A single layer graphene electrode has been successfully grown by the chemical vapour deposition (CVD) method using a liquid chlorobenzene carbon source trapped in a PMMA polymer matrix at a growth temperature of 450°C. Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and Ultraviolet-Visible (UV-vis) absorption spectroscopy have been used to identify the graphene based composition. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been used to characterize the film quality and growth dynamics. SEM snapshots show a preferential edge growth mechanism of single layer graphene has been observed as a function of growth time with distinct domains where only the edges parallel to the growth front are active to accept incoming carbon source. This work paves a potential pathway for an easier and cheaper production of large area conductive and transparent electrodes.
Determining the Mechanism of Low Temperature Graphene Growth

A single layer graphene electrode has been successfully grown by the chemical vapour deposition (CVD) method using a liquid chlorobenzene carbon source trapped in a PMMA polymer matrix at a growth temperature of 450 °C. Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and Ultraviolet-Visible (UV-vis) absorption spectroscopy have been used to identify the graphene based composition. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been used to characterize the film quality and growth dynamics. SEM snapshots show a preferential edge growth mechanism of single layer graphene has been observed as a function of growth time with distinct domains where only the edges parallel to the growth front are active to accept incoming carbon source. This work paves a potential pathway for an easier and cheaper production of large area conductive and transparent electrodes.
Determining the Mechanism of Low Temperature Graphene Growth

May 27, 2014

**Name of Principal Investigators:** Paul C Dastoor, Warwick J Belcher, Xiaojing Zhou

- e-mail address: Paul.Dastoor@newcastle.edu.au
- Institution: University of Newcastle
- Mailing Address: Centre for Organic Electronics, University of Newcastle, Callaghan, NSW 2308, Australia.
- Phone: +61-2-49215426

**Period of Performance:** 03/06/2013 – 03/06/2014

**Abstract:** A single layer graphene electrode has been successfully grown by the chemical vapour deposition (CVD) method using a liquid chlorobenzene carbon source trapped in a PMMA polymer matrix at a growth temperature of 450 °C. Raman spectroscopy, X-ray photoelectron spectroscopy (XPS) and Ultraviolet-Visible (UV-vis) absorption spectroscopy have been used to identify the graphene based composition. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been used to characterize the film quality and growth dynamics. SEM snapshots show a preferential edge growth mechanism of single layer graphene has been observed as a function of growth time with distinct domains where only the edges parallel to the growth front are active to accept incoming carbon source. This work paves a potential pathway for an easier and cheaper production of large area conductive and transparent electrodes.

**Introduction:** Graphene is the most promising alternative conductive and transparent electrode material to indium tin oxide (ITO) for organic photovoltaics (OPVs) and organic light emitting diodes (OLED). Chemical vapour deposition (CVD) either under low pressure (<1 Torr) or at atmospheric pressure has been used widely in recently a few years to produce graphene [1-6]. Although other metals are used as the catalysis [7-15] Nickel and copper are the two most chosen catalysts to promote graphene formation [1, 16]. Due to the low carbon solubility in nickel or copper, higher temperatures than 800 °C are generally required and a critical cooling process is essential to form high quality graphene films that are useful as electrodes for the OPV or OLED device fabrications [1]. Methane gas is the most selected carbon source used in the CVD to form single layer or multiple layer graphene, which highly depend on the growth conditions used in the CVD. Kinetic parameters have been investigated in the CVD process to control the formation of uniform large area graphene [17]. Solid carbon sources such as poly(methyl methacrylates) (PMMA), Sucrose and Fluorene, have also been reported by Sun et.al to produce monolayer graphene [2]. A minimum growth temperature of 800 °C has been used in this work to eliminate the defect formation in the graphene film. For a mass production of conductive transparent electrodes, the lower the temperature used to produce high-quality graphene, the better in the effective-cost management and the less challenges in the device process. Recently, using liquid sources such as benzene or pyridine, Li et al [3] [18] and Liu et al reported that a single layer of graphene can be fabricated at the temperature as low as 300 °C. However, more work is still needed to understand the underlying growth mechanism at such low temperature compared to the well investigated high temperature growth model. In addition, it is also important to demonstrate these low temperature grown films to be a good conductive and transparent electrode material after transferring or processing. Here we report a comparison study by varying a precursor temperature that can directly controls the incoming carbon precursor using either PMMA or chlorobenzene as the carbon source, centimetre size, high conductive and transparent graphene electrodes can be produced. Comparing to graphene growth using the high temperature CVD process, the mechanism of graphene growth at such a low temperature has been carefully examined in our study.
Experiment: Copper foil was purchased from Sigma-Aldrich with a thickness of 25 µm, and cut into 2 × 1 cm². The copper foil was then transferred to a CVD system and annealed at 900 °C for 90 min in an ambient of 10 sccm hydrogen gas and retaining the total pressure of 500 mTorr. This pre-thermal anneal allows Cu to form large domain crystalline on the surface. The annealed copper foils are then used as the catalyst for growing graphene film with temperatures in the range of 300 to 500 °C in a 2-inch diameter quartz tube furnace of CVD system, where a PMMA-coated glass is also loaded as the carbon source. Cu foil were firstly spin-coated (75 µL, 5000 rpm for 1 min) with PMMA (dissolved in chlorobenzene with a concentration of 50 mg/mL), which was then cured on a hot plate at 180 °C for 1 min. The grown graphene films were separated from the Cu foil by etching away the copper in an aqueous iron nitrate solution (0.05 g/mL) for ~ 48 hours, resulting in the floating PMMA/graphene film. The PMMA/graphene film can be picked up by a clean glass substrate and transferred it to in a petri dish containing deionized (DI) water for 30 min. The clean film was subsequently transferred onto a substrate and dried in a vacuum oven at 70 °C for 2 h. To dissolve the pre-coated PMMA, a new layer of PMMA with a 10-mg/mL concentration was spin-coated (75 µL, 5000 rpm for 1 min). The new PMMA film was slowly cured at room temperature for ~ 30 min and then removed by a slow flow of acetone and IPA 3 times, respectively, leaving the graphene film on the target substrate and storing it in dry N2 chamber for characterization, such as Ultraviolet-Visible, Raman, X-ray photoelectron spectroscopy, Scanning/transmission electron microscopy (SEM/EM) and electrical property measurements. A four-point technique was used to evaluate the conductance of the grown films.

Results and Discussion:
PMMA is known to be thermally decomposed to monomers at 220 °C and undergo further C-C scission above 300 °C [19]. Our thermogravimetric analysis as shown in figure 1 is in consistence with the literature. A small weight loss starts at 220 °C with the accelerated weight loss above 300 °C. In contrast, for a spin coated PMMA film, weight loss starts almost from room temperature, which is due to the chlorobenzene used as the solvent to dissolve PMMA. Two temperatures at 140 °C and 400 °C with one below the PMMA decomposition temperature and one above the PMMA decomposition temperature have been selected as the precursor temperatures.

![Figure 1 Thermogravimetric measurement of the weight loss percentage of PMMA only and chlorobenzene trapped PMMA.](image)

Our previous studies have shown that a critical annealing temperature above 800 °C is essential to activate the catalytic activity of the copper surface [20-21] to grow graphene but the growth temperature which is the substrate temperature during the graphene growth can be below 500 °C. In order to achieve the best graphene growth, an annealing temperature of 900 °C has been used to obtain micro-sized copper single crystal domains. Growth temperature at 450 °C was used. PMMA with trapped chlorobenzene was heated to 400 °C to generate carbon precursors. Three grown films were prepared with a growth during of 1s, 30s and 60s. SEM graphs show the surface morphologies of these films (still on copper foils) in figure 2a, figure 2b and figure 2c, respectively. Figure 2a clearly shows the graphene flakes for a growth time of 1 s. It appears some islands of graphene growth of various sizes are present, while the white dots are contaminants which possibly result from PMMA precursor fragments. After annealing for longer times, the copper surface is fully covered by graphene films (figure 2b and figure 2c) on which new growth domains with lobed shapes are formed. The size...
of the new growth domains increases with increasing annealing times due to the occurrence of domain coalescence, but does not completely cover the copper surface. In addition, figure 2b and 2c also show the overgrowth of carbon islands. All three films were transferred to quartz substrates. Transmittance of all the three films have been measured to be less than 92%, indicating that even with 1s duration the grown graphene film is multilayer. Figure 2d shows the SEM image of the transferred film in figure 2a. Figure 2e and figure 2f show the TEM images of the same film, which show a 2-5 three layers of graphene sheets and is consistent with the transmittance measurement.

Figure 2 Scanning electron microscopy images of graphene growth on copper foil with a growth temperature 450 °C and precursor temperature at 400 °C for 1s (a), 30s (b), 60 s(c), and transferred film (d) and Transmission electron microscopy images of transferred film showing a 4-layer graphene film. The scale bars are 1 µm for (a), 100 nm for (b) and 200 nm for (c).

Figure 3 shows the Raman spectroscopy of the same film in figure 2a. Three features are the G-band (~1582 cm⁻¹), D-band (~1350 cm⁻¹), and 2D-band (~2690 cm⁻¹). The sharp 2D-band confirms the graphene formation. The 2D/G ratio of less than 2 suggests again a multilayer growth [1, 22-24].

Figure 3 Raman spectroscopy of the transferred graphene on a glass substrate (the growth temperature at 450 °C, the precursor temperature 400 °C). The intensity ratio of 2D/G < 2 is consistent with the TEM measurement in Figure 2.
Using precursor temperature above the PMMA decomposition temperature 300 °C, no successful single layer graphene has been obtained at 450 °C growth temperature. This could be due to high concentration of carbon precursors that promote a multilayer overgrowth, or even amorphous carbon deposition, when limited catalytic atoms are accessible relative to incoming carbon atoms. To reduce the incoming precursor concentration, a relative low precursor temperature of 140 °C was used to eliminate any PMMA decomposition and only allow the trapped chlorobenzene as the carbon source. Figure 4 shows the Raman spectra of the graphene film in two regions. From the optical images as shown in figure 4, there are dark and bright regions, both with sharp 2D-band feature. The absence of G feature suggests the grown graphene is highly defect-free. Unlike previous study using hexachlorobenzene as the carbon source where more defect-containing monolayer and multilayer graphene mixture was obtained at the growth temperature of 460 °C and 560 °C[26], graphene film under the 140 °C precursor temperature is monolayer only when measured at different regions of the film as shown in figure 4a and figure 4b.
The transmittance of 97.4% at the 550 nm is also in a good accordance of the predicted single layer graphene opacity of ~2.3% [27]. The XPS measurement in figure 5b shows that there is a single peak for C1s with the binding energy at 284.5 eV, indicating a carbon sp$^2$ π-π stack of the graphene film [25-26]. No oxygen 1s XPS has been observed, in agreement with the Raman spectrum measurements that the graphene film is defect-free.

Figure 6 shows a series of SEM images of graphene growth stages on a copper foil catalyst by growing at a temperature of 450 °C with exposure times of 1, 10, 30, 60, 300 and 3600 s and a precursor temperature of 140 °C. In these images, graphene appears dark since the emission of secondary electron for copper is significantly higher than that for graphene. On the other hand, the appearance of white dots in the images is due to the presence of contaminants. After an exposure time of 1 s, (figure 6a) these appears a few growth domains about 30 nm in size. Between exposure time of 10 s and 30 s, the domain size increases as a result of additional carbon atoms being adsorbed on the edges of the growth sites. In particular, figure 6b shows the growth front (black arrows) of the graphene domain with domain size in micrometres in the parallel to the growth front direction and a few hundreds nanometres in the perpendicular to the growth front direction. Distinct domain edges (white arrows) are also clearly shown in figure 6b. This increase continues until the domains start to coalesce and then form larger islands as shown in figure 3c. The coalesced graphene flakes fully cover the surface of the copper foil after synthesizing for exposure times longer than 30 s, as seen in Figure 6 d-f. Using benzene as the carbon source to grow graphene, Li and co-workers [3] proposed that an initial adsorption step and followed by a dehydrogenation step and coalescence of the active species are required. By monitoring the time evolution grown process, our work directly demonstrates not only the initial adsorption as shown in figure 6a but also the preferentially active sites for graphene growth front indicated by the black arrows in the figure 6b which could be due to the copper surface mediated effect and coalesce in figure 3c. After 60 s, fully covered graphene surface starts to form carbon clusters and multilayer graphene shown in figure 6e and 6f.
It is believed that the failure of high purity single layer graphene growth when using PMMA as the main carbon source and working at temperatures below 500 °C might be due to the high concentration of precursor fragments deposited on the catalyst are not completely decomposed for arrangement to a graphene film. Optically, the resulting films had high quality with above 85% transparency. However, the electrical properties of the films were not bad, which could provide a reasonable performance if used as an electrode in an OSC. Size of transferred graphene films is generally 2×1 cm². The lowest sheet resistance of graphene films made from PMMA is ~ 600 Ω at the transmission of 93%. In comparison, for single layer graphene from chlorobenzene precursor, the resistance is in the range of a few kΩ, relatively high for OPV and OLED device fabrication. Future work will focus on the bilayer growth to further decrease the sheet resistance while retains the high transparency of ~95% and eliminate the carbon clusters.

**Conclusions:**

Previous studies of graphene growth on copper substrates have shown that the quality of graphene growth is dependent upon growth temperature. Indeed, for deposition of graphene from gas phase precursor (such as methane), temperatures of around 1000 °C are typically used. Much recent effort has focused on reducing graphene growth temperature by changing to different precursors and by optimizing the CVD growth parameter. The results presented in this work reveal that rather than a single growth temperature, there are actually three critical temperature parameters that need to be optimized independently. Firstly, there is the annealing temperature (T\textsubscript{ANNEAL}) of the Cu foil trial to graphene deposition, which needs to be sufficiently high (> 900 °C) to cause the recrystallization of large Cu grains in the substrate surface. Secondly, there is the precursor temperature (T\textsubscript{PRECURSOR}), which needs to be low enough to produce limited amount of volatile precursor fragments which subsequently decompose on the catalyst surface. In the case of carbon sources, chlorobenzene provides carbon fragments to form single layer graphene films at T\textsubscript{PRECURSOR} ~ 140 °C. Finally, there
is the Cu foil growth temperature ($T_{\text{GROWTH}}$), which has to be sufficiently high to activate carbon diffusion and rearrangement on the catalyst surface. For a Cu foil catalyst, this temperature needs to be at least 450 °C.

References:


List of Publications and Significant Collaborations that resulted from your AOARD supported project: In standard format showing authors, title, journal, issue, pages, and date, for each category list the following:


Attachments: Publications b)