestanding SiN membrane. Red boxes mark the broken sites of SiN membrane after transferring by PMMA (scale bar, 200 μm). (b) Array of micro pores on one freestanding SiN membrane after graphene film transferring using PMMA. A crack was captured on the transferred graphene film (scale bar, 4 μm).

Table 1. Success rate of two freestanding graphene transfer methods.

Samples	PMMA			Fullerene		
	SiN	Total	Gr	SiN	Total	Gr
#1	√	7	5	√	7	7
#2	×	7	0	√	7	7
#3	√	7	6	√	7	7
#4	√	9	8	√	9	8
#5	√	9	5	√	9	7
#6	√	9	9	√	9	9
#7	×	4	0	√	4	4
#8	×	5	0	√	5	4
#9	√	4	4	√	4	4
Rate	66.7%		**60.7%**	100.0%		**93.4%**

*The “total” column shows the number of micro pores in one freestanding SiN membrane and the “Gr” column shows the number of intact freestanding graphene films after transferring. If the SiN membrane was broken, the “SiN” column would be marked with an “×”. The last line shows the percentages of intact SiN membrane or freestanding graphene films in which the damage of SiN membrane was taken into account.

Smoothness and elementary composition of the freestanding graphene films transferred by these two methods were further evaluated and compared by SEM photography. **Figure 3a** shows the freestanding area of graphene films transferred by PMMA after etching Cu foil. There were many cotton-like and

white granular residues on the freestanding area and these residues even joined together to form lumps outside suspended area. This was typical feature of PMMA residues. We have tried to extend the reaction time and elevate temperature of PMMA removal, but the improvement was not obvious. On the contrary, the success rate of transferring further decreased by the intensified reaction conditions. **Figure 3b** and **3c** show one of the freestanding areas of graphene film before and after removing fullerene film. As seen in **Figure 3b**, small wrinkles on the Cu foil were amplified by fullerene film. The main reason of appearing these wrinkles is morphological replication of Cu foil during graphene synthesis and this situation can be improved by the advances in the CVD synthesis of graphene films.[26, 27] This phenomenon suggested that before fullerene film was removed, graphene film kept the same as the existence of Cu foil. Interestingly, after removal of the fullerene film, these winkles disappeared and the graphene film turned to be smooth (**Figure 3c**). Compared to the contact between PMMA film and graphene film by hard-coating and curing, the contact between fullerene film and graphene film is much softer[16] ,which is more conducive to graphene film returning to be flat. In addition, the graphene film transferred by fullerene showed a better homogeneity than PMMA, which can be further improved by optimizing the transfer process and upgrading the experimental environment. The Raman spectroscopy of the transferred graphene at 532nm (Figure 4) also revealed the characteristic peaks of graphene. No D peak was observed in the graphene films revealed the absence of a significant number of defects.

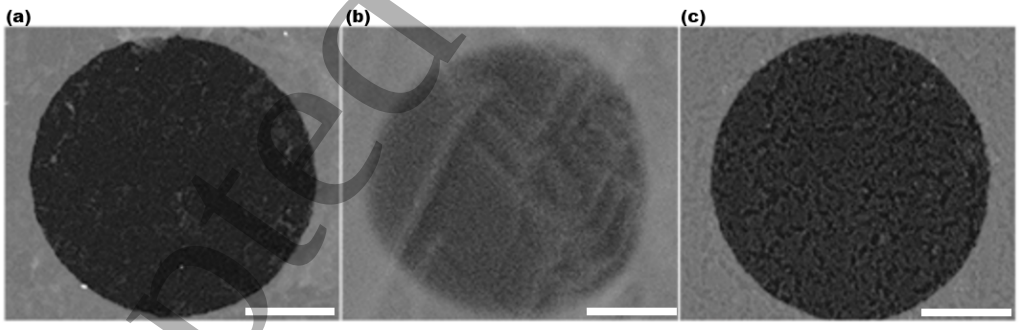

Figure 3. SEM images of freestanding graphene films transferred by two methods. The scale bar is 1 μm. (a) The image of graphene film transferred by PMMA method. (b) The image of graphene film transferred by fullerene before removing of support layer (fullerene). (c) The image of graphene film after removing the support layer (fullerene film). Regular and straight lines observed in (b) disappeared in (c).

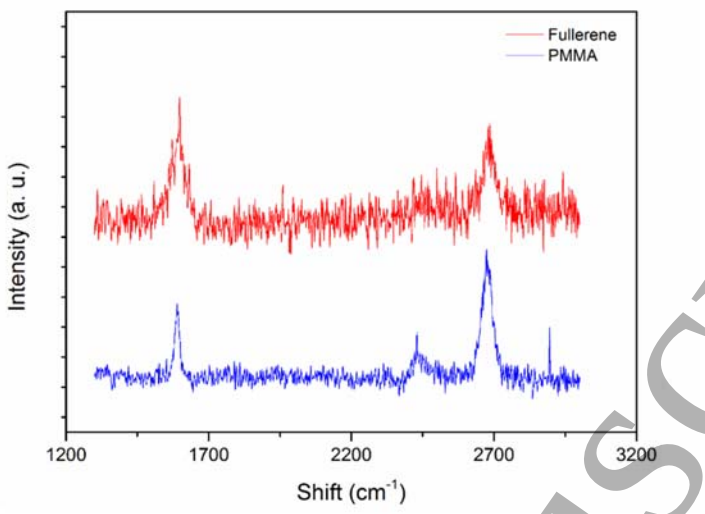

Figure 4. The Raman spectra of graphene films transferred by fullerene and PMMA measured at 532 nm. The two most intense features are the G peak at 1580 cm^{-1} and the 2D peak at 2700 cm^{-1}. The spectra also showed that no D peak is observed in the graphene films.

In order to further evaluate the residues produced by these two transfer methods, energy disperse spectroscope (EDS) was used for elemental analysis of transferred graphene films. **Figure 5c** shows the elemental map of the freestanding areas and nearby after two methods of transferring, and the regions being analyzed are shown in **Figure 5a** and **5b**. Besides silicon, nitride and carbon which belong to the targeted substrate and graphene film respectively, and the rest of elements in two transfer methods were mostly oxygen and an element causing a very small peak at about 1.5keV. The type of this element was unclear and the amount was too little to get a specific percentage of it. In PMMA method, the percentage of these two elements was 14.73% in total and in fullerene method, it was less than 1%. This result showed fullerene transferred graphene film has better cleanliness compared to PMMA transferred. The efficiency difference is partly attributed to the different thickness of support layers. PMMA films were coated to graphene films by rotating in this work, and by spraying in some other works. No matter which method used, the PMMA film is at least hundreds of nanometers thick. In contrast, the fullerene films formed by evaporation in our method were only about 50 nm. The elemental map illustrated the differences in carbon and oxygen elements between two methods. In PMMA transfer method, residual oxygen element was found, which represented the presence of PMMA and other organic solute on the transferred graphene films. PMMA has been confirmed to have adsorption effect on many biological

macromolecules such as proteins and DNAs.[28-31] Therefore, the presence of PMMA is unfriendly to the application of graphene films in biosensor experiments. This situation can be improved markedly by using fullerene instead. The low oxygen peak revealed that there was rare oxygenated compound on the surface of graphene film. Even the high temperature did not produce noticeable oxycarbides. We also noticed that the carbon peak of fullerene transfer method was higher than that of PMMA, which indicated the presence of fullerene on the graphene film. As a stable allotrope of graphene, the remained fullerene will not have great impact on the biochemical reactions. In EDS analysis, the fullerene transfer method shows better elemental cleanliness and greater prospect in the field of bio-sensing.

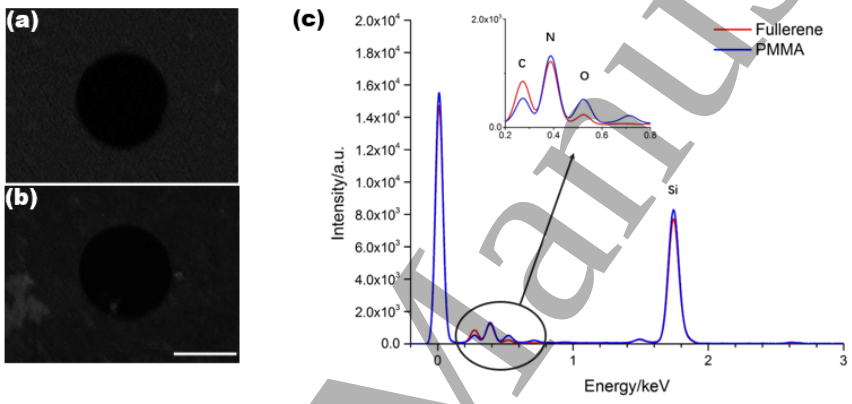

Figure 5. Energy disperse spectroscope (EDS) analysis of the freestanding area of two methods. (a) The analytical region of freestanding graphene film transferred by fullerene. (b) The analytical region of freestanding graphene film transferred by PMMA. (c) Elemental map of the freestanding area and nearby. In (c), the red curve is the elemental map of the freestanding film transferred by fullerene method, and the blue curve is the elemental map of the freestanding film transferred by PMMA method.

In summary, we have developed an improved method for transferring graphene films to substrates with large freestanding areas. The intact rate of fabricated freestanding films was significantly increased by using the improved method. And the simplicial elementary composition and inert chemical properties of fullerene make the innovated transferring method an attractive candidate for fabricating large-area freestanding graphene films using in the field of biochemistry analysis and biosensors.

Methods

Transfer of graphene films using fullerenes. (1) About 50 nm thick fullerene film was evaporated on the as-grown graphene film on 25 μm thick Cu foil in a vacuum thermal evaporator, which was under

about 600 ℃ for half an hour. (2) The Cu foil was then etched away by an aqueous solution of ferric trichloride (mass fraction of 20%) over a period of about 4 hours. After the Cu foil was totally etched, we used deionized water to replace the ferric trichloride solution for several times to wash the graphene/fullerene film. Then the combined film was transferred to the targeted substrate and dried. (3) We putted the combined film into the vacuum thermal evaporator again to remove the fullerene film. Before applying high temperature, we needed to pump excess inert gas into the chamber to make sure there was little oxygen gas in the reactor. (4) At last, we vacuumized the chamber, evaporated at 600 ℃ for half an hour and elevated the temperature by the step of 50℃ until the temperature achieved 900 ℃.

Transfer of graphene films using PMMA. (1) A layer of PMMA (MicroChem, 950,000 MW, 9-6 wt. % in anisole) was spin coated on the substrate prior to the transfer. (2) The Cu foil was then etched away by an aqueous solution of ferric trichloride (mass fraction of 20%) over a period of about 4 hours. After the Cu foil was totally etched, we used deionized water to replace the ferric trichloride solution for several times to wash the graphene/fullerene film. Then the combined film was transferred to the targeted substrate and dried. (3) Then we immersed the PMMA/graphene/targeted substrate into acetone carefully to dissolve the PMMA layer. (5) At last, the transferred graphene film was cleaned by isopropanol and dried in natural atmosphere.

Conflicts of interest

There are no conflicts to declare.

Acknowledgment

This work was supported by the National Key R&D Program of China (No. 2016YFA0501602) and the Fundamental Research Funds for the Central Universities of China.

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