



## Matrix assisted low temperature growth of graphene



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### ARTICLE INFO

#### Article history:

Received 26 February 2016

Received in revised form

23 May 2016

Accepted 30 May 2016

Available online 2 June 2016

### ABSTRACT

Single layer graphene has been successfully grown via chemical vapour deposition (CVD) at low temperature by using chlorobenzene trapped in a PMMA polymer matrix as the carbon source. By varying the carbon source temperature, we are able to vary the dominant carbon source from just chlorobenzene to PMMA. Raman spectroscopy and atomic force microscopy (AFM) have been used to characterize the as-grown graphene layer, while scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have been used to characterize film quality and growth dynamics. Lower source temperatures (corresponding to a chlorobenzene carbon source) result in high quality single layer graphene whereas higher source temperatures (PMMA carbon source) produce disordered multilayered graphene films. SEM imaging reveals that a preferential surface mediated edge growth mechanism for single layer graphene is observed as a function of growth time. This development offers a new methodology for graphene synthesis at low temperatures with implications for the development of printed graphene structures.

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### 1. Introduction

The unique electronic and structural properties of graphene mean that it is one of the most promising materials for use as transparent and flexible electrodes in electronic devices [1]. Chemical vapour deposition (CVD), either under low pressure (<1 Torr) or at atmospheric pressure, has been widely used over the last few years to produce graphene via growth on metal catalysts [2,3]. Although a number of metals have been studied [4–13], nickel [14] and copper [15–17] are the two most common catalysts used to promote graphene formation. Graphene formation on both nickel and copper usually involve growth temperatures higher than 800 °C but for different reasons. In the case of nickel, the carbon solubility is relatively high and the growth mechanism involves carbon segregating to the surface upon cooling [18]. By contrast, the solubility of carbon in copper is relatively low; consequently graphene growth occurs via a surface mediated mechanism with high temperatures typically used to generate the carbon surface active

species [19,20].

Methane is the most common carbon source used in CVD growth to form single layer or multiple layer graphene [21], the formation of which is highly dependent upon the CVD growth conditions. Kinetic parameters have been investigated to control the formation of uniform large area graphene surfaces during the CVD process [22]. For the production of conductive transparent electrodes from graphene [23], reducing the growth temperature needed to produce high-quality graphene would be desirable in terms of cost management and also to ensure compatibility with other steps in the device fabrication process. Recently, using liquid carbon sources such as benzene [24] or pyridine [25], it has been shown that a single layer of graphene can be fabricated at growth temperatures as low as 300 °C. Solid carbon sources, such as pristine bulk poly(methyl methacrylate) (PMMA) have also been reported to produce monolayers of graphene at temperatures as low as 400 °C, although a growth temperature of 800 °C was needed to eliminate defect formation in the graphene films [24]. High quality graphene films can be prepared from PMMA films as the carbon source when the PMMA is cast from aromatic solvent systems [26,27].

The effect of different solvents upon cast PMMA films has been

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the subject of a number of studies in the literature. It is well known that PMMA can act as a host matrix for a variety of organic non-chlorinated and chlorinated solvents, such as toluene, acetone and chloroform [28]. The solubility parameter of different organic solvents was shown to have an effect on the electrical properties of PMMA films [29]. In addition, residual solvent in drop-cast PMMA films is known to have a plasticizing effect on the bulk polymer, with the solvent-PMMA interaction being stronger for solvents with a strong Lewis acid character [30].

Despite the fact that PMMA is a known matrix host for organic solvents, to date there have been no studies to determine whether these entrapped solvents can act as a carbon source for graphene formation at low temperatures. Here, we show that by using chlorobenzene entrapped in a drop-cast PMMA matrix as the carbon source it is possible to control directly the incoming carbon precursor flux at a low growth temperature to produce high quality single layer, nearly defect-free graphene thin films. By carefully examining the growth process, we show that graphene formation occurs via a low temperature surface mediated growth mechanism.

## 2. Experimental details

Copper foil with a thickness of 25  $\mu\text{m}$  was purchased from Sigma-Aldrich, and cut into 2 cm  $\times$  1 cm rectangles. The Atomate CVD system has a quartz sample tube divided into three different zones, each zone with its own heating control program. The copper foil was then transferred to a thermal CVD system and annealed at 700  $^{\circ}\text{C}$ , 800  $^{\circ}\text{C}$ , 900  $^{\circ}\text{C}$  for 10 min in an atmosphere of 100 sccm hydrogen gas and retaining the total pressure of 500 mTorr. This annealing step allows Cu to form large crystalline domains on the surface. The annealed copper foils were then used as the catalyst for growing graphene films with temperatures in the range of 300–500  $^{\circ}\text{C}$  in a 2-inch diameter quartz tube furnace of CVD system located in zone 1, where a PMMA film drop-coated on glass was also loaded as the carbon source in zone 3. Zone 2 was left at room temperature to eliminate excess of heat leaking from zone 3 to zone 1. It also should be noted that PMMA has been dissolved in chlorobenzene with a concentration of 50 mg/mL. After drop-casting, PMMA was then cured on a hot plate at 180  $^{\circ}\text{C}$  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  $\sim$ 48 h, resulting in the floating PMMA/graphene film. The PMMA/graphene film can be picked up by a clean glass substrate and transferred into 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  $^{\circ}\text{C}$  for 2 h. To dissolve the pre-coated PMMA, a new layer of PMMA with a 10 mg/mL concentration was spin-coated onto the PMMA side of the graphene/PMMA film (75  $\mu\text{L}$ , 5000 rpm for 1 min). The new PMMA film was slowly cured at room temperature for  $\sim$ 30 min and then removed by a slow flow of acetone and IPA 3 times, respectively, leaving the graphene film on the target substrate. The films were stored in a dry  $\text{N}_2$  chamber prior to being characterized. The Raman measurements are performed at room temperature with a Renishaw spectrometer at 514 nm with notch filters cutting at 100  $\text{cm}^{-1}$ .

## 3. Results and discussion

Fig. 1 shows the thermogravimetric analysis (TGA) of: (a) PMMA powder, (b) PMMA drop cast from a chlorobenzene solution and air-dried and (c) PMMA drop cast from a chlorobenzene solution, air-dried and subsequently cured at 180  $^{\circ}\text{C}$ . Bulk PMMA is known to thermally decompose into monomers at 220  $^{\circ}\text{C}$  and undergo further C–C scission above 300  $^{\circ}\text{C}$  [31]. Our data is entirely consistent with the literature, with the TGA exhibiting a small

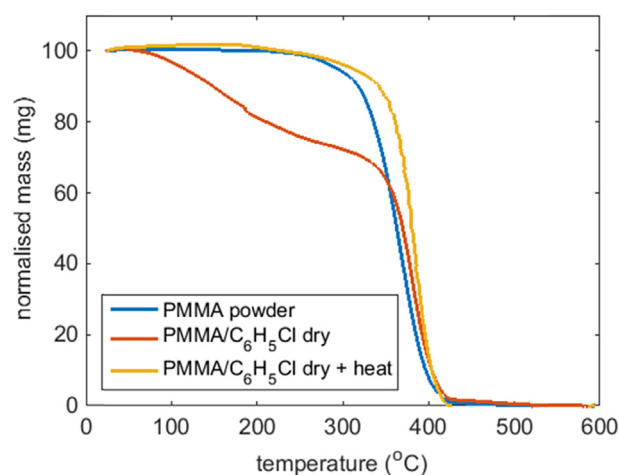


Fig. 1. TGA of the percentage weight loss for: (a) PMMA powder (solid blue line), (b) PMMA drop cast from a chlorobenzene solution and air-dried (solid orange line) and (c) PMMA drop cast from a chlorobenzene solution, air-dried and subsequently cured at 180  $^{\circ}\text{C}$  (solid yellow line). (A colour version of this figure can be viewed online.)

weight loss that starts at 220  $^{\circ}\text{C}$  followed by accelerated weight loss above 300  $^{\circ}\text{C}$ . By contrast, for the air-dried drop-cast PMMA film, the TGA data shows that the weight loss starts almost from room temperature and exhibits an inflexion at around 200  $^{\circ}\text{C}$ , followed again by accelerated weight loss above 300  $^{\circ}\text{C}$ . Upon curing at 180  $^{\circ}\text{C}$ , the TGA profile reverts back to that of the pristine PMMA powder suggesting that entrapped chlorobenzene is liberated during the heating process. In addition, the mass loss profile for the cured PMMA sample is shifted to slightly higher ( $\sim$ +20  $^{\circ}\text{C}$ ) temperatures suggesting that the curing process also most likely liberates the more volatile PMMA fragments.

While it is well-known that PMMA can readily entrap organic solvents in its structure [28], early work by Ouano and Pecora using depolarized dynamic light scattering showed that chlorobenzene in PMMA exists in distinct states with different dynamics ('fast' and 'slow') of rotational freedom [32]. In particular, the chlorobenzene molecules can be considered to exist as clusters or pools of various sizes in the PMMA matrix [33]. As such, the chlorobenzene molecules in the PMMA structure do not exist as bulk chlorobenzene with a distinct boiling point, but rather as collections of molecules which can be liberated from the PMMA host matrix across a broad temperature range. This model is consistent with the data shown in Fig. 1, which reveals that there is a 20% decrease in the mass of the drop cast film that occurs monotonically from room temperature up to approximately 200  $^{\circ}\text{C}$ .

In order to confirm that the release of entrapped chlorobenzene is responsible for the observed mass loss in the air-dried drop cast PMMA sample, mass spectrometry was used to identify the volatile species liberated during the TGA process. Mass spectra of the pristine PMMA and chlorobenzene were recorded and characteristic peaks were obtained from the measured cracking pattern (supporting information). The mass 69 ( $\text{C}_4\text{H}_5\text{O}^+$ ) and mass 111 ( $\text{C}_6\text{H}_5\text{Cl}^+-\text{H}$ ) peaks were used as the signatures of the PMMA and chlorobenzene fragments respectively. Fig. 2 superimposes the normalized mass loss from the TGA with the thermal desorption spectroscopy (TDS) for the characteristic PMMA and chlorobenzene fragments. As expected, Fig. 2a exhibits only a TDS spectrum for PMMA which directly correlates with the main mass loss observed in the TGA spectrum. By contrast, Fig. 2b displays an additional TDS spectrum for chlorobenzene, which correlates well with the mass loss observed between room temperature and  $\sim$ 300  $^{\circ}\text{C}$ . Upon curing the drop-cast PMMA sample at 180  $^{\circ}\text{C}$ , the TDS spectrum

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