Synthesis of Continuous Graphene Film Using Liquid Pyridine Precursor

Cheong Kang and Jin Seok Lee

Department of Chemistry, Sookmyung Women’s University, Seoul, 140-742, Korea

ABSTRACT

Due to unique structural and electrical properties of graphene, it has attracted noteworthy attention. Among various synthetic approach methods of graphene, the metal-assisted chemical vapor deposition (CVD) method is the most sensible method to produce graphene films of low-defect and large-scale. Until now, the CVD method using hydrocarbon sources of gas state has synthesized as the large-scale graphene; however, a high temperature above 1000 °C is required for such synthesis. In a recent study, monolayer graphene domains were obtained at a low temperature (300 °C) using liquid pyridine. However, graphene films were not synthesized and the graphene domains of high defects density were only synthesized. Herein, we report the first successful growth of low-defect and monolayer graphenes using liquid pyridine on a Cu foil by CVD method. The effects of the growth temperature, gas flow rate, gas flow ratio, and growth time on the synthesized graphene were also investigated. The micro-Raman analysis indicated that these reaction parameters affected the number of layers and the defect degree of the synthesized graphene.

KEYWORDS: Graphene Film, Defect, Liquid Pyridine, Micro-Raman Analysis.

1. INTRODUCTION

Graphene is a two-dimensional (2D) material of $sp^2$-bonded carbon sheet of a honeycomb crystal lattice. It has been attracting noteworthy interest, because of its unique structural and electrical properties.1 Moreover, the particularly high electron mobility and tunable band gap of graphene make it a potential substance for electronics and sensing applications.2-5 Among various synthetic approach methods of graphene, the metal-assisted chemical vapor deposition (CVD) method is the most sensible method to produce graphene films of low-defect and large-scale.6,7 The synthesis of graphene by CVD method on a Cu foil has shown significant potential due to the low solubility of carbon in Cu. And it is believed to strongly depend on the partial pressure of hydrogen that acts both as the activator of surface bound carbon and etchant for graphene during the growth process.8 Thus, the graphene domain size fundamentally matches to the equilibrium between the growth of graphene and hydrogen etching.

Owing to different carbon sources, catalysts, and other parameters, the CVD method was complicated. Nevertheless, the fundamental physical principles of this method are relatively simple. In the CVD method, the synthesis of graphene occurs either by surface catalytic reaction7,8 in the case of the substrate with the low carbon solubility, or by bulk carbon precipitation on the substrate surface during the cooling process10,11 in the case of the substrate with a high carbon solubility. In the cases, the graphene nucleation on a substrate surface is one of the decisive steps for the growth process. In principle, several elements affect the nucleation initiation including the micro-structure for surface of the metal substrate,9,12 carbon source,13 carbon separation from metal-carbon melts,14 and reaction parameters adapted during the synthesis by CVD method.15-17

In a previous study, graphene was synthesized by the CVD method of gas state hydrocarbons such as methane,7 acetylene,18 and ethylene.19 However, the synthesis of graphene using a liquid carbon source is more advantageous than using a carbon source of gas state, because most of the derivatives and their organic compounds are easily found in a liquid phase at room temperature. Moreover, a liquid carbon source is more variable by adjusting the electronic properties of graphene by doping boron or nitrogen. Because boron- or nitrogen-containing organic solvents are easy to use and cheap, while organic gases are rather uncommon for containing dopant atoms.

Due to these reasons, high quality graphene synthesis was recently proved by liquid precursors such as pyridine,20 benzene,21 alkyl alcohols,22 and hexane.23 Hydrocarbons of gas state require a high temperature above 1000 °C to produce the graphene by the CVD method;21 however, liquid carbon sources have the
Synthesis of Continuous Graphene Film Using Liquid Pyridine Precursor

Kang and Lee

Fig. 1. SEM images of the graphene flakes synthesized at growth temperatures of (a) 250 °C, (b) 300 °C, and (c) 350 °C. The scale bars represent 1 μm. The graphenes were transferred on SiO₂/Si substrates.

potential for the growth of graphene at low temperature. Very recently, using pyridine as the liquid precursors, graphene domains were obtained at a low temperature of 300 °C.²⁰,²¹ It is evident that the use of liquid carbon sources will be favorable owing to the economical and convenient graphene growth method. And the synthesis of low defect monolayer graphene film was important for application such as electronic devices. However, the high defect graphene domains were only synthesized and the graphene film was not synthesized at the current report using pyridine precursor.²⁰ And it was essential that the optimization of the growth parameter such as the growth temperature, gas flow ratio, gas flow rate, and growth time to remove defect. Thus, the optimization of the growth parameter was essential for the synthesis of low defect monolayer graphene film.

In this article, we report the first successful synthesis of low-defect and monolayer graphenes films on a Cu foil using liquid pyridine as the carbon sources and hydrogen as the carrier gas. Varying reaction parameters such as H₂/Ar gas flow rate and ratio and the effects of the degree of defects on the growth of monolayer graphene film were investigated. Moreover, the role of the H₂ and Ar gases on the formation of graphene films was investigated by comparing the graphene domains by scanning electron microscopy (SEM) and micro-Raman spectroscopy.

2. EXPERIMENTAL DETAILS

2.1. Materials

Copper foils (99.999% purity, 0.025-mm (0.001 in) thickness) used for the synthesis of graphenes were purchased from Alfa Aesar. Pyridine (99.8% purity) used for the synthesis of graphenes was purchased from Sigma-Aldrich. Ammonium Persulfate and PMMA (MicroChem 950 PMMA C3, 3% in chlorobenzene) used for the transfer of the synthesized graphenes were purchased from Daikin. A 300 nm-thick SiO₂/Si substrate used for transferring the synthesized graphenes prior to SEM and Raman analyses was purchased from Hitisan.

2.2. Characterization of the Synthesized Graphene

The synthesized graphene domains and films were characterized by SEM and micro-Raman spectroscopy. The morphology of the synthesized graphene domains and films was observed using a field-emission scanning electron microscopy (SEM)

Fig. 2. SEM images and Raman spectra (obtained using an Ar ion laser at a wavelength of 514.5 nm) of the graphene domains synthesized at cooling rates (denoted as Rc-°C/sec) of (a, c) fast cooling (Rc-20) and (b, d) slow cooling (Rc-1). The scale bars represent 10 μm. The graphene domains were transferred on SiO₂/Si substrates.
microscope (FE-SEM, JEOL 7600F) at an acceleration voltage of 15 kV. Prior to SEM observation, the graphene domains and films were transferred on the SiO₂/Si substrates. Micro-Raman mapping of the synthesized graphene domains was obtained by an indigenously developed micro-Raman spectroscopy system. For this, 514.5 nm wavelength of an Ar ion laser was used as the excitation source at a power of ~1 mW. The heating effect was neglected in this power range. The laser beam was focused on the graphene sample using a 50 x microscope objective lens (0.8 N.A.), and the scattered light was collected in the backscattering geometry. The collected scattered light was dispersed using a Shamrock SR 303i spectrometer (1200 grooves/mm) and detected using a CCD detector.

3. RESULTS AND DISCUSSION

Graphene flakes were synthesized at different growth temperatures to investigate the effect of the growth temperature on the sizes of the graphene flakes. The graphene flakes synthesized at different reaction temperatures ((a) 250, (b) 300, and (c) 350 °C) are shown in Figure 1. The growth time was 5 min for all the samples.

In general, the graphene growth is began by the active carbon species supersaturation produced by carbon sources decomposition. So, this growth depends on the growth temperature because the carbon sources decomposition can happen at high temperatures. The sample synthesized at 250 °C has no graphene (Fig. 1(a)). In contrast, the sample synthesized at 300 °C has graphene flakes (Fig. 1(b)), and the sample synthesized at 350 °C has larger flakes.

![SEM images and Raman spectra](image-url)

**Fig. 3.** SEM images and Raman spectra (obtained using an Ar laser at a wavelength of 514.5 nm) of the graphene domains synthesized using H₂ to Ar gas flow ratios of (a, d) 5:0, (b, e) 5:1, and (c) 5:5, respectively. The inset images in panels (a) show the high magnification image for pinholes in the graphene film. (f) Table for the various gas flow ratio compositions of the synthesized graphene samples. The scale bars represent 10 μm. The graphene domains were transferred on the SiO₂/Si substrates.
Synthesis of Continuous Graphene Film Using Liquid Pyridine Precursor

Kang and Lee

Graphene flakes (Fig. 1(c)). Therefore, the average size of the graphene flakes increases with increasing growth temperature. Moreover, the graphene flakes using the liquid pyridine were achieved at a temperature > 300 °C.

Graphene flakes were synthesized at different cooling rates (denoted as $R_c$ °C/sec) to analyze the effect of the cooling rate on the sizes and defects of the graphene flakes. The graphene flakes synthesized at different reaction temperatures are shown in Figures 2(a) and (c) fast cooling ($R_c$-20 °C/sec) and (b), (d) slow cooling ($R_c$-1 °C/sec). The samples were cooled in 150 sccm H$_2$ and 30 sccm Ar atmosphere, and the growth time was 3 min.

Interestingly, the samples with larger graphene domains were synthesized at the slow cooling (Fig. 2(b)) than that at the fast cooling (Fig. 2(a)). To further evaluate the quality of the produced graphene, Raman spectra of the graphene domains synthesized at different cooling rates were recorded, as shown in Figures 2(c) and (d). Figure 2(c) shows the Raman spectra$^{25-29}$ of the graphene areas in Figure 2(a), with monolayer domains ($I_{2D}/I_G = \sim 1.89$) and D peak intensity ($I_D/I_G = \sim 0.16$). In comparison, Figure 2(d) shows the Raman spectra of the graphene areas in Figure 2(b), for monolayer domains with $I_{2D}/I_G$ and ($I_D/I_G$) of $\sim 1.71$ and $\sim 0.09$, respectively. Therefore, the sample with larger size and lower defect graphene domains was synthesized at the slow cooling ($R_c$-1) (Fig. 2(d)) than that at the fast cooling ($R_c$-20) (Fig. 2(b)).$^{30}$

Graphene domains were also synthesized at different gas flow ratios to investigate the influence of the gas flow ratio on the synthesis of the graphene domains. Graphene was synthesized at different gas flow ratio as shown in

---

**Fig. 4.** SEM images and Raman spectra (obtained using an Ar laser at a wavelength of 514.5 nm) of the graphene domains synthesized using gas flow rates of (a, d) 150 sccm H$_2$ and 30 sccm Ar, (b, e) 75 sccm H$_2$ and 15 sccm Ar, and (c, f) 50 sccm H$_2$ and 10 sccm Ar. The scale bars represent 10 μm. The graphene domains were transferred on SiO$_2$/Si substrates.
Figures 3(a) and (d) 50 sccm H₂ gas and 0 sccm Ar gas of 5:0, (b, e) 50 sccm H₂ gas and 10 sccm Ar gas of 5:1, and (c) 50 sccm H₂ gas and 50 sccm Ar gas of 5:5. The growth time was 2 min for the samples.

Figure 3(d) shows the Raman spectra of the graphene areas in Figure 3(a) for monolayer films with the $I_{2D}/I_G$ of $\sim 1.76$ and large D peak intensity with $I_D/I_G$ of $\sim 1.06$, due to the large number of pinholes in the graphene film. In comparison, Figure 3(e) shows the Raman spectra of the graphene areas in Figure 3(b), with monolayer domains ($I_{2D}/I_G = \sim 1.51$) and near defect-free. And, Figure 3(c) shows that the graphene was not synthesized. Due to Ar gas used as buffer gas, the increase of Ar amount resulted in the increase of collision number of H₂ and Ar molecules. And it prevented the synthesis of graphene (Fig. 3(c)). On the other hand, without Ar gas the graphene was synthesized high defect monolayer films. So, the graphene domains were synthesized when the ratio of H₂ gas to Ar gas was 5:1 for all the samples.

Graphene domains were also synthesized at different gas flow rates to investigate the effect of the gas flow rate on defects, and their structures are shown in Figures 4(a) and (d) 150 sccm H₂ and 30 sccm Ar, (b, e) 75 sccm H₂ and 15 sccm Ar, and (c, f) 50 sccm H₂ and 10 sccm Ar. The ratio of H₂ to Ar was 5:1 for all the samples, and the growth time was 2 min.

Figure 4(d) shows the Raman spectra of the graphene areas in Figure 4(a) with monolayer graphene domains ($I_{2D}/I_G = \sim 1.71$) and high D peak intensity ($I_D/I_G = \sim 0.17$). Figure 4(e) shows the Raman spectra of the graphene areas in Figure 4(b) with monolayer graphene domains ($I_{2D}/I_G = \sim 1.52$) and low D peak intensity.

![Figure 5](image_url)  
**Fig. 5.** SEM images and Raman spectra (obtained using an Ar laser at a wavelength of 514.5 nm) of the graphene domains synthesized at growth times of (a), (d) 2 min, (b, e) 5 min and (c, f) 10 min. The scale bars represent 10 μm.
(I_D/I_G = \sim 0.06). In comparison, Figure 4(f) shows the Raman spectra of the graphene areas in Figure 4(c) with monolayer graphene domains (I_D/I_G = \sim 1.57) and nearly defect free (I_D/I_G = \sim 0). And the graphene domains of the lower defect synthesized than D peak intensity (I_D/I_G = \sim 0.06) of the previous report. H_2 acts as both the activator of carbon and etchant during graphene synthesis. The probability of mismatch increases, because the increase of the H_2 amount resulted in the more reaction. And the decrease of the gas flow rate resulted in the decrease of the H_2. So, the D peak intensity ratio for the samples decreased from 150 and 30 sccm Ar to 50 sccm H_2 and 10 sccm Ar. Therefore, the graphene domains were synthesized when the gas flow rate was 50 sccm H_2 and 10 sccm Ar for all the samples.

Graphenes at different growth times were synthesized to investigate the effect on the graphene film synthesis, and their morphology are shown in Figures 5(a) and (d), 5 min, and (c), (f) 10 min. The gas flow rate was 50 sccm H_2 and 10 sccm Ar for the samples.

Figure 5 shows the SEM image and Raman spectrum of the graphene domains and films synthesized at growth times of 2 min (Figs. 5(a) and (d)), 5 min (Figs. 5(b) and (e)), and 10 min (Figs. 5(c) and (f)). The remaining reaction parameters were identical to the graphene samples in Figure 4(c). Figure 5(a) shows the growth of the graphene domains similar to the graphene prepared at limited growth time as shown in Figure 4(c). Figure 5(d) shows the Raman spectra of the graphene areas in Figure 5(a) for monolayer domains with I_D/I_G of \sim 1.57. Thus, the growth time was increased to maintain the flow rate of H_2 and Ar gases. Figure 5(b), shows the growth of the graphene domains, but not a graphene film, with a longer growth time than that in Figure 5(a). Figure 5(e), showing the Raman spectra of the graphene domains in Figure 5(b), reveals the monolayer domains with the I_D/I_G of \sim 2.12. Figure 5(c), shows the growth of full graphene films at higher H_2 bubbling gas flow than that shown in Figure 5(b). Figure 5(f), showing the Raman spectra of the graphene areas in Figure 5(c), reveals that the film consists of monolayer. The increase of the growth time resulted in the increase of the action time of H_2 as both the activator of carbon and etchant. So, the nearly defect free graphene domains were synthesized when the growth time was 10 min and the gas flow rate was 50 sccm H_2 and 10 sccm Ar (the gas flow ratio of 5:1) at 300 °C (Fig. 5(c)). Therefore, the growth temperature, gas flow rate, gas flow ratio, and growth time were the key controlling factor for the graphene film synthesis in the presence of liquid pyridine precursor as the carbon source.

4. CONCLUSIONS

Monolayer graphene domains were synthesized using the APCVD on Cu foils with H_2 and Ar as the dilution gas, H_2 as the bubbling gas, respectively, and liquid pyridine as the carbon source. The APCVD reaction parameters were varied to investigate their effect on the quality of the graphene domains. The gas flow rate was varied, and its effect on the synthesis of graphene domains was investigated. The results indicate that decreasing gas flow rate resulted in defect-free graphene domains, because the decrease of the gas flow rate resulted in the decrease of H_2 amount. The uniformity, number of layers, and degree of defects in the graphene domains were further quantified by analyzing the micro-Raman spectra. Based on the results obtained in this study, we conclude that the degree of the defect for the graphene domains and the synthesis of films can be controlled by varying the growth parameter such as the growth temperature, gas flow ratio, gas flow rate, and growth time during the APCVD. Thus, we was first successfully synthesized the low defect monolayer graphene film by the optimization of the growth parameter.

Acknowledgment: This work was supported by Nano-Material Technology Development Program (2012M3A7B4034986) funded by the National Research Foundation and the Pioneer Research Center Program through the National Research Foundation of Korea funded by the Ministry of Science, ICT and Future Planning (2012-0009562). Additionally, it was supported by the Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (2015R1A2A2A01005536).

References and Notes