Atmospheric Pressure Chemical Vapour Deposition Growth of Graphene for the Synthesis of SiO$_2$ Based Graphene Ball

(Pertumbuhan Grafin melalui Endapan Wap Kimia Tekanan Atmosfera untuk Sintesis Bebola Grafin Berasaskan SiO$_2$)

NURKHAIZAN ZULKEPLI$^{1,2}$, JUMRIL YUNAS$^1$, MOHD AMBRi MOHAMED$^1$, MOHAMAD SHUKRI SIRAT$^1$ & AZRUL AZLAN HAMZAH$^1$$^*$

$^1$Institute of Microengineering and Nanoelectronics (IMEN), Universiti Kebangsaan Malaysia, 43600 UKM Bangi, Selangor Darul Ehsan, Malaysia
$^2$Centre of Foundation Studies, Universiti Teknologi MARA, Cawangan Selangor, Kampus Dengkil, 43800 Dengkil, Selangor Darul Ehsan, Malaysia

Received: 28 February 2022/Accepted: 12 May 2022

ABSTRACT
Graphene is a prominent carbon nanomaterial with fascinating characteristics such as high conductivity and very high charge carrier mobility at low temperatures. Numerous synthesis methods for graphene have been established. Chemical vapour deposition (CVD) is among the most successful methods to fabricate high-quality graphene. However, metal-catalyzed growth is used in virtually all of the CVD techniques mentioned. To remove these metal catalysts and relocate the graphene to the necessary dielectric substrate (SiO$_2$/Si or quartz), complex and sophisticated post-growth methods must be used, which limits the usage of graphene in practical electronic components. In the present work, we conducted a preliminary study to determine the suitable methane(CH$_4$) flowrate, which could be used to synthesise SiO$_2$ based graphene ball. Few-layer graphene was grown on a large area of copper(Cu) surface using 20 sccm CH$_4$ in atmospheric pressure CVD (APCVD). The influence of CH$_4$ flowrate on graphene growth has been investigated. Graphene was deposited on a metal catalyst substrate at optimum temperatures of 1000 °C.

Keywords: Atmospheric pressure chemical vapour deposition; graphene; graphene ball; methane flowrate

INTRODUCTION
Graphene is a stunning two-dimensional carbon allotrope composed of a monolayer of sp$^2$ bonded carbon atoms with a carbon atom at each vertex in a hexagonal configuration. The key study of Novoselov et al. (2004) ignited interest in graphene. Three-dimensional graphite is formed by piling graphene layers; carbon nanotubes are formed by rolling graphene sheets, and fullerene is a zero-
Graphene is a two-dimensional material that has been extensively studied due to its unique properties and potential applications. It is characterized by its high electrical conductivity, mechanical strength, and thermal conductivity, making it a promising material for various technologies. However, in order to make practical electrical components, the as-grown graphene must be transferred from the metal catalyst surface to another suitable substrate via a series of complex operations. Various impurities, folds, defects, and cracks in graphene are unavoidable throughout this transfer technique. This might lead to a decrease in the quality and properties of graphene films. As a result, graphene sheets must be grown directly on dielectric substrates without any transfer step.

In this research, we show how to develop a few layers of graphene utilising the CVD technique over a broad area of Cu surface using CH₄ at atmospheric pressure. In particular, we conducted a preliminary investigation to establish the optimal methane (CH₄) flowrate for the production of SiO₂ nanoparticles-based graphene balls.

**EXPERIMENTAL DETAILS**

Before graphene growth, the Cu foil (99.9% purity; 50 µm thick) 10 by 10 mm is sonicated in ethanol for 5 min, then in distilled water for 5 min, subsequently in IPA for 5 min, and finally gently blown dry with nitrogen. The substrate was cleansed to eliminate any leftover organic elements and contaminants. As illustrated in Figure 1, the sample is immediately deposited on a porcelain boat placed into a horizontal quartz tube (inner diameter = 25.4 mm, length = 1200 mm) at room temperature. Before graphene growth, the quartz tube was sealed and then purged with Ar/H₂ for 30 min under atmospheric pressure. This procedure is carried out to flush the air contained in the quartz tube. While Ar/H₂ gas flowed, the system was heated to 1000 °C at a ramping rate of 33 °C/min. The Cu foil was annealed at 1000 °C for 30 min in an Ar/H₂ environment to enhance the Cu grain size and assure the elimination of native oxide and a smooth Cu surface. Graphene is then grown by admitting mixed gases of Ar/H₂ and CH₄ at various flowrates (Table 1) for 30 min. In this investigation, the overall flow rate was set at 100 sccm. After growth, CH₄ was shut off for the cooling step. The graphene/Cu samples were cooled from 1000 °C to room temperature using an Ar/H₂ environment, as illustrated in Figure 2.

Using the bubbling process, the graphene/Cu samples were subsequently transferred to glass substrates. To guarantee good adherence of the PMMA on the graphene/Cu samples, a thin layer of PMMA was spin-coated on them at 4000 rpm for 10 s before baking them at 140 °C for 4 min. Using an aqueous FeCl₃ solution, the PMMA/graphene was removed from the copper foil.
The floating PMMA/graphene film is washed in distilled water, transferred to a SiO$_2$ piece, and air dried. Finally, PMMA is removed from the sample by immersing it in acetone for 10 min.

To determine the existence of graphene on Cu substrates, Raman spectroscopy was performed using confocal micro-Raman imaging spectroscopy (DXR2Xi, Thermo Scientific). The wavelength of excitation was 532 nm, and the exposure duration was 0.1 s. A 900 line mm$^{-1}$ diffraction grating and a 50 µm spectrograph aperture were employed. These studies were carried out directly on Cu substrates, with no graphene transfer procedure. Field emission scanning electron microscopy (FESEM, Zeiss Merlin) was used to examine the sample’s morphology after they had been transferred to SiO$_2$ substrates.

![FIGURE 1. Experimental setup of APCVD graphene growth on Cu foil](image1.png)

![FIGURE 2. Graphene growth protocol](image2.png)

| TABLE 1. Evaluated flow rate for the growth process |
|-----------------------------------------|-----------------|-----------------|-----------------|-----------------|
| Heating | Purging | Growth flow rate [sccm] | Cooling |
| T (°C) | Time [min] | CH$_4$ | Ar/H$_2$ | Gas |
| 1000 | 30 | 60 | 40 | Ar/H$_2$ |
| 1000 | 30 | 20 | 80 | Ar/H$_2$ |
RESULTS AND DISCUSSION

Raman spectroscopy has advanced into a powerful, non-invasive tool for analyzing graphene and related materials (Childres et al. 2013). This spectroscopic approach has been used to assess the structural and physical characteristics of graphitic components, showing valuable information on the atomic structure of edges, the presence of disorder, defects, charges, and strain (Moreno-Bárcenas et al. 2018). Graphene Raman spectra are based on the D, G, and 2D bands, which are expected to be about 1350 cm\(^{-1}\), 1580 cm\(^{-1}\), and 2680 cm\(^{-1}\), respectively (Gajewski et al. 2016). D band provides a good indicator for determining the amount of disorder in the sample. The G band corresponds to the in-plane vibration of sp\(^2\) carbon atoms, whereas the 2D band represents graphene thickness (Dresselhaus et al. 2010). \(I_D/I_G\) ratio measurement is a well-known tool for determining defect density, whilst \(I_{2D}/I_G\) ratio measurement offers details on the number of layers in a graphene sample.

In this study, the CH\(_4\) gas flowrate was investigated by keeping all other parameters constant. Figure 3 depicts the Raman spectra of graphene produced at various CH\(_4\) flowrates. Only the sample grown with a flowrate of 20 sccm of CH\(_4\) shows the presence of standard graphene D, G, and 2D-bands, whereas the sample grown with a flowrate of 60 sccm of CH\(_4\) shows the formation of amorphous carbon. The 2D band was clearly visible in the 20 sccm sample but not in the 60 sccm sample when the flowrates were compared.

![Raman spectra of graphene grown with different CH\(_4\) flowrate](image)

The peak ratios of \(I_D/I_G\) and \(I_{2D}/I_G\) were calculated to assess the quality of graphene on Cu foil. Table 2 displays the computed ratios. Based on the high \(I_D/I_G\) ratios, defects were discovered in the 20 sccm sample (Childres et al. 2013). Its existence, however, is predicted due to surface imperfections in the Cu substrate (Zhang et al. 2016). Furthermore, in this work, our CVD reactors operate at atmospheric pressure where some oxygen will be present. The presence of oxygen in the CVD reactors most likely contributes to defects during the formation of graphene grains on the Cu foil (Robinson et al. 2013).

In the 20 sccm sample, the \(I_{2D}/I_G\) ratio was 0.324. The existence of graphene from a few layers to multilayers is indicated by an \(I_{2D}/I_G\) less than 1 (Nguyen et al. 2013). The \(I_{2D}/I_G\) ratio of the 20 sccm sample was 0.324, indicating the development of a few layers of graphene. This information is critical in understanding why low flow rates are required for higher graphene quality. This indicates that reducing the flow of CH\(_4\) gas results in fewer flaws and an increase in the thickness and uniformity of graphene quality.
TABLE 2. Evaluated flow rate for the growth process

<table>
<thead>
<tr>
<th>Flowrate [sccm]</th>
<th>$I_\text{D}/I_\text{G}$ ratios</th>
<th>$I_{2D}/I_{G}$ ratios</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>NA</td>
<td>NA</td>
</tr>
<tr>
<td>20</td>
<td>1.146</td>
<td>0.324</td>
</tr>
</tbody>
</table>

The morphology of graphene was examined using a field emission scanning electron microscope (FE-SEM). Figure 4 shows a 20 sccm sample with a continuous graphene sheet on SiO$_2$ substrates. Graphene domains tend to merge with one another, leaving only tiny gaps in between. Each graphene domain is usually flat and smooth, which is ideal for the production of graphene electrical devices.

**FIGURE 4.** FE-SEM images of grown with 20 sccm CH$_4$

**CONCLUSIONS**

We have explored the effect of CH$_4$ gas flow on the synthesis of graphene on the Cu surface. Before this investigation, all the other growth parameters were optimized. Two extreme conditions of CH$_4$ flow rate have been chosen, including 20 sccm and 60 sccm, which are predicted to give significant results to grow graphene at atmospheric pressure. Few layers of graphene were successfully synthesized on the Cu surface by the APCVD method in a vacuum-free system with 20 sccm of CH$_4$ flowrate. The outcome of this research provides a starting point to establish the optimal methane (CH$_4$) flowrate for the production of SiO2 nanoparticles-based graphene balls.

**ACKNOWLEDGEMENTS**

This research is supported by the Fundamental Research Grant Scheme (FRGS/1/2018/TK07/UKM/02/7) research fund from the Ministry of Education, Malaysia.

**REFERENCES**


*Corresponding author; email: azlanhamzah@ukm.edu.my