Journal of Materials Chemistry C

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Received 00th January 20xx, Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

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Pore-free Bubbling Delamination of Chemical Vapor Deposited Graphene from Copper Foils

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The electrolytic bubbling-assisted transfer of graphene from metal catalysts in chemical vapor deposition provides a high efficiency, low cost and environmental benign alternative to the traditional chemical etching method. Despite its high potential, the yield of the bubbling delamination is yet low, mainly due to the induced pores in the graphene after the transfer. It is found that the water and protons transport through the poly(methyl methacrylate) (PMMA) supporting layer play a critical role in the pore formation. Once the water and protons reach the PMMA-graphene interface before the delamination is finished, the protons permeate the graphene and form trapped hydrogen bubbles between the graphene and the metal. The built-up gas pressure inside the bubbles is high enough to crack the PMMA/graphene sheet thereby creating pores in the graphene. An optmized PMMA layer not only reduces trapped hydrogen bubble generation, but is also mechanically stronger preventing cracking. This contributes significantly to the pore-free electrolytic bubbling-assisted delamination of graphene.

Introduction

Graphene, a novel two dimensional material consisting of single layer sp^2 hybridized carbon atoms with hexagonal lattice,¹ has been attracting plenty of attention since its first isolation in 2004,² because of its unique structure and excellent physical, electronic and chemical properties.¹⁻⁹ These properties enable graphene to find many applications, from post-silicon electronic devices,^{2,9} flexible electronics,¹⁰⁻¹² bio/chemical sensors,^{7,8,13,14} optoelectronics,^{3,4,11,15-19} energy generation and storage^{12, 20-23} to mechanics.²⁴⁻²⁷ To realize these applications, large scale, controllable production and subsequent transfer of graphene to arbitrary substrate are necessary.

There are several strategies developed to produce graphene, including the mechanical exfoliation,^{2, 5} chemical oxidization and reduction of graphite,^{25, 28-30} and chemical vapor deposition (CVD).^{5, 6, 31} Among them, CVD which has been used to grow high-quality nanostructures, including carbon nanotubes,³²⁻³⁶ and semiconductor nanostructures,^{37, 38} is now considered to be the most promising method to obtain large-scale graphene that could be transferred to arbitrary substrate with the help of polymer mechanical support.^{10, 39-41} The conventional methods of separating

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Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x graphene from metal catalysts usually involve chemical etching to remove the metal.^{10, 39-41} The chemical etching process typically requires several hours to remove the metal, which increases the production cost and causes environment concerns. Moreover, for several refractory-metals and platinum catalysts, the metal etchant severely damages the graphene.

Very recently, a new electrolytic delamination method by H₂ bubbles evolving at the interface between the metal and graphene, has been proposed and systematically investigated by several groups.^{31, 42, 43} The graphene/metal substrate is used as the cathode in a water-based electrolysis cell, where H₂ bubbles generated therein are used to delaminate the graphene from the metal. Compared with the chemical etching method, the electrolytic delamination is able to separate graphene from the metal catalyst much faster, obtain cleaner graphene, and allow for reuse of the catalyst many times. However, the electrolytic delamination tends to create more pores in graphene after transfer, which will hurdle the practical application of graphene. Up to now, although this technology has obvious advantages in terms of cost and ecofriendliness, the reason for the damage in graphene is yet unclear, preventing the technique to be widely used in industry. Recently, it has been found that protons can permeate through graphene and react with metal catalyst to generate hydrogen bubbles, although no gas or liquid are able to permeate this one-atom-thick layer.44 Here, we argue that in the electrolytic delamination, if the water and protons could permeate the polymer capping layer and reach the polymer-graphene interface, the protons can permeate the graphene and form hydrogen bubbles at the interface between graphene and metal substrate. The expansion of hydrogen bubbles constrained at the graphene-metal interface will generate mechanical stresses and, eventually, cracks and pores in the polymer/graphene sandwich layer. The proposed mechanism of the graphene damage is supported by calculations and experimental

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data. Furthermore, in this paper we propose a strategy to effectively reduce the amount of pores in the electrolytic delaminated graphene. We have found that the pore formation can be greatly suppressed by increasing the thickness of the polymer supporting layer. To the best of our knowledge, the proposed graphene-transfer failure mechanism has not been reported before. Our solution to the problem will help large-scale production of defect-free graphene.

Experimental Section

CVD Growth of graphene on Cu foil. The CVD growth condition of graphene was similar to those reported in our previous publications, ^{43, 45, 46} but with minor modifications. In brief, 50 mm thick 99.99% pure Cu foils (Advent) and a cold-wall low-pressure CVD reactor (Black Magic, AIXTRON) were used. After being cleaned by acetic acid, acetone, and isopropanol in sequence, the Cu foil was heated to around 1000 °C, and annealed for 10 min in a flow of 40 sccm H₂ and 1000 sccm Ar. Then, the graphene growth started by introducing 30 sccm diluted CH₄ (5% in Ar) as carbon source. After 10 min growth, the heating was immediately switched off and the reactor was evacuated to <0.1 mbar.

Transfer of Graphene by electrolytic bubbling method. Similarly to our previous published work, a semi-rigid plastic frame was employed to provide mechanical support and facilitate the subsequent handling in cleaning and transfer of graphene.⁴³ A schematic diagram of the graphene transfer process can be seen in Figure 1. In this work, PMMA layers of different thickness were prepared by spin-coating PMMA (950 A4, in anisole) onto graphene/Cu at 500, 1000, 1500, and 2000 rpm. Then the PMMA layers were cured at 180 °C for 10 min on a hotplate. For the supporting frames, we used 100-200 μ m thick polyethylene terephthalate (PET) (see Figure 1(a)) which was found to be intact during the electrolysis. We used PMMA as glue to attach the frame to the PMMA/graphene/Cu stack and then cure it at 180 °C on a hotplate. In this way, the two PMMA layers were fused together and the frame was firmly attached to the PMMA/graphene/Cu stack. Finally, the graphene at the bottom side of the Cu foil was removed by dry etching using oxygen plasma (50 W for 30 s).

The electrolytic delamination was performed at 8 V of cathode to anode dc voltage, in an electrolytic cell filled with 0.2 M NaOH solution as an electrolyte. A Pt foil was used as the anode while the frame/PMMA/Graphene/Cu complex as the cathode. Once the power supply was turned on, bubbles would evolve at both electrodes (see Figure 1b). After separation from the Cu foil, the frame/PMMA/Graphene stack was rinsed in deionized water for several times, and then transferred to SiO₂/Si substrate. Subsequently, the sample was dried naturally, and baked at 120 °C for 10 min to improve the adhesion between the graphene and the SiO₂/Si substrate. The frame was removed by mechanically cutting the PMMA/graphene along the inner edges of the frame, as shown in Figure 1c. Finally, the PMMA was removed using acetone and isopropanol in sequence, leaving behind a clean graphene film on SiO₂/Si substrate (Figure 1d). The graphene transfer by chemical etching method was conducted in 0.2M ammonium persulfate solution (APS). The frame/PMMA/graphene/Cu stacks were floating on the surface of the APS solution after 4 hours of etching; the subsequent cleaning and transfer processes were the same as that of the electrolytic bubbling method described above.

Characterizations. The as-grown graphene/Cu foils were analyzed by scanning electron microscopy (SEM, Zeiss Supra 60 VP) operating at acceleration voltages from 1 to 2 kV. The transferred graphene on SiO₂/Si substrates were characterized by SEM, optical microscopy (Olympus MX40) and Raman spectroscopy (Horiba XploRA) equipped with a 633 nm laser. The laser spot was ~1 μ m for a ×100 objective lens and the laser power was ~5 mW. The step size in the Raman mapping was 2 μ m for both x and y directions. The sheet resistances of graphene films transferred by different processes were measured with 4 point probe method.

3. Results and Discussion



Figure 1. Schematic diagram of the electrolytic bubbling delamination of graphene from Cu foil. (a) Deposition of the PMMA layer and mounting of the semi-rigid plastic frame onto the PMMA/graphene/Cu. The graphene at the bottom side of the Cu foil was etched away by oxygen plasma. (b) Electrolytic delamination of the frame/PMMA/graphene from the Cu foil in a NaOH solution. The hydrogen bubbles generated between the frame/PMMA/graphene and the Cu foil provided a gentle force to separate the frame/PMMA/graphene from the Cu foil. (c) Transfer of the frame/PMMA/graphene to SiO₂/Si and removal of the semi-rigid plastic frame. (d) PMMA removal in acetone.

The electrolytic bubbling delamination of graphene from copper (Cu) foil process is schematically shown in Figure 1. Although graphene was proven to have reasonably good quality, it remains a question whether this quality is always well preserved after the transfer process. If not, then the induced defects in graphene can modify the electronic properties,⁴⁷ and affect the charge transport,⁴⁸ rendering a problem for many applications. Before mitigating pore generation in graphene during the transfer, the origin of these pores should be first identified. We first looked into the graphene transfer by the traditional chemical etching method. Figure 2a and 2c show SEM images of graphene with many micron-

sized pores due to incomplete growth and pore-free graphene (perfect growth), respectively. Figure 2b and 2d are the corresponding images after the etching based transfer to SiO_2/Si substrates. Apparently, the holey graphene was still holey, and the continuous graphene was still continuous. The morphology was well preserved after the transfer. The chemical etching method seemed to be a relatively gentle process and tended to add only a few structural defects to the graphene.



Figure 2. Images showing that the chemical-etching transfer was relatively benign to the structure and morphology of the CVD graphene (a) SEM image of a graphene/Cu sample where the graphene did not fully cover the Cu foil; (b) The corresponding optical image of sample (a) after being transferred onto SiO₂/Si by the chemical etching method. (c) SEM image of a hole-free graphene/Cu sample; (d) the corresponding optical image of sample (c) after transfer by the chemical etching method.

The image was, however, entirely different when using the electrolytic bubbling method to delaminate the graphene. We found that there was a direct correlation between the thickness of the PMMA support layer and the detrimental effect which the transfer process imposed on the morphology of the graphene. The PMMA thickness was controlled by the rotation speed during the spin casting, where the thickness is approximately proportional to the square root of the spinning speed.⁴⁹ According to the spin curve of PMMA 950 A4, the thickness at 500, 1000, 1500 and 2000 rpm were approximately 600, 420, 340 and 290 nm(PMMA Datasheet, MicroChem), respectively. The SEM images of the as-transferred graphene are shown in Figure 3. Here the graphene films were all transferred from the same type of samples where the graphene were grown using the recipe guaranteeing the full coverage. For the 600 nm thick PMMA samples, no pores could be observed, as shown in figure 3a. However, when the PMMA thickness decreased to 420 nm, a certain amount of tiny pores with the size of 1-2 μm appeared on the graphene (marked by the red circles), as displayed in figure 3b; further decreasing the thickness to 340 nm, the size of pores raised to 4-6 µm (marked by the red circles) and the number of pores also increased slightly(see figure 3c); for the 290 nm case, the pores accounted for a large portion of the graphene surface and the diameter of pores augments to tens of microns(figure 3d). These observations were indicative of the crucial role of the PMMA supporting layer for integrity of the graphene during the electrolytic



bubbling transfer. Notwithstanding, there was always a trade-off

between the thickness and the flexibility of the PMMA layer.

Figure 3. SEM images of the graphene on SiO_2/Si transferred with help of PMMA-support of different thickness during the electrolytic bubbling. In each image, the graphene was known to be pore-free before the transfer. The PMMA thicknesses were (a) 600 nm; (b) 420 nm; (c) 340 nm; and (d) 290 nm. Red circles indicate the positions of the pores.

20µm



Figure 4. Characterization of the graphene before and after the electrolytic transfer. (a) SEM image of the as-grown graphene on Cu. (b) Optical image of the graphene transferred onto SiO₂/Si. (c) SEM image of the graphene transferred onto Si/SiO₂. (d) Raman spectrum of the graphene transferred onto SiO₂/Si. The inset shows a typical Raman map of 2D/G over a 20 μ m × 20 μ m area.

Figure 4a shows the morphology of a perfect growth graphene/Cu material before electrolytic delamination. It is evident that the graphene film uniformly and fully covered the Cu foil. The wrinkles in graphene are believed to be formed during the cooling down, considering the large difference in the thermal expansion coefficients between graphene and Cu foil (graphene has negative

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thermal expansion).⁵⁰ Figure 4b-c show images of the graphene transferred onto SiO₂/Si substrate by the electrolytic bubbling method with the optimized parameter (PMMA thickness 600nm), where no holes could be identified, confirms the integrity of the graphene film. Figure 4d, a typical Raman spectrum, reveals a 2D/G ratio of 2.2 with the full width at half maximum (FWHM) of the 2D peak being around 31.9 cm⁻¹. These are strong evidences that the graphene is a monolayer and with reasonable material quality.^{40, 51} The inset of Figure 4d shows a 2D/G ratio map of the transferred graphene on SiO₂/Si substrate. In a 20 μ m × 20 μ m area, the ratio of 2D/G is approximately in the range from 2 to 3.5, indicating a good uniformity of the graphene film after bubbling delamination.

One might expect that the electric potential applied on the electrodes would also affect the delamination process and the final graphene quality. To test this, we applied 8, 10, 15, and 20 V to the similar samples all protected by 600 nm thick PMMA. Nevertheless, after the transfer and cleaning, the graphene films did not show any significant dependence on the voltage during the delamination, as shown in Figure 5a-d. The graphene morphology was confirmed to be not sensitive to the applied voltage between the two electrodes in the wide range of 8-20 V.



Figure 5. The morphology of transferred graphene for voltages of (a) 8 V; (b) 10 V; (c) 15 V; and (d) 20 V during the electrolytic bubbling graphene delamination. PMMA thickness was 600 nm.

The sheet resistance of graphene transferred by different processes is another indicator for the structural integrity characterization in graphene. The average sheet resistance of graphene transferred by wet etching with 0.2M APS and bubbling delamination with 600 nm, 420 nm, 340 nm and 290 nm PMMA are 1.2, 2.0, 3.7, 12.1 and 16.2 k Ohm respectively, as shown in figure 6. It shows that the resistance of graphene transferred by bubbling delamination with 600 nm PMMA is comparable with that of wet etching. However, if the PMMA thickness decreases, the sheet resistance will increase drastically, indicative of the increase in the pore numbers in graphene. The transferred graphene films have also been used as transparent electrode for light emitting diodes (LED) circuits, as shown in figure 7a-c, the graphene transferred onto glass slide with gold contact could light up a LED, and the figure 7d shows the experimental setup. In Figure 7a the LED was lighted up by

graphene transparent electric circuit transferred by chemical etching method; and figure 7b and c display the LED lighted up by the graphene transparent electrode made by bubbling delamination with 600 nm PMMA and 340 nm PMMA respectively. It is found that the brightness of LED in figure 7b is comparable with that of figure 7a, indicating that the resistance of graphene transferred by bubbling delamination with 600 nm PMMA is comparable with that of the etching method, which agrees well with the sheet resistance measurement result in figure 6; however, the LED brightness in figure 7c is much lower than those of figure 7a and b, which is indicative of a high resistance in graphene transferred by bubbling delamination with 340 nm PMMA.



Figure 6. Sheet resistance of graphene films transferred by different processes. A: wet etching; B-E: Bubbling delamination with PMMA thickness of 600 nm, 420 nm, 340 nm and 290 nm respectively.

Here we propose a mechanism based on the trapped hydrogen bubble formation at the graphene-Cu interface via water and proton penetration through the PMMA layer. This direct transport of water and protons through the PMMA layer has thus far been completely overlooked in literature. In the common and oversimplified description of the electrochemical bubbling transfer, the hydrogen bubbles are said to be only evolving at the sample edges which are in contact with the electrolyte. Smaller bubbles are prone to merge into larger bubbles and escape through the wedge at the graphene-Cu interface at the sample edge into the liquid. With more and more bubbles being produced, the wedge at the sample edge grows and propagates towards the interior of the sample eventually delaminating graphene from Cu. This seemingly perfect scenario, however, cannot explain the fact that pores are much easier to be generated in the electrolytic transfer compared with the traditional etching transfer. If the bubbles are only to be produced starting from the edge, they are always untrapped. The bubbles are always free to escape from the wedge. The internal pressure in these untrapped bubbles cannot build up because the pressure is just determined by the surface tension at the bubble surface and the hydrostatic pressure from the electrolyte.

Figure 7. Demonstration of graphene-based transparent electrode for a LED electrical circuit by transferring graphene onto glass with different processes. (a) Etching method; (b) Bubbling delaminated, with 600 nm PMMA layer; (c) Bubbling delaminated with 340 nm PMMA; (d) Optical Image of Graphene/glass transparent electrodes.

In our model, the direct penetration process via the whole surface of the PMMA results in a considerably large amount of hydrogen bubbles that are trapped in the interior of the sample. The augmentation of these trapped hydrogen bubbles will cause an increase in the internal gas pressure and bulging of the graphene/PMMA sheet. We note that the hydrogen bubble generation at the graphene-Cu interface in the interior of the sample indeed happened during the electrolytic delamination, indicating that the PMMA was a very poor barrier against water penetration. Indeed, Sutandar et al have investigated water uptake in PMMA and found that PMMA is not a good barrier to water penetration, in their observation, water first penetrated and then diffused at a certain speed in the PMMA. ⁵² The pore generation and its strong dependence on the PMMA thickness appear to be very natural in our model. If the PMMA is thin (e.g. 290 nm), the water and protons absorbed by PMMA would diffuse to the PMMAgraphene interface before the frame/PMMA/graphene stack is detached from the Cu foil. For the 600 nm thick PMMA layer water and protons would need roughly four times longer time to diffuse to the interface while delamination could be completed earlier than that (the diffusion time of water in PMMA is proportional to the square of PMMA thickness). As it can be seen later, the high pressure in the trapped bubbles caused the graphene to break and accounted for the pore generation during the bubbling.

To check the validity of this hypothesis, we investigated the effect of PMMA thickness on water blocking. As before, the PMMA films were prepared by spin casting at speeds of 500, 1000, 1500, and 2000 rpm on one side of bare Cu foils, with the corresponding thickness of about 600, 420, 340, and 290 nm, respectively. After the PMMA was cured, a layer of polydimethylsiloxane (PDMS, weight ratio of monomer to curing agent is 10:1) was coated to the backside and edges of the PMMA/Cu foil and cured at 100 $^{\circ}$ C for 1

hour. The PDMS film protected the backside and edges of the PMMA/Cu stack. It is well known that PDMS is strongly hydrophobic. Therefore, the thick PDMS was expected to offer a sealing effect against water penetration (and hence bubble generation) at the backside and edges. The electrochemical tests were conducted in the same set-up as before. The PMMA/Cu/PDMS stack was used as the cathode, and the counter electrode was a platinum foil, where the potential applied between the two electrodes was 8 V. After 5 min of electrolysis, photographs of the cathode were captured as shown in Figure 8a-d. There were almost no bubbles in the sample with 600 nm thick PMMA, as displayed in Figure 6a. However, there yet existed a certain amount of bubbles at the edges of the Cu foil. It could be ascribed to the higher density of defects (pinholes, cracks) in the PDMS at the sample edges, which were very difficult to completely avoid and led to imperfect sealing. When the PMMA thickness decreased to 420 nm, small amount of bubbles could be observed along the PMMA area, indicating that the water and protons had penetrated the PMMA film and generated the hydrogen bubbles. If the PMMA thickness was further reduced, more and larger bubbles appeared on the PMMA layer, as shown in Figure 8c-d. This figure serves as a direct evidence of the water and proton penetration and transport through the PMMA layers, which is dependent on the thickness of the PMMA.



Figure 8. Effect of PMMA thickness on water blocking during the electrolytic delamination (8V, 5 min). The backside and edges of the PMMA/Cu stacks were sealed by PMDS. The thicknesses of the PMMA layers are (a) 600 nm; (b) 420 nm; (c) 340 nm and (d) 290 nm.

Despite the well-known impermeability to water and gases, however Hu *et al* have observed a high transport rate of protons across graphene then the protons reacted with metal catalysts to form hydrogen molecules,⁴⁴ that is to say, graphene is transparent to protons. Therefore, in our case, when the water and protons permeated the PMMA layer and reached the PMMA-graphene interface, the protons would continue to move and reach the

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graphene-Cu interface. Trapped hydrogen bubbles (THBs) were thereby produced and would continue expanding as the electrolysis went on. The augmenting THBs bulged the PMMA/graphene membrane. Note that the fracture strain of PMMA at room temperature is around 3%.⁵³ Thus, the bulging of PMMA/graphene would first cause cracks in the PMMA layer, considering the fracture strain of graphene could reach 15% or higher.⁵⁴ The pressure difference across the bulged membrane as the function of the deflection can be expressed as follows:⁵⁵⁻⁵⁷

$$\delta p = \frac{k(v)Etd^3}{a^4} \tag{1}$$

Here *E* is the Young's modulus, *v* is the Poisson's ratio, *t* is the membrane thickness, *d* is the deflection of the PMMA/graphene membrane at the center, *a* is the radius of the pore and k(v) is the coefficient that depends only on the Poisson's ratio. As shown in Figure 9, when the PMMA layer started to crack at the elongation of 3%, the deflection *d* was approximately 0.24*a*. For a simple estimate, the PMMA/graphene membrane was treated to be a composite with two components with the pressure in the normal direction. To bulge the PMMA/graphene membrane and crack the PMMA layer, the pressure difference across the composite membrane δp for c.a. 290, 340, and 420 nm PMMA thickness, were estimated to be 5, 21, 65 MPa, respectively. The calculation of pressure difference indicated that it was considerably harder to bulge and crack thicker PMMA films during the electrolytic delamination of graphene.



Figure 9. Schematic diagram of the bulging the PMMA/graphene membrane due to hydrogen bubble. Here, 2a is the original dimensional of the bugled PMMA/graphene membrane, d is the deflection of the PMMA/graphene complex layer, and δP is the pressure difference across the PMMA/graphene membrane.

For etch transfer process, we found that the 290 nm thick PMMA is strong enough to keep the integrity of graphene and the increase of PMMA thickness only produce very similar, pore-free graphene by carefully handling(see figure S1). We have identified that the expansion of trapped hydrogen bubbles between the graphene and metal substrates is the main reason to the pore generation for the bubbling delamination method, but there is no trapped hydrogen bubbles generating during the etch process (here we use APS solution as etchant which could etch copper foil without generating hydrogen bubbles). Thus we attributed the poregeneration mechanism during the bubbling delamination of graphene to the trapped hydrogen bubble generation, rather than poor integrity of PMMA.

Based on the observation and analysis above, the mechanism for the pore generation during the electrolytic bubblingassisted delamination of graphene can be summarized as follows. The water and protons in the electrolyte diffuse towards the PMMA-graphene interface driven by the concentration gradient. If water and protons could reach the PMMA-graphene interface before the PMMA/graphene is fully detached from the Cu foil, due to the permeation of protons through graphene, trapped hydrogen bubbles evolve at the graphene-Cu interface and thereby bulge the PMMA/graphene membrane. The bulging tends to damage the PMMA supporting layer and create pores in the graphene, as shown in Figure 10a. For a thicker PMMA supporting layer, it takes much longer time for the water and protons to diffuse to the PMMAgraphene interface; reducing the possibility of the trapped hydrogen bubbles formation at the graphene-Cu interface. Also, from a simple estimation, thicker PMMA is much more robust against mechanical damage. The mitigation of the pore generation in graphene is therefore attributed to the reduced amount of bubbles in the interior of samples, by virtue of the thicker PMMA layer, as displayed in Figure 10b. Finally, we note that because graphene is conducting, it should be possible for some protons to be reduced already at the PMMA-graphene interface. However, graphene has a much lower catalytic efficiency for creation of hydrogen molecules than Cu. It is therefore assumed to be a minor effect in our experiments.



Figure 10. Schematic mechanism of pore formation in graphene separated by electrolytic delamination. (a) Thin PMMA, the water and protons penetrate and transport through the PMMA layer. The inset shows that protons in water propagate through graphene and react with Cu to form hydrogen bubbles which contribute to the pore formation in graphene as show in (c). (b) Thick PMMA layer provide better barrier against water and protons penetration and transport; the water and protons failed to reach the PMMA-graphene interface, no pores generation as shown in the (d).

Conclusions

In summary, we systematically investigated the process of graphene delamination by the electrolytic bubbling method and proposed a mechanism for the pore generation. We found that the water and protons diffusion through the PMMA supporting layer played a critical role in the pore formation in the graphene. For thin PMMA the diffusion is fast and the protons are able to permeate the graphene and form hydrogen bubbles that can be trapped between the graphene and the Cu foil. If the overall delamination process does not keep pace with the bubble formation, the build-up of gas

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pressure inside the bubbles can be high enough to crack the PMMA sheet and create pores in the graphene. On the other hand, if the PMMA layer is thick enough, the diffusion takes much longer time allowing for the full delamination of graphene by bubbles created at the edges before any bubbles would evolve in the interior parts of a sample; and the graphene tends to maintain its integrity after being separated from the metal. This seemingly straightforward mechanism has been so far overlooked in the community, since the bubbling delamination has been always described as a procedure that involves only bubble evolution from the edges of Cu foils. We believe that with our study of the failure mechanism and the corresponding technical solution, the full potential of the electrolytic bubbling method could be thoroughly explored. Also, the results of this paper should be easily extended to other relevant materials such as the electrolytic delamination of other 2D materials e.g. h-BN and MoS₂ from conducting substrates, not limited to Cu. Moreover, after optimization, the bubbling-assisted transferred process could replace the conventional wet transfer method, which is expected to be beneficial to develop wide spectrum applications such as graphene-based devices and transparent electrodes with high quality.

Acknowledgements

This work was supported by Chalmers Area of Advance Nano, Stiftelsen Olle Engkvist Byggmästare, Swedish Foundation for Strategic Research, and Carl Tryggers Stiftelse.

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Table of content



Water and protons permeate thin PMMA layer and form trapped hydrogen bubbles to crack graphene and create pores on graphene.