An Investigation of Growth Mechanism of Coal Derived Graphene Films

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Abstract

The growth mechanism of coal derived graphene films synthesized via chemical vapor deposition on copper substrates was investigated utilizing Raman spectroscopy, X-ray photoelectron spectroscopy, selected area electron diffraction, optical microscopy, and gas chromatography. The synthesis of coal derived graphene films is a two-step process, wherein the copper is annealed followed by flash pyrolysis of coal under hydrogen environment. The growth mechanism involves a copper catalyzed reaction to produce a carbon film within the first few minutes of synthesis, followed by a hydrogen catalyzed graphitization of the underlying carbon film to form graphene domains which merge together to form graphene films.

1.Introduction:

The discovery of graphene has created an increasing interest in developing an efficient synthesis route for high quality and large-scale production opening a new wave of research in targeting its use in diverse applications [1-8]. Chemical vapor deposition (CVD) has been demonstrated as a promising technique for high quality, large area, transparent, and scalable graphene synthesis [9-11]. Hydrocarbons, which includes gases (such as methane, ethylene, acetylene, etc.) [10, 12], solids (such as polymethyl methacrylate, polystyrene, etc.) [13, 14], and liquids (such as methanol, ethanol, benzene, etc.) [13, 15], are utilized as carbon sources for CVD synthesis of graphene. These carbon sources are unreliable for large-scale graphene production due to their limited supplies and high cost. Efforts are directed towards utilizing alternate carbon sources, which are inexpensive and readily available. Biomass waste and food waste showed the potential for graphene production at low cost [16, 17]. Initially, we demonstrated the use of coal as a carbon source to grow amorphous carbon thin films [18]. We further synthesized graphene films from coal and utilized the coal derived graphene films for battery applications [19, 20]. Coal is a naturally abundant inexpensive carbon source, which shows great potential for sustainable, low cost, and scalable synthesis of graphene films.

Studies of the growth mechanism of graphene are critical to tailor the graphene films as desired for various applications. The graphene growth mechanism is influenced by not only the synthesis conditions such as temperature, pressure, time, etc.; but also by the solubility of carbon on the metal substrate [12, 21-27]. The low carbon solubility on the copper substrate has been demonstrated to be ideal for monolayer synthesis of graphene [12, 22]. Previous studies of the graphene growth mechanism directly on copper substrates focused on the formation of monolayer graphene films utilizing pure hydrocarbon sources such as methane, ethylene, etc.

[12, 21-24]. It has been demonstrated that the mechanism involves copper catalyzed surface adsorption of carbon species from the pure hydrocarbon source, which undergoes nucleation to form graphene domains. These graphene domains grow and merge together to form a monolayer graphene film on the copper substrate [22, 24]. This surface mediated growth mechanism is thought to be self-limiting, and is attributed to the low solubility of carbon species on the copper substrate [12, 22]. However, various studies have demonstrated a change in graphene growth kinetics depending on the growth conditions leading to formation of bilayer or multilayer graphene films [25, 28, 29]. This confirms the self-limiting graphene growth mechanism does not hold for all the growth conditions.

Furthermore, there has been little focus on investigating the graphene growth mechanism using solid carbon sources such as coal. An understanding of the graphene growth mechanism using coal will have a significant impact on the optimization of the synthesis conditions, economics, and environment during the efficient scale up of the process. Unlike pure hydrocarbon gases, coal is a complex carbon source which when pyrolyzed releases a mixture of various gases including hydrocarbons with different molecular weights. Moreover, the partial pressure of gaseous hydrocarbons presumably influences the graphene growth [27, 28, 30] is challenging to control while utilizing a complex solid carbon source such as coal. Consequently, it is essential to elucidate the carbon nucleation, growth of domains, and coal pyrolysis products to better understand the growth mechanism of coal derived graphene films.

Within this context, the objective of the present work is to investigate the growth mechanism of coal derived graphene films, which will facilitate future production of high quality graphene films from various types of coal (such as anthracite, bituminous, etc.) as carbon source. Further, characterization of these graphene domains and the graphene films using optical

microscopy, transmission electron microscopy (TEM), selected area electron diffraction (SAED), Raman spectroscopy, and X-ray photoelectron spectroscopy (XPS) will assist in predicting a growth model for the coal derived graphene films.

2.Experimental:

2.1. Chemicals and materials

The coal used for the experimental work was Wyodak coal (Wyodak coal seam, Wyoming), a sub-bituminous type, which was purchased from the Penn state coal bank. The datasheet provided by the Penn state coal bank reported the elemental analysis of Wyodak coal as - carbon (69.74%), hydrogen (5.55%), nitrogen (0.94%), organic sulfur (0.35%), oxygen (14.83%), and mineral matter (8.59%) content.

Copper foils (99.8%, 0.025 mm thickness) obtained from Alfa Aesar were used as substrate for graphene synthesis. Acetone (> 99%) used for rinsing the copper foils was purchased from Fisher Scientific. Cupric sulfate (> 95%), and Hydrochloric acid (6 N) used for preparation of Marbles reagent were also procured from Fisher Scientific. Silicon wafers (SSP 0.025 mm Virginia Semiconductor Inc.) were used as substrate to transfer the graphene films for characterization. Copper grids (PELCO® Center-Marked Grids, 300 mesh, 3.0 mm O.D.) and lacey carbon grids (300 mesh, Copper) purchased from Ted Pella were used for transmission electron microscopy (TEM) characterization. 5 L Tedlar sampling bags with SS fittings were purchased from SKC Inc. for gas collection during the in-situ and flash coal pyrolysis process.

2.2. Sample preparation and synthesis

The sample preparation and synthesis were performed using the experimental procedure and setup described in our previous work [19]. Coal (10 mg) was loaded on one quartz boat and

placed outside the heat zone in a tubular furnace. Copper foil was placed on another quartz boat and placed inside the heat zone in the furnace. The furnace was evacuated with a vacuum pump and backfilled with hydrogen. The furnace was ramped to the desired synthesis temperature for annealing the copper followed by flash coal pyrolysis for the growth of graphene on the copper substrate. The carbon/graphene films were synthesized at various temperatures/time as shown in table 1. The dimensions of the tubular oven affect the synthesis time and the gas flow rates. The objective of this work is to provide a better understanding of the growth mechanism and not to optimize the synthesis conditions.

Table 1: Synthesis conditions (temperature and time) for the growth of carbon films.

Synthesis temperature (°C)	Synthesis time (min)	Material obtained	Synthesis temperature (°C)	Synthesis time (min)	Material obtained
455	30	C film	1055	6	hybrid C film
655	30	C film	1055	12	hybrid C film
855	30	C film	1055	18	Graphene
955	30	C film	1055	24	Graphene
1000	30	C film	1055	30	Graphene
1055	30	Graphene	1055	45	Graphene

The copper foils were then dropped to float in a petri dish containing Marble's reagent (10 g CuSO₄, 50 ml HCl, 50 ml deionized –DI- water) until the copper dissolved in ~2-3 h and the synthesized carbon films were observed to float in the solution. The carbon films were then lifted

using a clean glass slide and transferred to a petri dish containing DI water. The process was repeated twice to remove the contaminants from the surface of the carbon films before finally transferring onto desired substrates such as silicon wafer, TEM grids, etc. for further characterization. The transfer process is also described in our previous work [19].

2.3. *Gas collection*

The gases released as coal pyrolysis products were collected in a 5 L Tedlar gas sampling bag connected at the exhaust of the tubular furnace. Prior to the pyrolysis, the sampling bag was purged with helium and hydrogen three times each to remove excess air from the sampling bag.

2.4. *Graphene domain visualization*

In order to make graphene domains optically visible, the copper foils with the graphene films were placed on a hot plate at 100 °C for 1 min. The area with the presence of graphene domains remains unaffected, whereas other areas of the copper foil are oxidized [31-33]. The colour contrast between the oxidized region and non-oxidized region was visible under Alicona® InfiniteFocus Optical Microscope (IFM).

2.5. *Physical characterization:*

Raman spectroscopy/mapping is a powerful tool to investigate the structural properties and growth of graphene films [34, 35]. The carbon/graphene films synthesized at different temperatures/times were transferred onto silicon wafers for performing Raman spectroscopy/mapping. The Raman spectra of the carbon/graphene films were obtained using a Bruker Senterra Raman spectrometer. A 20X objective lens was used to acquire Raman spectra using an argon laser ($\lambda=532$ nm) with 20 mW power, resolution range of 3-5 cm^{-1} and integration time of 20 s; whereas Raman mapping measurements were obtained utilizing 2 mW power,

resolution range of 9-15 cm^{-1} and integration time of 10 s. Raman mapping over $100 \times 100 \mu\text{m}^2$ area with step size of 5 μm was selected for measurements. Transmission electron microscopy (TEM) images and the selected area electron diffraction (SAED) of the carbon/graphene films were obtained using the JEM 2100F Transmission Electron Microscope (TEM). The X-ray photoelectron spectroscopy (XPS) analysis of the various carbon/graphene films were conducted using Kratos XSAM 800 electron spectrometer with a 1484 keV Al X-ray source utilizing 120 W power and pass energy of 40 eV. The images of graphene domains on the copper foil were attained utilizing an Alicona® InfiniteFocus Optical Microscope (IFM). The images were then analyzed using ImageJ software. The collected gases were analyzed using Thermo Scientific Gas Chromatograph.

3. Results and Discussion:

The coal derived graphene films were synthesized using low pressure CVD at 1055 $^{\circ}\text{C}$ and 30 min synthesis conditions as demonstrated in previous work [19]. Raman spectrum of the coal derived graphene films (figure 1a) reveals D band at 1350 cm^{-1} , G band at 1575 cm^{-1} , and 2D band at 2700 cm^{-1} . The presence of D band in the graphene films is a mode in Raman spectra of first order originating from the disorder and defects such as point defects, subdomain boundaries, etc. [11, 25, 34-36]. These can be due to the breaking of hexagonal graphene structure caused by other functional groups such as C-O, C=O, etc. or by the sp^3 carbon [14, 37-39]. According to our synthesis method (Section 2.2), the solid coal sample is fed into the tubular oven; therefore, it is hypothesized that gaseous mixture generated from the in-situ pyrolysis of coal can contain the C-O groups that lead to defects in the synthesized graphene. The G band in the coal derived graphene film arises due to the tangential vibrations associated with the sp^2 bonded carbon atoms [25, 34, 35]. Another band at $\sim 2700 \text{ cm}^{-1}$ is designated as 2D band, which

is a mode in Raman spectra of second order and is associated with layers in the graphene films [25, 34, 35]. These bands in the Raman spectra are used to identify the quality and the number of layers associated with the graphene films [34, 35]. The relative intensity of 2D/G is ~ 1 and the FWHM of the 2D peak is $\sim 31 \text{ cm}^{-1}$, which demonstrates formation of bi-layer graphene films [11, 12, 14, 25, 34, 40].

Figure 1. (a) Raman spectra of coal derived graphene film synthesized at 1055 °C and 30 min exhibiting D, G, and 2D band. (b) Large area of coal derived graphene films on TEM grid showing wrinkles, overlapping, and backfolding; Inset: SAED with six diffraction spots demonstrating crystalline nature of coal derived graphene film. (c) High magnification TEM image with the edge of the coal derived graphene film exhibiting bi-layers.

TEM image in figure 1b illustrates large area of the graphene film on the TEM grid with wrinkles, back folding, and overlapping introduced due to the transfer process. The selected area electron diffraction (SAED - inset in figure 1b) reveals the six diffraction spots depicting the hexagonal diffraction pattern and the crystalline nature of the coal derived graphene films. The edge of the graphene film (TEM image in figure 1c) reveals the bi-layers of the coal derived graphene films, which is in agreement with the Raman analysis. In addition, the XPS survey spectrum of graphene film synthesized at 1055 °C and 30 min (Figure S1 - see supporting

information) reveals the presence of carbon, oxygen, and copper (from substrate). The XPS survey did not show any other impurities present in the graphene films.

In order to investigate the growth mechanism of coal derived graphene films, the synthesis was performed at different temperatures/times. Initially, the synthesis was conducted for 30 minutes at different temperatures as mentioned in Table 1. Raman spectra (figure 2) of the low temperature (455 °C, 655 °C, and 855 °C) synthesized films exhibit only D band and G band with broad shoulders demonstrating their amorphous nature [41, 42]. Increase in synthesis temperature to 955 °C and 1000 °C also yielded only carbon films exhibiting D band and G band in the Raman spectra as seen in supporting information figure S2. As the synthesis temperature is further increased to 1055 °C, a 2D peak is also detected along with D and G bands, confirming the formation of the graphene film. The 2D/G intensity and FWHM revealed formation of a bi-layer graphene film. The presence of a D peak in the Raman spectra of a graphene film is the result of defects and disorder due to C-O, C=O, sp^3 carbon, etc. within the graphene network of sp^2 carbon. As a comparison, the Raman spectra of raw coal is also included (figure 2), which shows a broad D band at 1365 cm^{-1} and G band at 1575 cm^{-1} indicating the amorphous nature of the coal [41].

Figure 2. Raman spectra of films synthesized at different temperatures and 30 min synthesis time demonstrating formation of graphene films when the temperature is increased to 1055 °C.

Further, Raman mapping was conducted in order to validate the results of Raman measurements over large areas of the carbon films. A $100 \times 100 \mu\text{m}^2$ area was selected on each sample for the mapping. The results were analyzed in terms of 2D band intensity only, since the interest was to detect the temperature required for graphene formation. Figure 3 shows the 2D band intensity map area of films synthesized at different temperatures and 30 min synthesis time. It can be observed that the 2D peak intensity is close to zero for films synthesized at 455 °C (figure 3a), 655 °C (figure 3b) and 855 °C (figure 3c) indicating no formation of graphene films. However, the 2D peak intensity is dominant over large area of films synthesized at 1055 °C (figure 3d) revealing the continuous and large area graphene formation. Raman mapping

(measurements with respect to the 2D peak intensity) was also conducted on the replicate samples synthesized at different temperatures in order to determine the uniformity of the films. Figure S3 (see supporting information) shows that the 2D peak intensity is negligible for films synthesized at 455 °C, 655 °C, and 855 °C without significant variation. However, the 2D map shows high intensity and uniformity for the replicates synthesized at 1055 °C.

Figure 3. Raman map measurements showing the 2D band intensity over $100 \times 100 \mu\text{m}^2$ area of films synthesized at 455 °C (a), 655 °C (b), 855 °C (c), and 1055 °C (d) demonstrating the presence of 2D band over large area for films produced at 1055 °C.

X-ray photoelectron spectroscopy (XPS) is an ideal technique not only used to determine the elemental composition of monolayer-scale carbonaceous materials, but also to provide information regarding the chemical composition [43, 44]. Therefore, XPS was employed to detect the core level C1s carbon spectra directly on the copper surface. Figure 4 represents the C1s spectra of the carbon/graphene films synthesized at different temperatures and 30 min synthesis time. The C1s spectra of the various carbon films were found to be around 284 eV - 286 eV. The background of the peaks was subtracted using the nine point Shirley background and deconvoluted using a Gaussian-Lorentzian fit. The C1s spectra for the various films were deconvoluted into four peaks. The decomposed peaks and their corresponding components are: sp^2 graphitic carbon (284.5 eV), sp^3 amorphous carbon (285.5 eV), C-O (286.5 eV), and O-C=O (288.5 eV) [21, 43-48]. The oxygen related components and the sp^3 carbon are dominant and have high intensity for low temperature films (figure 4a-455 °C, and 4b-655 °C). As the temperature is increased see figure 4c(855 °C) and figure 4d (1055 °C), the peak intensity of the oxygen related components and the sp^3 carbon decreases and is found to be lowest for the graphene films synthesized at highest temperature (figure 4d-1055 °C). Conversely, the peak representing sp^2 carbon has low intensity for low temperature films (455 °C and 655 °C). The peak intensity of sp^2 carbon increases with temperature and shows the highest concentration for graphene films.

The XPS analysis is consistent with the results from Raman measurements, indicating that the presence of sp^3 carbon and various carbon-oxygen functional groups within the graphene network is correlated with defects in the graphene films. The difference in concentrations of sp^2 carbon, sp^3 carbon, and oxygen related components, follows the phase change from amorphous (low temperature films - 455 °C, 655 °C, and 855 °C) to crystalline (high temperature films -

1055 °C). The peaks corresponding to the oxygen components are calculated to occupy an area of ~20% of the total area of the carbon C1s spectra of the graphene films. This can be attributed to various reasons such as oxidation of the copper foil, adsorption of air on the graphene films, or the oxidation of carbon atoms near the domain boundaries [43-45]. Furthermore, the gaseous mixture generated during the flash pyrolysis of coal contain C-O groups that can also induce defects in the graphene films.

Figure 4. XPS C1s spectra of carbon films synthesized at 455 °C (a), 655 °C (b), 855 °C (c), and 1055 °C (d) and 30 min. synthesis time. C1s spectra of the graphene films (1055 °C) show low amounts of sp^3 carbon and oxygen related components as compared to carbon films synthesized at low temperatures (455 °C, 655 °C, and 855 °C).

Selected area electron diffraction (SAED) was conducted on the films synthesized at

different temperatures and 30 min synthesis time for investigating the nature and phase change. Figure 5 a-d shows the SAED pattern of the synthesized films. The SAED reveals an intense ring without any presence of diffraction spots for low temperature films (figure 5a - 455 °C, and 5b - 655 °C), indicating their amorphous nature. The SAED pattern of films synthesized at 855 °C (figure 5c) shows a combination of diffraction spots and intense rings indicating a hybrid structure of amorphous and crystalline carbon. Similar SAED pattern was observed by Cui et al., for their low temperature synthesized hybrid films [49]. However, only hexagonal diffraction spots are observed for the graphene films (figure 5d - 1055 °C), demonstrating their crystalline nature. The SAED characterization is in agreement with the Raman and XPS measurements.

Figure 5. Selected area electron diffraction of films synthesized at 455 °C (a), 655 °C (b), 855 °C (c), and 1055 °C (d). Amorphous rings present for low temperature films (455 °C and 655 °C), a hybrid film is synthesized at 855°C, and crystalline graphene films is formed at 1055 °C.

After investigating the synthesis temperature required for graphene formation, it was essential to observe the growth and evolution of the graphene films. This was achieved by increasing the synthesis time from 6 min up to 45 min. Figure 6 shows the Raman spectra of the graphene films synthesized at 1055 °C and different synthesis times. The 2D peak intensity is negligible for films synthesized at 6 min. However, as the synthesis time is increased the 2D

peak becomes sharper and peak intensity increases. This behaviour is caused by the increase in graphitization/crystallization of amorphous carbon films and increase in the size of graphene domain with corresponding increase in synthesis time. In order to verify the size of graphene domain optical microscopy was utilized, which is discussed in the later part.

Figure 6. Raman spectra of films synthesized at 1055 °C and different time demonstrating graphitization and increase in domain size as synthesis time is increased.

The evolution of the 2D band is also evidenced from the map measurements (figure 7a-e) demonstrating the intensity of 2D/G ratio over $100 \times 100 \mu\text{m}^2$ area of the graphene films. The intensity of 2D/G ratio is negligible for films synthesized at 6 min (figure 7a). However, with progressively longer time duration the 2D/G intensity ratio increases from ≤ 0.4 for 12 min (figure 7b), ≤ 0.6 for 18 min (figure 7c), ≤ 0.8 for 24 min (figure 7d) up to ≥ 1 for 30 min and

45min synthesis (figure 7e and f). The 2D/G map results indicate that a large fraction of the area is covered with bi-layer graphene films for 1055°C and 30/45 min synthesis. Raman mapping was also conducted on the replicate samples to validate if the 2D/G intensity ratio is uniform and repeatable across the replicates. The 2D/G intensity ratio among the replicate samples increases with increase in synthesis time without significant variation as shown in figure S4 (see supporting information).

Figure 7. 2D/G intensity Raman map over $100 \times 100 \mu\text{m}^2$ area of films synthesized at 1055 °C and 6 min (a), 12 min (b), 18 min (c), 24 min (d), 30 min (e), and 45min (f) demonstrating bi-layer to few layer formation of graphene films produced at 1055 °C and 30/45 min.

Figure 8 a-e demonstrates SAED pattern obtained for the films synthesized at 1055 °C and different times. The SAED for 6 min (figure 8a) and 12 min (figure 8b) synthesis films show

intense rings with diffraction spots. These films are hybrid films composed of amorphous and crystalline carbon. However, the films synthesized at 18 min (figure 8c), 24 min (figure 8d), 30 min (figure 8e), and 45min (figure 8f) reveal only hexagonal diffraction spots indicating the crystalline nature of the graphene films.

Figure 8. Selected area electron diffraction of films synthesized at 1055 °C and 6 min (a), 12 min (b), 18 min (c), 24 min (d), 30 min (e), and 45min (f). Hybrid films with combination of amorphous rings and diffraction spots is observed for 6 min and 12 min synthesis time; while, crystalline graphene films obtained for longer synthesis times (18 min, 24 min, 30 min, and 45min).

Optical microscopy was demonstrated to be a simple and direct technique to visualize graphene domains on the copper substrate [31-33]. Optical detection is a fast approach to

observe the development of graphene domains and their growth to form graphene films, under various experimental conditions. The domain visualization can be obtained with the assistance of an intrinsic property of the graphene, which is to act as an oxidation barrier [31-33]. The copper substrate when heated in air gets oxidized, whereas the sites with graphene domains remain unaffected. The copper foils with graphene films synthesized at 1055 °C and different times were placed on a hot plate maintained at 100 °C for 1 min to visualize the evolution of the graphene domains. After this exposure, the sites with graphene domains were unaffected, whereas the other region of copper was oxidized. Optical microscopy images (Figure 9) shows the evolution of these graphene domains synthesized at 1055 °C and different time intervals. The coal derived graphene domains appears to be oval shaped as seen from figure 9. The graphene domain is similar to one of the many different shapes of graphene domain synthesized by Wu et. al., controlling various process parameters [50]. Graphene domains are hardly visible for 6 min synthesis times. The graphene domains grow in size as the synthesis time is increased and eventually merge together to form a continuous graphene film covering the surface of the copper foil.

Figure 9. Graphene domains observed utilizing optical microscope. The graphene domains hardly observed for 6 min synthesis (a). With progressive synthesis times, the evolution of graphene domains can be observed for 12 min (b), 18 min (c), and 24 min (d) synthesis. Graphene film is formed by merging of graphene domains for 30 min (e) and 45min (f) synthesis.

Raman spectroscopy was used to verify the graphene domains. Figure 10a shows an isolated oval shaped graphene domain synthesized at 1055°C and 30 min. Raman spectra obtained from domain and non-domain region directly on the copper substrate is illustrated in Figure 10b. The Raman spectra of the graphene domain reveals a low intensity D band, G band observed at 1585 cm^{-1} , and the 2D band at 2700 cm^{-1} . The spectra of the non-domain region (figure 10b) only shows the presence of D band and G band, as an indication of an amorphous carbon film surrounding the graphene domain.

Figure 10. Graphene domain on the copper foil (a) with corresponding Raman measurements (b) indicating the presence of the graphene domain and an amorphous carbon in the background.

The optical microscopy images demonstrated that the domains increase in size and merge together, thus increasing in coverage on the copper substrate. Optical images were also obtained from the replicate samples to determine the uniformity and consistency of the surface area coverage of graphene films as the synthesis time was increased. Figure S5 (see supporting information) illustrates this increase in surface area coverage of graphene domains to form graphene films. The graphene film covers ~95 % surface area of the copper substrate at 30 min and 45 min synthesis. Previously, it was observed from the Raman mapping that the 2D intensity increases with increase in synthesis time. This behaviour is attributed to an increase in the size of graphene domain with corresponding increase in synthesis time. The optical images were obtained from the replicate samples of films synthesized at different times. The image analysis assisted in validating the increase in domain size as synthesis time increased. Figure S6 (see supporting information) shows that the domain size increases from few micrometers at 12 min synthesis to hundreds of micrometers at 30 min and 45 min synthesis.

The mechanism of the graphene growth in this rather simple coal heating approach is

certainly intriguing. The hydrocarbons released during the pyrolysis of coal act as the precursors for the graphene synthesis. In order to determine these hydrocarbon gases, the Wyodak coal was pyrolyzed at the graphene synthesis conditions and the gases collected in a gas sampling bag using the setup and procedure mentioned in the experimental section. The gases were then analyzed using gas chromatograph. The chromatography analysis reveals the following gaseous products from the coal pyrolysis at the graphene synthesis conditions: Hydrocarbon gases methane, ethane, ethene, propane, and propene, apart from carbon dioxide and carbon monoxide. The hydrocarbon gases (methane, ethane, ethene, propane, and propene) lead to the formation of active carbon species, thus acting as an indirect carbon source for the growth of graphene films.

Thermogravimetric analysis (TGA) on coal was performed utilizing SDT600 TGA (TA instrument) with argon as a carrier gas. 1055 °C was selected as target temperature under isothermal conditions (30 min pyrolysis time) in order to mimic the synthesis conditions of graphene film. Figure S7 (see supporting information) shows the TGA curve (weight loss % v/s time), which includes the weight loss occurred during the ramp process as well. Majority weight loss occurs within 6 min during the ramp to 1055 °C demonstrating that all the bulk gases are released within the 6 min of the ramp process. This indicates that during the graphene synthesis process (1055 °C) the coal when exposed to flash pyrolysis will release bulk gases within the first 6 min. According to the TGA there is no other gases coming out of the coal even with further increase in pyrolysis time after the ramp step.

Based on these results from the Raman spectroscopy/mapping, TEM SAED, and optical microscopy, we propose a growth mechanism of coal derived graphene films as demonstrated in the following schematic figure 11.

1. Carbons atoms from the various hydrocarbon gases released during coal pyrolysis undergo

copper catalyzed adsorption [21, 23, 51].

2. This is followed by catalytic dissociation and desorption to form an amorphous carbon film on the copper substrate within the first few minutes of the synthesis.
3. As time progresses, the hydrogen catalyzed dehydrogenation and graphitization of the underlying amorphous carbon occurs to form graphene domains.
4. With further increase in time, the graphene domains grow in size and merge together to form a continuous graphene film on the substrate of copper [21, 23].

Figure 11. Schematic of growth mechanism of coal derived graphene films showing the formation of amorphous film followed by hydrogen catalyzed graphitization to form graphene domains. As time progresses, the graphene domains grow in size and merge together forming a continuous graphene film on the copper substrate.

Hydrogen also plays a key role for the synthesis of graphene on metals with low solubility of carbon and has been investigated [21, 46]. It has been described as hydrogen induced graphitization/crystallization of the carbon layer on the copper foil to form graphene [21,

46, 52]. We believe that in the present work as the synthesis proceeds with time, hydrogen graphitizes the underlying hybrid carbon film produced within the first 6 min of the growth process to form graphene domains. In order to confirm the hydrogen-induced graphitization, synthesis was performed at the same conditions (1055 °C and 30 min) as graphene growth, except replacing hydrogen with argon. A continuous carbon film was obtained in the absence of hydrogen at the graphene synthesis conditions. Figure S8 (see supporting information) shows the Raman spectrum of the carbon film revealing the presence of broad D band and G band. However, no 2D band was observed, thus validating the copper assisted growth of a-C films and that copper does not induce crystallization as previously confirmed by various studies [46, 53, 54].

The results prove that coal derived graphene growth is not just a consequence of copper catalyzed self-limiting growth and carbon saturation, but it also involves hydrogen induced graphitization of the carbon films.

4. Conclusion

Large area and uniform graphene films were obtained utilizing coal as solid carbon source via chemical vapor deposition. The growth mechanism was investigated by implementing Raman spectroscopy/mapping, TEM/SAED, optical microscopy, and gas chromatography. The results show coal pyrolysis release hydrocarbon gases, which act as indirect precursor. The carbon species from the hydrocarbon gases adsorb on the copper to undergo copper catalyzed reaction to form hybrid carbon film. This is followed by graphitization of carbon film to form graphene domains with the aid of hydrogen, eventually leading to formation of graphene films.

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Coal

CVD

Graphene

500 nm