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# Crystallization of Size-Selective Nanopores in Graphene for Gas Separation

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### Abstract

Nanoporous single-layer graphene (N-SLG) membranes, owing to their single-atom thinness, have the potential to exceed the permeance and selectivity limits of gas separation membranes. However, two key issues in the top-down N-SLG synthesis need to be addressed to achieve scalable, high-performance membranes: a) reproducible synthesis of high-quality SLG film by chemical vapor deposition (CVD) on a low-cost Cu substrate, and b) introducing high-density of pores with a narrow pore-size-distribution (PSD). This dissertation addresses these issues by developing a method to prepare smooth and oriented Cu foil by a facile approach to obtain high-quality SLG membranes. On the fundamental science front, it explores two novel methods of tuning the PSD in graphene for gas separation.

Low-cost Cu foils are rough, and result in membranes with large nonselective intrinsic vacancy defects which hampers their application in gas separation. Herein, we conduct a systematic high-temperature annealing study on two separate, commercial, low-cost Cu foils leading to their transformation to smooth Cu(111), decreasing their surface roughness by ~ 2-fold. The smooth, oriented Cu foils yielded SLG with a significantly lower defect density with  $I_D/I_G$  ratio decreasing from  $0.18 \pm 0.02$  to  $0.04 \pm 0.01$ . The intrinsic defects in these SLG films were H<sub>2</sub> selective with H<sub>2</sub> permeance reaching 1000 gas permeation units (GPU; flux normalized with transmembrane pressure difference) and attractive H<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> selectivities of 13 and 26, respectively.

To decouple the pore nucleation and expansion in SLG, we utilize  $CO_2$  as a mild etchant to expand the existing pores at temperatures ranging 750 – 1000 °C.  $CO_2$  could uniformly expand the intrinsic pores in SLG in a controlled manner, down to a few Å/min, without nucleating new defects in the SLG basal plane. Furthermore, we revealed two distinct kinetic zones for the reaction of  $CO_2$  with graphene edges, with the transition happening around the pore diameter of ~ 2 nm. Etching rate of the larger expanded-pores was constant and independent of the pore size. The expansion was thermally activated with an activation energy of 2.71 eV, consistent with the literature based on ab-initio calculation for  $CO_2$  dissociative chemisorption on zigzag edges. In comparison, the etching rate was an order of magnitude slower in smaller pores indicating that geometrical confinement in smaller pores play an important role. An exponential relation between the density of expanded pores and etching temperature, with an activation energy of 3.58 eV, was observed.

Next, we develop a novel method to fabricate N-SLG with a high pore-density while maintaining a narrow PSD. We exposed the highly porous SLG (treated by  $O_2$  plasma) with a broad PSD to graphene CVD condition in presence of both CH<sub>4</sub> and CO<sub>2</sub>. The pore expansion (as a result of etching) and shrinkage (as a result of growth) reached a comparable rate. Moreover, CO<sub>2</sub> suppressed the graphene grain nucleation, leading to high-quality graphene synthesis. Membranes with H<sub>2</sub> permeance reaching 10000 GPU and H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> selectivity of 26 were fabricated by optimizing the CH<sub>4</sub>/CO<sub>2</sub> ratio at 800°C.

In summary, we address the current obstacles in SLG membrane development by utilizing  $CO_2$  in graphene CVD environment to tune the PSD of SLG membranes. Moreover, a simple annealing method to optimize the morphological and crystallographic properties of Cu foils for high-quality SLG synthesis is proposed.

#### Keywords

single-layer graphene, pore size distribution, CO<sub>2</sub> based etching, graphene etching, competitive etching and growth, vacancy expansion, intrinsic vacancy defects

## Résumé

Les membranes en graphène monocouche à nanopore (N-SLG), étant donné leur épaisseur atomique, ont le potentiel de surpasser la limite des membranes en termes de perméabilité et sélectivité pour la séparation des gas. Néanmoins, deux problèmes majeurs dans la synthèse « top-down » se doivent d'être résolus pour être en mesure d'obtenir des membranes de hautes performances : a) Synthèse de haute qualité du graphène monocouche (SLG), en utilisant la méthode du dépôt chimique en phase vapeur (CVD) sur un substrat en cuivre peu couteux, et b) l'incorporation de nanopores sélectifs avec haute densité et distribution uniforme (PSD). Cette dissertation répond à ces problématiques, par l'élaboration d'une méthode pour générer une feuille lisse et orientée de cuivre (Cu), permettant l'élaboration de N-SLG de haute qualité. Du point de vue fondamental, ce travail se focalise sur deux nouvelles méthodes permettant de modifier la PSD du graphène monocouche pour la séparation de gas.

Les feuilles de Cu bon marché sont rugueuses, générant des membranes avec des larges défauts intrinsèques, limitant leur application pour la séparation des gas. Dans ce travail, une étude sur un traitement de recuit « annealing » à haute température pour deux feuilles de Cu bon marché. Ce procédé a permis la transformation des deux feuilles en lisse Cu (111), permettant la réduction de leur rugosité par un facteur deux. Cu(111), obtenu après le traitement, permet l'obtention de graphène monocouche avec une réduction de densité de défaut, démontré avec un  $I_D/I_G$  ratio réduit de 0.18 ± 0.02 à 0.04 ± 0.01. Ces défauts étaient sélectifs pour H<sub>2</sub>, avec une perméabilité atteignant 1000 unités de perméation de gas ou GPU et des sélectivités H<sub>2</sub>/CH<sub>4</sub> et H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> surpassant 13 et 26, respectivement.

Pour découpler la nucléation des pores avec leur expansion, le CO<sub>2</sub> a été utilisé comme graveur d'intensité modérée, permettant l'expansion des pores existants pour des températures entre 750 et 1000 °C. Le CO<sub>2</sub> pouvait expandre les pores dans le graphène monocouche de manière contrôlé : quelques A/min, sans générer de nouveaux pores. De plus deux zones cinétiques distinctes ont été identifiées pour la réaction du CO<sub>2</sub>, avec la transition se manifestant autour d'un diamètre du nanopore de 2 nm. La vitesse d'expansion des nanopores de plus grande taille était constante et indépendante de la taille du pore. L'expansion était thermiquement activée et consistante avec les calculs « ab-initio » reportés dans la littérature. Néanmoins, la vitesse d'expansion était d'un ordre de magnitude plus lent pour des plus petits nanopores, en raison du confinement géométrique.

Pour le développement de membrane N-SLG avec une haute densité de nanopores, tout en maintenant leur distribution uniforme, le graphène de haute porosité, a été exposé aux conditions CVD en présence de CH<sub>4</sub> et CO<sub>2</sub>. L'expansion des pores et leur rétrécissement ont démontré des vitesses comparables. Le CO<sub>2</sub> supprime la nucléation des grains du graphène, permettant l'obtention d'une synthèse de haute qualité. Des membranes avec une perméabilité  $H_2$  de 10000 GPU et  $H_2/C_3H_8$  sélectivité de 26.

En résumé, ce travail répond aux obstacles rencontrés par les membranes en graphène monocouche en utilisant le  $CO_2$  pour modifier la PSD. En outre, un simple traitement « annealing » permet d'optimiser la morphologie des feuilles de cuivre pour obtenir des membranes en graphène monocouche de haute qualité.

#### **Mots-clés**

single-layer graphene, pore size distribution, CO<sub>2</sub> based etching, graphene etching, competitive etching and growth, vacancy expansion, intrinsic vacancy defects

# **Table of Contents**

Acknowledgments	1		
Abstract	2		
Résumé			
Table of Contents			
1. Chapter 1. Introduction			
1.1. Graphene membranes: challenges and opportunities	8		
1.2. Gas separation mechanism1	1		
1.3. Graphene crystallization1	4		
1.3.1. Introduction1	4		
1.3.2. Graphene growth mechanism1	5		
1.3.3. Graphene growth kinetics1	6		
1.4. Incorporation of nanopores by etching1	7		
1.4.1. Physical etching1	8		
1.4.2. Chemical etching2	1		
1.5. Current bottlenecks of graphene membrane fabrication for gas separation2	9		
1.6. Thesis outline	2		
2. Chapter 2. Hydrogen-sieving single-layer graphene membranes obtained b crystallographic and morphological optimization of catalytic copper foil	у 4		
Abstract	4		
2.1. Introduction	5		
2.2. Methods	6		
2.2.1. Annealing and smoothening of commercial Cu foils	6		
2.2.2. Graphene synthesis	8		
2.2.3. Membrane fabrication	9		
2.2.4. Characterization	0		
2.3. Results and discussion	1		
2.3.1. Intrinsic defects in graphene	1		
2.3.2. The orientation of Cu grains	2		
2.3.3. Surface morphology of Cu	4		
2.3.4. Gas separation performance from intrinsic vacancy-defects in graphene4	7		
2.4. Conclusions	1		
Appendix I			
3. Chapter 3. Demonstrating and unraveling a controlled nanometer-scale expansion of the vacancy defects in graphene by $CO_2$			

Abstract.		54
3.1. Introduction		
3.2. Me	ethods	56
3.2.1.	Graphene synthesis	56
3.2.2.	CO <sub>2</sub> etching	57
3.2.3.	O3-treatment of SLG on Cu	
3.2.4.	O <sub>2</sub> -plasma treatment	
3.2.5.	AC-HRTEM sample preparation	
3.2.6.	Characterization	60
3.3. Re	sults and discussion	61
3.4. Co	onclusion	73
Appendix	۲ I	74
4. Chapte 78	r 4. Competitive etching and growth of single-layer graphene fo	r molecular sieving
Abstract.		
4.1. Int	roduction	
4.2. Me	ethods	
4.2.1.	Graphene synthesis	
4.2.2.	CO <sub>2</sub> etching	81
4.2.3.	Regrowth by CH <sub>4</sub> -CO <sub>2</sub>	
4.2.4.	O2 plasma treatment	
4.2.5.	Membrane fabrication	
4.2.6.	AC-HRTEM sample preparation	
4.2.7.	Characterization	
4.3. Re	sults and discussion	
4.4. Co	onclusion	
Appendix	ς Ι	
5. Chapte	<ol> <li>Chapter 5. Summary and perspective</li> </ol>	
5.1. Su	mmary of the thesis	
5.2. Pe	rspective	
References.		
Curriculum	Vitae	

### 1. Chapter 1. Introduction

### 1.1. Graphene membranes: challenges and opportunities

Membrane separation has been progressively gaining more attention due to its potential to cut down the energy consumption of the separation industry by 90%, thus, decreasing the carbon footprint of the separation industry at the current environmental-friendly regulations (Figure 1-1a).<sup>1</sup> Moreover, membranes can be retrofitted to existing processes due to their simple steady-state operation. The separation driving force in membranes is the chemical potential gradient across the membrane layer, that is, the difference in partial pressure of the components in feed and permeate sides. This makes membrane a compelling choice for applications with high feed pressure or high concentration of the permeable component.<sup>2,3</sup>

Currently, polymeric membranes dominate the gas separation applications, however, their potential is limited due to an intrinsic tradeoff between permeance and selectivity.<sup>4,5</sup> Twodimensional (2D) membranes operating in molecular-sieving regime can overcome this issue by eliminating the effect of molecular solubility and free volume in polymeric chains.<sup>6</sup> The permeance and selectivity of the 2D membranes can be controlled and adjusted separately, enabling fabrication of the ultimate membrane possessing high selectivity and permeability. In particular, single-layer graphene (SLG) is predicted to play a major role in shaping the future of membrane separation due to its ultimate thinness, flexibility, mechanical strength, and chemical stability.<sup>7,8</sup> The component flux across a membrane can be described by a derivation of the Fick's law for thin films (Equation 1.1). Thus, SLG possesses the least theoretical resistance on the diffusion path of the permeating component due to its one-atom thickness.

$$J_{i} = \frac{DH}{l} (C_{i,feed} - C_{i,permeate})$$
Equation 1.1

where *J* is the diffusive flux, *D* is the diffusion coefficient, and *H* is the adsorption coefficient of component i. *l* is the membrane thickness, and  $C_{i,feed}$  and  $C_{i,permeate}$  are the concentration of component *i* at the feed and the permeate sides, respectively.

Graphene's extreme flexibility provides unique opportunities in its synthesis process (e.g., rollto-roll production) and fabrication of membranes with high surface area (e.g., possibility of a spiral-wound membrane modules). In addition, SLG's flexibility enables it to conform to the topology of the target substrate, hence exhibiting an ultra-high adhesion energy to even smooth substrates. For instance, an adhesion energy of 0.45 J.m<sup>-2</sup> for SLG and silicon oxide substrate is reported (Figure 1-1b,c).<sup>9</sup>

Graphene's high mechanical strength (Young's modulus of 1 TPa and tensile strength of 125 GPa)<sup>10</sup> simplifies the handling and transfer of the SLG from its growth substrate to any desired surface such as porous substrates during membrane fabrication without deforming the graphene's lattice. Moreover, nanoporous SLG (N-SLG) maintains its mechanical strength even at 15% porosity (Young's modulus of 500 GPa),<sup>11</sup> making it a suitable material for membranes operating at a wide range of feed pressures (Figure 1-1d).



Figure 1-1. (a) Separation processes ranked based on their energy consumption.<sup>12</sup>. Thermal separation processes require higher energy compared to nonthermal separation processes as at least one component must vaporize. Reprinted with permission; copyright 2019, The National Academies Press. (b) A schematic of the high-speed roll-to-roll production of graphene.<sup>13</sup> Reprinted with permission; copyright 2015, Springer Nature BV. (c) 3D rendering of the AFM image of SLG film on holey SiO<sub>2</sub> substrate displaying its deformed shape due to the high pressure difference between its two sides.<sup>9</sup> This shows high mechanical strength and flexibility of SLG along with strong adhesion to the SiO<sub>2</sub> substrate. Reprinted with permission; copyright 2011; Springer Nature BV. (d) A schematic of the roll-to-roll production/transfer of graphene to an arbitrary substrate.<sup>14</sup> Reprinted with permission; copyright 2010; Springer Nature BV.

Pristine graphene is inherently impermeable (even to He);<sup>15</sup> however, gas permeation across membranes made from SLG grown by chemical vapor deposition (CVD) method were reported.<sup>16–18</sup> Huang et al. reported SLG membranes with H<sub>2</sub>/CH<sub>4</sub> selectivity of up to 25 and H<sub>2</sub> permeance of ~100 gas permeation unit (GPU).<sup>16</sup> they reported membranes with H<sub>2</sub>

permeance of up to ~1000 GPU, although at the expense of the decline in selectivity. These intrinsic defects were formed due to a) the etching effect of the residual oxygen in the CVD system,<sup>19</sup> and b) the incomplete intergrowth of the adjacent graphene grains with different orientations, leading to grain boundary defects.<sup>20,21</sup> Nonetheless, these membranes are far from the theoretically predicted performance of the N-SLG membranes (H<sub>2</sub> permeance of 10<sup>7</sup> GPU, He/H<sub>2</sub> selectivity of 10<sup>3</sup>, and H<sub>2</sub>/CH<sub>4</sub> selectivity of 10<sup>23</sup>).<sup>22,23</sup>

Incorporating a high density of pores with narrow pore-size-distribution (PSD) in SLG is crucial to realize this material's true potential fully. The first proof-of-concept of gas separation across SLG was reported by Koenig et al. by exposing a micron-sized graphene membrane to ultraviolet, thus creating a small number of angstrom-sized pores.<sup>24</sup> Several groups, including ours, have been actively investigating the fundamentals of gas transport and gas separation by graphene, Recently, molecular-sieving N-SLG membranes in nanometer and centimeter scale were successfully demonstrated.

Nanopores can be incorporated in SLG film by bottom-up or top-down approaches. In the bottom-up approach, the density of the vacancy defects is increased by tuning the CVD synthesis parameters, mainly by decreasing the CVD temperature. Kidambi et al. first reported the fabrication of N-SLG membranes for ion separation by reducing the CVD temperature from 1000 to 900 °C.<sup>25</sup> Yuan et al. further manipulated the CVD temperature and carbon precursor concentration and fabricated gas separation membranes with H<sub>2</sub>/CH<sub>4</sub> selectivity of > 2000 and H<sub>2</sub> permeance of > 4000 GPU.<sup>26</sup>

Various chemical etching top-down approaches were explored to tune the PSD in SLG. O'Hern et al. and Cheng et al. utilized ion bombardment to nucleate high density of vacancy defects in SLG film and subsequently expanded the pores by oxidative etching in acidic potassium permanganate solution, resulting in membranes suitable for ion separation and nanofiltration.<sup>27,28</sup> Zhao et al. used O<sub>3</sub> etching to fabricate gas-sieving N-SLG membranes with H<sub>2</sub> permeance of up to 6000 GPU and H<sub>2</sub>/CH<sub>4</sub> selectivity of up to 25. Hsu et al. further optimized the O<sub>3</sub> etching parameters, resulting in membranes with CO<sub>2</sub> permeance of up to 8700 GPU and CO<sub>2</sub>/N<sub>2</sub> selectivity of up to 33.<sup>29</sup>

N-SLG membranes possess the potential to become the ultimate membrane; however, further development in tuning their PSD is required to realize their true potential in diverse separation applications.

#### **1.2.** Gas separation mechanism

Membranes act as selective barriers by allowing a molecule (or set of molecules) to pass across their semi-permeable layer faster than other molecules. Gas separation membranes can be classified based on the structure of the selective layer: a) dense films with solution-diffusion mechanism, b) films prepared by stacking of layers such that interlayer spacing forms a transport pathway, and c) nanoporous membranes hosting selective pores.

Selectivity in solution-diffusion-based membranes depends on the difference in gases solubility and diffusivity.<sup>30</sup> Molecules with higher solubility and diffusivity in the membrane layer pass through it faster, resulting in separation. Molecules' path across the membrane includes absorption from feed gas bulk into the membrane, diffusion through the membrane, and desorption to the permeate gas bulk. Polymeric membranes operate by this mechanism.<sup>4,31</sup>

In layered films, separation is realized by tuning their interlayer spacing to allow the passage of smaller molecules while blocking the larger molecules. Graphene oxide (GO) and reduced GO (rGO),<sup>7,32</sup> MXenes,<sup>33,34</sup> and transition metal dichalcogenides (TMDs)<sup>35,36</sup> are notable examples of membranes operating with this mechanism.

Separation in nanoporous membranes is achieved by allowing the smaller molecules to pass through the pores while rejecting the larger molecules. N-SLG,<sup>16,37</sup> metal-organic frameworks (MOFs),<sup>38</sup> covalent organic frameworks (COFs),<sup>39</sup> and zeolites<sup>40</sup> belong to this group. These membranes operate by three mechanisms based on their pore size relative to the permeating gas molecules.

When the kinetic diameter of the molecule  $(d_{mol})$  is close to the membrane's pore size  $(d_{pore})$ , the highest selectivity can be obtained by operating in the molecular sieving regime. When the  $d_{pore}$  is bigger than the  $d_{mol}$  but smaller than the molecule's mean free path  $(\lambda_{mol})$ , Knudsen transport mechanism is dominant and separation is achieved due to the faster average speed of the lighter molecules compared to the heavier ones. The Knudsen selectivity is calculated by Equation 1.2.<sup>41</sup> When  $d_{pore}$  is bigger than the  $\lambda_{mol}$ , viscous flow is dominant and separation is based on the viscosity. The selectivity can be calculated by Equation 1.3.<sup>3</sup> A graphical summary of the various gas transport mechanisms across membranes is shown in Figure 1-2. Schematic of various transport mechanisms across the membranes.Figure 1-2.

where  $\alpha_{A/B}$  is the selectivity of the gas A over gas B, and  $M_A$  and  $M_B$  are the molecular weight of the gas A and B, respectively.

$$\propto_{A/B} = \frac{\mu_B}{\mu_A}$$
 Equation 1.3

where  $\alpha_{A/B}$  is the selectivity of the gas A over gas B, and  $\mu_A$  and  $\mu_B$  are the viscosity of the gas A and B, respectively.





Gas transport across N-SLG cannot be explained by conventional continuum equations based on the mass transport resistance in a membrane with a significantly thicker layer than SLG.<sup>42</sup> In addition, contrary to the conventional gas transport mechanisms, the effect of surface adsorption and diffusion in N-SLG membranes should not be neglected. Several molecular dynamics (MD) studies emphasized the importance of the external surface in N-SLG membranes.<sup>43-45</sup> The suggested transport models in N-SLG can be classified as a) models based on analytical expressions of adsorption, surface diffusion, pore translocation, and desorption;<sup>42,46-48</sup> and b) transport models based on steric constraints.<sup>8,49</sup> In its simplest form, in a unified model, gas molecules can cross the N-SLG film in two ways:<sup>50</sup> a) the gas molecule adsorbs on the graphene surface and diffuses on the surface to the pore opening (overcoming resistance of  $R_1$ ). Then, it crosses the pore by overcoming the energy barrier of translocation (resistance of  $R_3$ ); b) the gas molecule directly transports to the pore opening from the gas bulk (overcoming resistance of  $R_2$ ) and translocates across the pore (overcoming resistance of  $R_3$ ). A schematic of the mechanism is shown in Figure 1-3.



Figure 1-3. (a) Schematic of the gas transport in N-SLG membranes and (b) the corresponding resistance model.

The net permeation rate across the pore can be expressed by  $^{50}$ 

$$N_p = \frac{\Delta P}{R}$$
 Equation 1.4

where  $N_p$  is the net permeation rate across the pore,  $\Delta P$  is the transmembrane pressure difference, and *R* is the total gas transport resistance. *R* can be expressed as

$$R = \frac{1}{R_1^{-1} + R_2^{-1}} + R_3$$
 Equation 1.5

The resistances can be calculated by

$$R_1^{-1} = \sqrt{\frac{\pi}{2Mk_BT}} \frac{D_p^2}{4}$$
 Equation 1.6

$$R_2^{-1} = \sqrt{\frac{\pi k_B T}{2M}} D_P H_{sur}$$
 Equation 1.7

$$R_3^{-1} \propto C_i \operatorname{erfc}\left(\sqrt{\frac{E_{act}}{k_B T}}\right)$$
 Equation 1.8

where  $D_p$  is the pore's effective diameter, M is the molecular weight,  $k_B$  is the Boltzmann constant, T is temperature,  $H_{sur}$  is Henry's coefficient for gas molecule adsorption on the graphene surface,  $C_i$  is the concentration of gas molecules at the pore, and  $E_{act}$  is the energy barrier of the translocation.

#### **1.3.** Graphene crystallization

#### 1.3.1. Introduction

Nobel prize award-winning discovery of graphene in 2004<sup>51</sup> was a momentous point in material science not only due to graphene's extraordinary physical, chemical, optical, and electrical properties<sup>52</sup> but also by falsifying a long-standing belief that strictly 2D materials were not thermodynamically stable and thus could not exist in isolation.<sup>53–56</sup> Graphene is an allotrope of carbon with planar sp<sup>2</sup> C-C bonds.<sup>57</sup> Its hexagonal 2D crystal lattice consists of two carbon atoms (Figure 1-4), giving it a honeycomb-like structure. Each carbon atom possesses three sp<sup>2</sup>-hybridized orbitals that form three  $\sigma$  bonds with three adjacent carbon atoms at 120° angles, and the 2P orbitals form half-filled  $\pi$  bonds<sup>58</sup>. The C-C bond length in graphene is 0.142 nm, which is double the resonance bond atomic radius of 0.71 Å.<sup>59</sup>





Chemical vapor deposition (CVD) has been the method of choice to synthesize large-area polycrystalline monolayer graphene films. In the absence of catalysts, graphene formation by the decomposition of hydrocarbon precursors requires temperatures higher than 1500 °C to form a highly-crystalline graphitic lattice, thus, necessitating the existence of a catalytic surface to assist the precursor dissociation and sp<sup>2</sup> bonding arrangement.<sup>60</sup> Typical metal catalysts that can lower the activation pathway of graphene crystallization are Cu,<sup>14,61–64</sup> Ni,<sup>65–67</sup> Ru,<sup>68,69</sup> and Ir,<sup>70,71</sup>. Cu foil has emerged as the substrate of choice due to its low C solubility (leading to the synthesis of predominantly SLG), ease of etching (resulting in ease of SLG transfer to a desired substrate), and most importantly, low cost.<sup>61</sup>

Additional graphene domains and adlayers can nucleate and grow at the interface of the metal and first graphene layer<sup>72</sup> when the carbon precursor partial pressure is higher than a certain threshold.<sup>73</sup> This is primarily due to the carbon precursor leakage to the interface from graphene

defects and grain boundaries. To prevent this, low-pressure CVD (LPCVD) can be employed to benefit from its self-limiting mechanism after the first layer of graphene is formed. Graphene growth is a surface-mediated phenomenon,<sup>74</sup> and CH<sub>4</sub> is the precursor of choice in high-quality graphene growth as pyrolysis at elevated temperatures can be prevented due to its thermal stability.<sup>75</sup> Li et al. paved the way by developing the first LPCVD method to synthesize large-area high-quality SLG.<sup>61</sup> Later, Bae et al. demonstrated roll-to-roll production of 30-inch high-quality graphene film.<sup>14</sup> Recently, a high-speed roll-to-roll synthesis of CVD graphene was reported, increasing its attraction for future scale-up efforts.<sup>13</sup>

#### 1.3.2. Graphene growth mechanism

Graphene growth mechanism and kinetics via LPCVD on Cu have been studied via ex-situ time-dependent growth experiments<sup>76,77</sup> and gained much more attention in the past few years due to advancements in in-situ observation techniques.<sup>19,78-80</sup> Graphene nucleation occurs as a result of localized active carbon supersaturation on the Cu surface.<sup>81</sup> The density of nuclei can be manipulated by the amount of atomic oxygen in the reactor, <sup>19,82</sup> the extent of existing carbon contamination on the Cu surface,<sup>83</sup> and the level of Cu surface roughness.<sup>84</sup> Li et al. investigated the growth processes of graphene/Cu, graphene/Ni, and graphene/Cu-Ni systems using CH<sub>4</sub> as the carbon precursor with a carbon-isotope labeling technique.<sup>79</sup> Two growth mechanisms have been proposed: i) a surface segregation/precipitation process of C for metals with high carbon solubility such as Ni, and ii) a surface adsorption process for metals with low carbon solubility such as Cu (Figure 1-5). In the latter mechanism, CH<sub>4</sub> first adsorbs on the metal surface and decomposes to generate CH<sub>x</sub> radicals or C. Then, active carbon species diffuse on the Cu surface and attach to the edges of the existing nuclei, leading to two-dimensional growth of graphene domains, or form new nuclei where supersaturation occurs.<sup>85</sup> Moreover, LPCVD graphene growth on Cu substrate is a self-limiting process as supply of active carbon species stops when the catalytic Cu surface is covered with graphene and CH<sub>4</sub> decomposition cannot take place.<sup>79</sup> On the contrary, high CH<sub>4</sub> partial pressure, e.g., atmospheric pressure CVD (APCVD), can result in bi- and multi-layer graphene domains due to the possibility of additional CH<sub>4</sub> decomposition in the gas phase.<sup>86</sup>



Figure 1-5. Schematic of the spatial distribution of C isotopes in graphene films for sequential exposure of Cu substrate to the C isotopes (<sup>12</sup>C and <sup>13</sup>C). (a) Surface segregation and/or precipitation, and (b) surface adsorption.<sup>79</sup> Reprinted with permission; copyright 2009, American Chemical Society.

#### 1.3.3. Graphene growth kinetics

Graphene growth rate depends on many factors such as temperature, growth precursor partial pressure, presence of impurities in the reactor, morphology and cleanness of the catalytic surface, and the percentage of the available catalytic surface.<sup>26,61,87–89</sup> Graphene growth follows the following three steps: i) dissociative chemisorption of CH<sub>4</sub> on Cu surface, ii) surface diffusion of the growth species, and iii) attachment of the said species to the graphene nuclei.<sup>81</sup> The rate-limiting step has the highest energy barrier and controls the overall rate of the reaction as these three steps are in series. At the beginning of the growth process, which most of the studies focused on, the graphene domains are far apart. Depending on the reaction condition, surface diffusion or attachment of the growth species to the edges of the existing domains is likely the rate-limiting step (energy barrier of 2.4 - 3.1 eV).<sup>76,80,81</sup> Moreover, the competition between the surface diffusion rate and the reaction rate determines the shape of the graphene grains (dendritic graphene grains in case of slow surface diffusion and faceted graphene grains in case of slow reaction).<sup>90</sup> At the beginning of the growth process, when ample catalytic Cu surface area is available, a high number of growth species are available; thus, the rate of the attachment of these species to the graphene grain determines the overall rate of the process. However, at the later stages of the growth (when a certain area of the Cu is covered and consequently the CH<sub>4</sub> decomposition rate is slower), the overall process is limited by the rate of surface diffusion of the available growth species to reach the edges of the graphene domains prior to their attachment.

Wang et al.<sup>80</sup> utilized a modified environmental scanning electron microscope (ESEM) to directly observe the LPCVD graphene growth cycle from substrate annealing to graphene growth and the subsequent cooling on a polycrystalline Cu substrate. They used the in-situ-recorded images to investigate the nucleation and growth behavior (Figure 1-6). During phase I, a large catalytic surface area was available, resulting in an abundance of decomposed growth species leading to a constant growth rate limited by the attachment rate of these species to the existing nucleus. The rapid consumption of the growth species depleted the growth precursors at the immediate distance of the graphene domain edges resulting in the initiation of phase II, in which the surface diffusion of the species limited the growth rate. Phase III begins when the diffusion zone of the adjacent domains intersects, further lowering the growth rate. In addition, their study revealed a much slower growth rate at the growth fronts of the adjacent domains.



Figure 1-6. (a) Graphene growth phases and nucleation rates. The nucleation rate was calculated based on the number of new nuclei per recorded frame. (b) Evolution of the graphene grains displayed by the superposition of a series of subsequent recorded frames (the scale bar measures 5  $\mu$ m). (c) Left: a scheme of the graphene growth phases (mentioned in panel a), and right: the corresponding in-situ SEM images (the scale bar measures 5  $\mu$ m).<sup>80</sup> Reprinted with permission; copyright 2015, American Chemical Society.

#### **1.4.** Incorporation of nanopores by etching

Perfect graphene lattice is impermeable to gas molecules; thus, incorporation and expansion of nanopores are necessary to realize its potential for separation applications. The majority of the graphene etching methods can be categorized as either physical etching or chemical etching techniques (Figure 1-7). Physical etching is obtained by using a high-energy electron/(focused) ion beam to knock out the C atoms from the graphene lattice, and chemical etching is achieved

by reaction of C atoms in graphene lattice with oxidative gases leading to gasification and release of CO and CO<sub>2</sub> molecules.



Figure 1-7. Diagram of the widely used graphene etching methods.

#### 1.4.1. Physical etching

#### 1.4.1.1. Electron beam

Bombardment of graphene lattice by high-energy electrons can break the C-C bonds and knockout C atoms if the transferred energy exceeds the C-C bond energy. The transferred energy is always lower than the electron source energy due to several factors, such as the angle of the incident electron beam and the direction of ejection. Smith and Luzzi<sup>91</sup> and Kotakoski et al.<sup>92</sup> reported a minimum incident electron energy of 86 and 100 keV, respectively, to displace one sp<sup>2</sup> C atom bonded to three C atoms in the graphene basal plane. The energy barrier of C atom knock-out (transferred energy) from graphene basal plane is reported to be 23 eV.<sup>93</sup> However, much lower energy (<14 eV) is needed to expand the existing pore edges in graphene lattice as each C atom is only bonded to two C atoms.<sup>94</sup>

Fischbein and Drndić were one of the first to demonstrate the physical etching of graphene by creating 3.5 nm-sized nanopores, slits, and nanobridges utilizing a converged 200 keV electron beam.<sup>95</sup> Warner et al.<sup>96</sup> and Robertson et al.<sup>97</sup> irradiated multilayer graphene films to selectively

remove the top graphene layer using an 80 keV electron beam. Schneider et al.,<sup>98</sup> Merchant et al.,<sup>99</sup> and Garaj et al.<sup>100</sup> created 5 - 23 nm nanopores in graphene using 200 - 300 keV electron beams to study their membrane performance in ion separation and DNA sequencing. Examples of physical etching in graphene are shown in Figure 1-8. As mentioned above, the required energy for expanding the existing pores is much lower than that needed to nucleate new pores. As pore nucleation and expansion of the existing pores co-occur, achieving the desired pore size with narrow PSD is complicated, deteriorating the membrane performance. This complexity has been observed by aberration-corrected transmission electron microscope (AC-HRTEM) displaying the dynamic behavior of graphene edges.<sup>85</sup>



Figure 1-8. (a) A sequence of HRTEM images showing the evolution of a pore in bilayer graphene under electron beam exposure (scale bar measures 1 nm).<sup>96</sup> Reprinted with permission; copyright 2009, Springer Nature. (b) TEM images of the nanopores drilled in a multilayer graphene sheet by an electron beam.<sup>98</sup> Reprinted with permission; copyright 2010, American Chemical Society.

#### 1.4.1.2. Focused ion beam

Focused ion beam (FIB) working mechanism is similar to electron beam bombardment, in that, the collision of high-energy particles (ions) knocks out the C atoms from the graphene basal plane. Heavier ions (e.g., Ga<sup>+</sup>, Ar<sup>+</sup>, and Kr<sup>+</sup>) exhibit a higher yield of sputtering than lighter ions (e.g., He<sup>+</sup>) at the same working voltage.<sup>93</sup> Celebi et al. demonstrated this by revealing the higher average removal rate of the carbon atoms from graphene lattice using Ga<sup>+</sup> compared to the He<sup>+</sup>.<sup>101</sup> This can be explained by the kinematical relationship used to estimate the minimum required ion energy to knock out a C atom in a head-on collision.<sup>102</sup>

$$E_{min} = E_d \frac{(M_i + M_c)^2}{4M_i M_c}$$
 Equation 1.9

where  $E_{min}$  and  $E_d$  are the minimum ion energy to knock out a C atom and the displacement energy of a C atom, respectively.  $M_i$  and  $M_c$  are the mass of the ion and the C atom, respectively.

Celebi et al. created 16 - 1000 nm-sized nanopores in the graphene lattice by varying the dose between  $0.5 - 5 \times 10^{-5}$  pA/nm<sup>2</sup>.<sup>101</sup> They fabricated bilayer graphene membranes with a mean pore size of ~ 7.6 nm using He<sup>+</sup> and studied their gas permeation behavior. Similar to the electron beam, simultaneous pore nucleation and expansion limits the potential of FIB. Russo and Golovchenkoa addressed this issue by utilizing a 3 keV Ar+ beam to create 1 - 2 missing C atom defects and further expanded them by electron beam exposure.<sup>94</sup> A parallel 80 keV electron beam inside a TEM device was used for the pore expansion (expanded to ~ 1.7 nm). Examples of the pore nucleation and expansion by FIB are shown in Figure 1-9.

These microscopy methods are of great use in fundamental research. However, they are highly challenging in pore fabrication with angstrom control of PSD required in gas separation. In addition, their method of application (inside TEM) makes them impractical for treating surfaces larger than a few micrometers and further scale-up.



Figure 1-9. (a) SEM images of the left: 50-nm-sized and right: 7.6-nm-sized FIB drilled nanopores in graphene (left scalebar: 500 nm; right scalebar: 100 nm) and the various PSD obtained by FIB in graphene sheets.<sup>101</sup> Reprinted with permission; copyright 2014, American Association for the Advancement of Science. (b) Diagram of the steps of nanopore creation by FIB in graphene and (c) an example of I) atomic model, II) simulated, and III) experimental nanopore created by this method.<sup>94</sup> Reprinted with permission; copyright 2012, National Academy of Sciences.

#### **1.4.2.** Chemical etching

In contrast to the physical etching techniques, the chemical etching of graphene is intrinsically scalable and can create small nanopores appropriate for gas separation membranes. Several oxidizing etchants such as plasma, gas molecules (O<sub>2</sub>, O<sub>3</sub>, H<sub>2</sub>O, CO<sub>2</sub>, etc.), ultraviolet (UV)/O<sub>3</sub>, etc. have been studied to incorporate vacancy defects in graphite and graphene. Thermal reaction of oxidative gases with carbon has been experimentally investigated by observing the etching effect of O<sub>2</sub> on graphon<sup>103,104</sup> and graphite;<sup>105–109</sup> chlorinated oxygen on graphite;<sup>110</sup> air on graphite;<sup>111,112</sup> steam on graphite,<sup>113–116</sup> activated carbon,<sup>117,118</sup> and coke;<sup>119</sup> CO<sub>2</sub> on graphite;<sup>120–123</sup> CO/CO<sub>2</sub> mixture on graphite;<sup>124</sup> CO<sub>2</sub> and steam on activated carbon,<sup>125</sup> graphite,<sup>126,127</sup> and charcoal;<sup>128</sup> NO on graphite;<sup>129</sup> NO, NO<sub>2</sub>, N<sub>2</sub>O, and O<sub>2</sub> on graphite;<sup>130</sup> N<sub>2</sub>O on graphite;<sup>131</sup> and NO, O<sub>2</sub>, H<sub>2</sub>O, and CO<sub>2</sub> on graphite<sup>132</sup> at elevated temperatures.

#### 1.4.2.1. Plasma

Plasma treatment has gained more attention in recent years due to its ability to introduce nanoto micro-meter size pores in graphite and graphene. Several studies investigated the etching behavior of O<sub>2</sub>-plasma on highly oriented pyrolytic graphite (HOPG)<sup>133–137</sup> and graphene<sup>63,138,139</sup> to produce a high density of defects in their lattice or to remove the unwanted graphene during the lithography procedure. Paredes et al.<sup>137</sup> achieved a high density of nanometer size defects in HOPG ranging from  $\sim 5 \times 10^2$  to  $3 \times 10^5 \,\mu\text{m}^{-2}$ . The main reactions in O<sub>2</sub> plasma are a) ionization of an oxygen molecule with an energetic electron (Equation 1.10), b) formation of a negative ion (Equation 1.11), and c) recombination reaction (Equation 1.12).<sup>140</sup>

$$O_2 + e \rightarrow O_2^+ + 2e$$
 Equation 1.10

$$O_2 + e \rightarrow O^- + O$$
 Equation 1.11

$$O_2^+ + O^- \rightarrow O_2 + O$$
 Equation 1.12

Surwade et al. fabricated ~ 1-nm-sized nanopores in a 5- $\mu$ m-sized SLG sheet by optimizing the O<sub>2</sub> plasma condition.<sup>136</sup> They investigated the performance of these membranes in water desalination. Bai et al. fabricated 5 – 15 nm pores in graphene nanomesh by exposing the graphene templated by a block copolymer to O<sub>2</sub> plasma.<sup>141</sup> Later, they optimized their method leading to graphene with ~ 0.63 nm pores used for water purification.<sup>142</sup> Jang et al. decoupled the nucleation and pore expansion by utilizing Ga<sup>+</sup> to nucleate the defects and further expand

them by  $O_2$  plasma leading to 0 - 1 nm PSD.<sup>143</sup> They used these nanopores to investigate the transport of water and solute in nanoporous graphene. Recently, He et al. created nanopores in SLG by  $O_2$  plasma and utilizing the synergetic behavior of these pores with a polymer with intrinsic microporosity (PIM) reported attractive membranes for carbon capture.<sup>50</sup>

In radio frequency (RF) plasma, the high-energy  $O_2^+$  ions physically sputter carbon atoms away from the graphene surface (physical etching). In addition, the  $O_2^+$  ions may dissociate into reactive neutral oxygen atoms (or an oxygen atom and a cation) via collisional energy transfer.<sup>133,138,144</sup> These reactive oxygen atoms adsorb onto the graphene surface and react with the C atoms in the graphene lattice, producing CO and CO<sub>2</sub> gases.<sup>133</sup> Activated sites, i.e., lessordered carbon atoms and the graphene edge, have higher reactivity and oxidize significantly faster than pristine graphene lattice when exposed to atomic oxygen.<sup>145</sup>

Xie et al.<sup>146</sup> and Yang et al.<sup>147</sup> utilized H<sub>2</sub>-plasma to etch graphene, and both reported anisotropic etching behavior with a constant etching rate under the same etching condition. Xie et al. performed H<sub>2</sub>-plasma at elevated temperatures, e.g., 300 °C, to selectively etch the reactive graphene edges without introducing new defects in the graphene basal plane to narrow down the nanoribbons prepared by the standard lithography technique.<sup>146</sup> Hydrogen radicals attack the C atoms at both edges and surface defects via C-H covalent bond formation and C-C bond breakage, producing CH<sub>4</sub> as the main product. Examples of graphene etching by plasma are shown in Figure 1-10.



Figure 1-10. (a) TEM images of the graphene nanomeshes (top; scale bars measure 100 nm) with their corresponding PSD (bottom).<sup>141</sup> Reprinted with permission; copyright 2010, Springer Nature BV. (b)

Schematic of the plasma treatment of the suspended SLG on a 5 µm hole, and (c) aberration-corrected scanning transmission electron microscopy (AC-STEM) image of the corresponding graphene exposed to O<sub>2</sub> plasma for 1.5 s.<sup>136</sup> Reprinted with permission; copyright 2015, Springer Nature BV. (d) AC-HRTEM image of SLG exposed to O<sub>2</sub> plasma for 3 s.<sup>50</sup> Reprinted with permission; copyright 2020, John Wiley and Sons. (e) Atomic force microscopy (AFM) images of the graphene nano ribbons before and after exposure to H<sub>2</sub> plasma.<sup>146</sup> Reprinted with permission; copyright 2010, American Chemical Society.

#### 1.4.2.2. Oxygen

Reaction of  $O_2$  with carbon materials at elevated temperatures has been extensively studied by investigating its interaction with graphite.<sup>105–109,130,132</sup> In its simplest form, the reaction of  $O_2$  with carbon is as follows:<sup>148</sup>

$$C + O_2 \rightarrow CO_2$$
 Equation 1.13

$$C + \frac{1}{2}O_2 \rightarrow CO$$
 Equation 1.14

Thermal oxidation by  $O_2$  is quite uniform and scalable due to its gaseous nature, expanding its application to pore creation and expansion in graphene.<sup>149–151</sup> Etching initiates from the existing defects and pore edges below the nucleation temperature threshold due to bond disorders and functional groups at the edges of the graphene (leading to their higher chemical reactivity than the perfectly bonded sp<sup>2</sup> carbon atoms in the basal plane).<sup>152,153</sup> Linear oxidative behavior, under the threshold temperature of pore nucleation, has been reported<sup>106,126,154</sup>. The threshold temperature, above which oxidative carbon atom removal from the basal plane is significant, is reported to be ~ 600<sup>106</sup> and 700<sup>126</sup> for C-O<sub>2</sub> reaction. However, O<sub>2</sub> is capable of reacting with graphene basal plane at 200 – 250 °C, albeit at a much slower rate.<sup>155</sup> The activation energy of pore creation and expansion by O<sub>2</sub> are reported as 2.1 and 1.32 eV, respectively.<sup>130</sup> The difference in the energy barrier of nucleation and expansion is much lower than that of physical etching methods.

Liu et al. exposed multilayer graphene to  $O_2$  at 200 – 600 °C and reported a strong dependence of  $O_2$  etching kinetics with the number of graphene layers (Figure 1-11a).<sup>156</sup> They created 20 nm-sized pores by exposing SLG to 350 Torr of  $O_2$  at 450 °C for 2 h. Yamada et al. fabricated sub-nanometer (10 – 13 missing C atoms) pores by exposing SLG to  $O_2$  at 220 – 260 °C for 5 h (Figure 1-11b).<sup>155</sup> They proposed ether, carbonyl, and lactone groups based on the resemblance of AC-HRTEM images and simulation. Agrawal et al. demonstrated the  $O_2$ etching at 1077 °C CVD temperature creating sub-nanometer size pores in SLG by adjusting the amount of air leak to the system (Figure 1-11c).<sup>18</sup> Raising the amount of  $O_2$  from 130 ppm (exposed for 6 – 8 h) to 7 % (exposed for 1 min) increased the defect density from 47 ± 37  $\mu$ m<sup>-2</sup> to 325 ± 173  $\mu$ m<sup>-2</sup>. Recently, Schlichting and Poulikakos utilized O<sub>2</sub> at 250 – 350 °C to further expand the pores generated by ion beam in suspended bilayer graphene, decoupling the pore nucleation and expansion (Figure 1-11d).<sup>157</sup> They reported H<sub>2</sub>/CH<sub>4</sub> selectivity of up to 9.3 at 0 bar transmembrane pressure difference. However, the selectivity dropped close to their Knudsen selectivity by pressurizing the membrane to 1 bar, indicating the existence of huge pores/cracks in the membrane.



Figure 1-11. (a) AFM image of nanopores created in graphene by exposure to O<sub>2</sub> at 500 °C for 2 h.<sup>156</sup> Reprinted with permission; copyright 2008, American Chemical Society. (b) HRTEM images of SLG oxidized in O<sub>2</sub> for 5 h at 240 (left) and 260 °C (right).<sup>155</sup> Reprinted with permission; copyright 2014, American Chemical Society. (c) Scanning tunneling microscopy (STM) images of the defects in assynthesized SLG with O<sub>2</sub> leak to the system.<sup>18</sup> Reprinted with permission; copyright 2017, American Chemical Society. (d) Schematic of the bilayer graphene membrane fabrication process utilizing ion beam irradiation and O<sub>2</sub> etching.<sup>157</sup> Reprinted with permission; copyright 2020, American Chemical Society.

#### 1.4.2.3. Ozone

 $O_3$  has been widely used as an oxidant to control pollution in contaminated aqueous solutions.<sup>158–160</sup> Moreover,  $O_3$  is a promising alternative to  $O_2$  plasma when a sample is

sensitive and cannot be heated to higher than room temperature.  $O_3$  generation was developed by Siemens in 1875 by a corona discharge in a tube.<sup>161</sup> An altering voltage is applied between the two electrodes leading to the formation of O<sup>•</sup> and ultimately  $O_3$ . The reactions can be described as below (M is the substrate):

$$e^{-1} + O_2 \rightarrow 2O^{-} + e^{-1}$$
 Equation 1.15

$$O^{\cdot} + O_2 + M \rightarrow O_3 + M^*$$
 Equation 1.16

Lee et al. investigated the reaction of graphene with  $O_3$  by density functional theory (DFT) and reported energy barriers of 0.25 and 0.72 eV for physisorption and chemisorption of  $O_3$  on graphene, respectively.<sup>162</sup> The oxygen functional groups on graphene lattice (due to  $O_3$  exposure) prefer to form clusters to minimize their energy.<sup>163,164</sup> DFT studies suggested the following steps in defect generation in SLG by  $O_3$ :<sup>164–166</sup> i) epoxy group formation, ii) formation of clusters by these epoxy groups, iii) transformation of epoxy groups to ether groups, iv) C-C bond breakage enabled by lattice strain resulting in semiquinone groups, and v) transformation of semiquinone groups to lactone groups releasing CO and CO<sub>2</sub>. Huang et al. observed both functional group clusters and vacancy defects after exposing SLG to O<sub>3</sub> and suggested that the cluster formation is an intermediatory step in vacancy defect formation.<sup>163</sup>

Koenig et al. demonstrated the first proof-of-principle of gas-sieving by nanopores in SLG created by chemical etching.<sup>24</sup> They created sub-nanometer pores in 5- $\mu$ m suspended mechanically exfoliated single- and bi-layer graphene sheets by UV/O<sub>3</sub> exposure and investigated their gas separation performance, reporting H<sub>2</sub>/CH<sub>4</sub> selectivity exceeding 1000. Kumar et al. fabricated 5- $\mu$ m suspended CVD-grown SLG membranes with intrinsic defects and exposed them to O<sub>3</sub> during the measurement.<sup>18</sup> They observed an increase in permeance and estimated a mean pore size of ~ 1 – 100 nm based on the observed Knudsen gas pair selectivity. Huang et al. reported 1 mm<sup>2</sup> CVD-grown SLG membranes hosting intrinsic defects and reported a 3-fold increase in permeance by in-situ O<sub>3</sub> treatment at 80 – 100 °C.<sup>16</sup> Interestingly, the permeance was decreased and the H<sub>2</sub>/CH<sub>4</sub> selectivity was raised by 50 % when samples were treated at room temperature, suggesting that O<sub>3</sub> can etch the graphene film at elevated temperatures and functionalize the defect edges near the room temperature.

Zhao et al. utilized the synergetic effect of  $O_2$  plasma and  $O_3$  treatment to fabricate CVD-grown SLG membranes reaching high H<sub>2</sub> permeance of ~ 2600 GPU along with attractive H<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> selectivities of 30 and 207, respectively.<sup>37</sup> They demonstrated a similar rate of pore

expansion and pore nucleation by O<sub>3</sub> resulting in a narrow PSD, contrary to the well-known trade-off between the pore-density and the percentage of the nonselective pores in O<sub>2</sub> plasma exposure. Later, Hsu et al. further modified the O<sub>3</sub> treatment technique by developing a multipulsed millisecond O<sub>3</sub> gasification reactor.<sup>29</sup> They investigated the effect of O<sub>3</sub> partial pressure on nucleation and etching rates and concluded O<sub>3</sub> treatment at higher pressures increases the pore density while maintaining the narrow PSD. Membranes with CO<sub>2</sub> permeance of 4400 ± 2070 GPU and CO<sub>2</sub>/N<sub>2</sub> selectivity of  $33.4 \pm 7.9$  were reported. These membranes are quite attractive for post-combustion carbon capture applications. Recently, Huang et al. optimized their method by in-situ exposing the CVD-grown SLG membranes to O<sub>3</sub> at 200 °C for 1-2 h to slowly expand the nanopores in graphene leading to membranes with above 10000 GPU CO<sub>2</sub> permeance and CO<sub>2</sub>/N<sub>2</sub> selectivity of over 20.<sup>163</sup> Examples of graphene etching by O3 are shown in Figure 1-12.



Figure 1-12. (a) AFM image of the suspended graphene etched by UV/O<sub>3</sub> (nanopores are colored red to enhance the visualization).<sup>24</sup> Reprinted with permission; copyright 2012; Springer Nature BV. (b) Top: schematic of the pore nucleation by O<sub>2</sub> plasma and expansion by O<sub>3</sub> process in SLG; bottom: schematic of the membrane fabrication steps including O<sub>2</sub> plasma and O<sub>3</sub> treatment steps.<sup>37</sup> Reprinted with permission; copyright 2019, American Association for the Advancement of Science. (c) Left: schematic of the millisecond gasification reactor setup; middle: O<sub>3</sub> dosing profile; and right: Raman spectroscopy of the treated SLG films at various O<sub>3</sub> dosages.<sup>163</sup> Reprinted with permission; copyright 2021, American Association for the Advancement of Science.

#### 1.4.2.4. Carbon dioxide

Most of the early studies were focused on the interaction of oxidizing etchants such as O<sub>2</sub> and steam with graphite.<sup>109,114,167</sup> However, these etchants are highly reactive and difficult to

control. Most importantly, they are less suitable for decoupling the defect nucleation and expansion as they are limited by their defect nucleation temperature threshold (~ 220 °C). Above this temperature, carbon removal from the graphite basal plane occurs along with the expansion of the existing defects and edges, rendering these etchants ineffective where precise control of the defect expansion is required.<sup>106,115</sup> As an alternative,  $CO_2$  is a fitting mild etchant as it can expand the existing defects without nucleating new vacancies due to its significant energy barrier (ca. 5 eV) for single-vacancy defect formation.<sup>120</sup> Understanding the etchantgraphene reaction and its kinetics is the key to tune the etching condition to achieve the desired outcome, such as varying the band gap in graphene nanoribbons (GNR) by controlling the GNR's width;<sup>168</sup> realizing the unique properties of graphene nanomeshes,<sup>141</sup> quantum dots,<sup>169</sup> and nano disks;<sup>170</sup> and nucleating and expanding nanopores in graphene for membrane fabrication.<sup>136,163,171,172</sup>

In principle, carbon gasification by CO<sub>2</sub> is the boudouard reaction (Equation 1.17) and has been widely studied since the 1970s.<sup>121</sup> Ergun was one of the first to focus on the kinetics of the reaction between CO<sub>2</sub> and carbon.<sup>122</sup> He investigated the etching rate of graphite and activated carbon at atmospheric pressure and temperatures ranging 700 – 1400 °C and concluded that i) the reaction rate is proportional to the concentration of CO<sub>2</sub> occupied sites, ii) CO decreases the reaction rate by reducing the number of CO<sub>2</sub>-occupied sites, and iii) release of CO from adsorbed phase to gas phase is the rate-determining step (RDS). The last claim has been debated, and other studies have indicated the possibility of a different RDS. Several studies by Yang and coworkers revealed the kinetics of the graphite-CO<sub>2</sub> reaction.<sup>127,147,173</sup> They showed that the reaction rate follows the Langmuir-Hinshelwood model, and etching is highly anisotropic along the c-axis of graphite. Nevertheless, despite all studies on carbon gasification by CO<sub>2</sub>, the RDS is still inconclusive. Biederman and co-workers suggested the rate of CO<sub>2</sub> chemisorption as the RDS as release of the gaseous CO is believed to be much faster.<sup>120</sup>

$$C + CO_2 \leftrightarrow 2CO$$
 Equation 1.17

Most of the published data are based on the reaction of  $CO_2$  with graphite,<sup>122,126,127,132,148</sup> and to the best of our knowledge, the only experimental investigation of  $CO_2$ -graphene interaction was done by Yang et al. recently.<sup>174</sup> They exposed SLG films to  $CO_2$  at various elevated temperatures and flowrates and reported that the  $CO_2$  etching rate depends on both of these parameters. Confirming the result of the previous studies on graphite, they demonstrated that  $CO_2$  does not nucleate new defects in the graphene basal plane up to the probed temperature of 1000 °C. However, they could not control the reaction effectively, leading to areas of fullyetched graphene, areas of graphene with etched trenches, and faceted pores. As a result, the kinetics of the  $CO_2$ -graphene reaction could not be studied and remained unexplored.

Several DFT studies were published recently to elucidate the mechanism and kinetics of the CO<sub>2</sub>-graphene reaction. Cabrera-Safelix investigated the interaction of CO<sub>2</sub> with a defective SLG film and proposed a three-step mechanism: a) physisorption of CO<sub>2</sub> parallel to the graphene surface and on top of the defective site, b) chemisorption of CO<sub>2</sub> on the graphene's defective site by lactone group formation, and c) desorption of gaseous CO.<sup>175</sup> Release of the second CO molecule leads to the successful etching.<sup>176–178</sup> To date, other researchers have agreed with Cabrera-Safelix's analysis aside from the nature of the oxygen-containing groups at transition and final states and the value of the energy barrier for each step. Generally, the activation energy of the physisorption step (ca. 0.2 eV) is believed to be an order of magnitude lower than that of other steps. <sup>179</sup> Typically, the chemisorption and the first CO release steps are combined in studies and called the dissociative chemisorption step. Selection of different oxygen-containing groups (e.g., lactone, semiquinone, ether, carbonyl, epoxy, etc.) as the intermediatory species at the chemisorption step led to a range of calculated activation energy values (1.7 - 3.3 eV).<sup>180,181</sup> Nature of the defective site (i.e., single vacancy, double vacancy, and zigzag and armchair edges) and the underlying assumptions of various computational methods led to the observed variance in the computed energy barriers and stable species. Desorption of the second CO molecule requires an activation energy of 2.3-3.6 eV.<sup>178,182,183</sup> Similarly, the structure of graphene computed at the preceding steps and the selected computational method generated the observed variance. Among the recent DFT studies, only Zhao et al. investigated the entire process of graphene gasification by CO<sub>2</sub> and reported the overall activation energy of 2.72 eV and 3.11 eV for gasification of zigzag and armchair edges, respectively.<sup>184</sup> Examples of the reaction of CO<sub>2</sub> with carbon are shown in Figure 1-13.



Figure 1-13. (a) TEM image of the gold-decorated etched pores on graphite by CO<sub>2</sub>.<sup>127</sup> Reprinted with permission; copyright 1985, Elsevier Science & Technology Journals. (b) Top: optical images of the oxidized Cu foil hosting etched SLG at 1000 °C with increasing CO<sub>2</sub> flow rate, and bottom: their corresponding SEM images.<sup>174</sup> Reprinted with permission; copyright 2017, John Wiley and Sons. (c) Reaction mechanism of CO<sub>2</sub> with the zigzag edge of graphene, leading to the gasification of edge C atoms and release of CO (the numbers written under each structure shows the potential energy of the system at that state; unit: kJ/mol).<sup>184</sup> Reprinted with permission; copyright 2018, Elsevier Science & Technology Journals.

It is quite challenging to etch graphene nanopores to obtain extremely high pore-density (~ $10^{13}$  cm<sup>-2</sup>) while maintaining a narrow PSD that allows molecular differentiation. Recently, Dutta et al. simulated a unique CVD approach in the presence of CO<sub>2</sub> as an etchant to generate high density (3 ×  $10^{13}$  cm<sup>2</sup>) of gas-selective pores.<sup>185</sup> Briefly, the concept dealt with a competitive etching (by CO<sub>2</sub>) and growth (by CH<sub>4</sub>) to arrive at a narrow PSD. A high density of elongated pores was predicted when the crystallization was modeled using the kinetic Monte Carlo simulations.

# **1.5.** Current bottlenecks of graphene membrane fabrication for gas separation

There are three major bottlenecks in realizing the true potential of SLG membranes for gas separation in real-world applications: a) synthesis of high-quality SLG from commercially available cost-effective Cu foil, b) tuning the pore density and PSD in SLG to achieve high permeance and selectivity for a desired gas pair separation, and c) developing a crack-free

transfer method to support the SLG film during the transfer from Cu foil to the membrane module and during the operation.

Synthesis of high-quality SLG film is the first step in fabricating membranes with high-reaching selectivities, i.e., operating in the gas-sieving regime.<sup>171</sup> The Cu substrate and the CVD environment influence the PSD and density of the intrinsic defects of the graphene, subsequently affecting the quality of the graphene. Generally, gas-sieving SLG membranes are synthesized on expensive high-purity Cu foil, hindering their application beyond fundamental research due to economic factors.<sup>16,25,37,186,187</sup>

A controllable graphene PSD tuning at high temperatures, i.e., CVD and near CVD temperatures, has not yet been realized. This enables the incorporation of a high-density pores with narrow PSD inside the very CVD reactor used for graphene synthesis, eliminating the handling- and transfer-related complications and contamination from exposure to the lab environment.<sup>185</sup> In addition, developing a clean process to precisely etch the graphene edges at near CVD temperatures without nucleating new defects brings about a unique method to optimize the width of GNRs for bad-gap optimization<sup>168,170</sup> and to shape graphene nanomeshes,<sup>141</sup> quantum dots,<sup>169</sup> and nano disks<sup>170</sup> with a high degree of control.

Finally, developing a robust mechanical reinforcement layer for graphene transfer from the Cu foil to the membrane module and support provision during membrane operation under high transmembrane pressure difference is needed to fabricate the market-ready large-scale graphene membranes. Figure 1-14 provides an overview of the recent advancements in ways to mechanically support the SLG film during membrane fabrication. More effort is needed to achieve the meter-scale graphene membranes suited for industrial applications. The first two issues are addressed in this dissertation.



Figure 1-14. (a) The first proof-of-principle graphene membrane made by suspending a mechanically exfoliated graphene flake on a 5  $\mu$ m hole in silicon oxide.<sup>24</sup> Reprinted with permission; copyright 2012, Springer Nature. (b) the First report of gas permeation through CVD-grown SLG suspended on a 5  $\mu$ m hole in a tungsten (W) foil.<sup>18</sup> Poly(methyl methacrylate) (PMMA) was used to transfer the SLG film from Cu foil to the W foil. Reprinted with permission; copyright 2017, American Chemical Society. (c) Crack-free transfer of 1 mm<sup>2</sup> CVD-grown SLG from Cu foil to a holey W foil (2500 × 5- $\mu$ m-sized holes) using nanoporous carbon (NPC) layer as the support.<sup>16</sup> Reprinted with permission; copyright 2018, Springer Nature BV. (d) Centimeter-scale transfer of SLG film using polymer (polyether sulfone; PES) casting and phase inversion reaction of PES in water to fabricate membranes for ion and dye separation.<sup>25</sup> Reprinted with permission; copyright 2018, John Wiley & Sons - Books. (e) Centimeter-scale transfer of SLG film using NPC/multi-walled carbon nanotube (MWNT)

composite layer for mechanical reinforcement for gas separation.<sup>188</sup> Reprinted with permission; copyright 2021<sup>,</sup> Elsevier Science & Technology Journals.

#### **1.6.** Thesis outline

This dissertation aims at addressing the current bottlenecks of SLG membrane fabrication for gas separation applications. First, an overview of graphene and its application in gas separation along with the current PSD tuning methods is provided. Then, a simple thermal annealing method is introduced to optimize the morphological and crystallographic properties of the catalytic Cu foil leading to the synthesis of high-quality SLG film on cost-effective commercial Cu foils. Next, a controlled etching of SLG by CO<sub>2</sub> is demonstrated, and its reaction kinetics is reported for the first time. Afterward, a competitive etching and growth method for the synthesis of N-SLG in CVD reactor for gas-sieving is introduced. Finally, a summary of the current work and the future direction of the SLG membrane fabrication for gas separation are provided.

Chapter 1 provides an overview of the challenges and opportunities in graphene membrane development and identifies the current bottlenecks of competitive large-scale SLG membrane fabrication for gas separation. In addition, fundamentals and recent advancements in graphene membrane fabrication are discussed, addressing subjects including graphene crystallization, graphene etching methods, and gas separation membrane theories.

Chapter 2 introduces a thermal-annealing-based crystallographic and morphological optimization protocol, applied to two different low-cost Cu foils, successfully transforming them from mixed-orientation to Cu(111) substrates while lowering their overall surface roughness, resulting in the synthesis of higher-quality SLG membranes capable of hydrogensieving. This slow annealing process conveniently fits into the CVD synthesis protocol by replacing the typical annealing step under H<sub>2</sub> atmosphere. This is the first step towards economical scale-up of the SLG membranes by decreasing the Cu foil cost by ~ 80-fold. In addition, no significant correlation between the Cu foil purity and its corresponding membrane performance was found, suggesting its potential application in treating other low purity metal foils.

Chapter 3 describes a controlled and uniform etching of SLG by CO<sub>2</sub> oxidative etching at elevated (near CVD and CVD) temperatures and investigates the kinetics of the graphene-CO<sub>2</sub>

reaction, extracting the experimental value of the activation energy of pore expansion for the first time. The temperature dependence of the etching rate is demonstrated and utilized to control the etching rate down to sub-nanometer per minute. Moreover, the etching behavior of  $CO_2$  at various initial pore sizes is probed, revealing an order of magnitude slower reaction kinetics at pores smaller than ~ 2 nm. Finally, the effect of  $CO_2$  treatment on the remaining SLG film and the Cu substrate are investigated, disclosing that  $CO_2$  does not nucleate new defects in pristine graphene basal plane and does not oxidize the exposed Cu substrate.

Chapter 4 investigates the interplay of CH<sub>4</sub> (growth precursor) and CO<sub>2</sub> (etchant) during CVD synthesis of SLG and demonstrates its application in the fabrication of gas-sieving membranes. This elucidates the effects of temperature and CH<sub>4</sub>:CO<sub>2</sub> ratio on the CVD chemistry and provides insight into the role of CO<sub>2</sub> in SLG crystallization process, utilizing various characterization techniques such as AC-HRTEM, SEM, gas permeation, and combination of carbon isotope labeling and Raman spectroscopy. Optimization of the temperature and CH<sub>4</sub>:CO<sub>2</sub> ratio led to high permeance membranes capable of H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> separation. In addition, the net growth rate was ~ 200-fold lower for nanometer-sized pores compared to that of micrometer-sized pores, exhibiting similar behavior to CO<sub>2</sub> etching kinetics described in chapter 3.

Chapter 5 summarizes the major achievements in optimizing the Cu substrate and developing a unique graphene etching and growth technique to eliminate the longstanding trade-off between the pore density and the desired narrow PSD in SLG membrane fabrication. Moreover, the potential future direction of the SLG membranes is discussed.

# 2. Chapter 2. Hydrogen-sieving single-layer graphene membranes obtained by crystallographic and morphological optimization of catalytic copper foil

Adapted with permission from <u>Mojtaba Rezaei</u>, Shaoxian Li, Shiqi Huang & Kumar Varoon Agrawal\*, Hydrogen-sieving single-layer graphene membranes obtained by crystallographic and morphological optimization of catalytic copper foil, Journal of Membrane Science, 612, 118406 (2020), DOI: 10.1016/j.memsci.2020.118406. Copyright © 2020, Elsevier B.V.

#### Abstract

Gas separation membranes based on single-layer graphene are highly attractive because the size of graphene nanopores can be tuned to separate gases by the size-sieving mechanism. A prerequisite for this is synthesis of high-quality polycrystalline SLG film by CVD is crucial. The quality of graphene in the context of membranes is reflected by the size and the density of the intrinsic vacancy defects, and is affected by the catalytic metal substrate and the CVD environment. Generally, expensive high-purity Cu foil is used to obtain gas-sieving performance from SLG. For the eventual scale-up of graphene membranes, it is highly attractive to use low-cost Cu foils; however, as we show here, these Cu foils are rough and graphene membranes derived from these foils do not yield gas-sieving performance. Herein, we conduct a systematic high-temperature annealing study on two separate, commercial, lowcost Cu foils leading to their transformation to Cu(111). The annealing process smoothened the Cu surface, decreasing the root mean square (RMS) surface roughness from over 200 nm to close to 100 nm. The RMS roughness on the individual Cu step, measured using the scanning tunneling microscopy (STM), was only 0.23 nm. The smooth, oriented Cu grains yielded SLG with a significantly lower defect density with  $I_D/I_G$  ratio decreasing from 0.18  $\pm$  0.02 to 0.04  $\pm$ 0.01. Finally, SLG films, synthesized on the annealed low-purity Cu foil, yielded H<sub>2</sub>-selective membranes with H<sub>2</sub> permeance reaching 1000 GPU in combination with attractive H<sub>2</sub>/CH<sub>4</sub> and  $H_2/C_3H_8$  selectivities of 13 and 26, respectively.

#### 2.1. Introduction

SLG hosting subnanometer-sized nanopores have shown attractive gas separation performances by molecular sieving where separation takes places based on differences in size of the molecule.<sup>8,24,171,189,190</sup> The ultrashort diffusion path of gas molecules across the sieving nanopore, involves only one rate-limiting transition state when the molecule arrives at the center of the nanopore.<sup>48</sup> With a narrow PSD in graphene, this manifests in a selective gas flux.<sup>22,46</sup> The development of graphene-based membranes is gaining momentum from the fact that the size of graphene nanopores can be tuned, increased or decreased, in a controlled fashion by various chemical or physical etching techniques and post-synthetic functionalization.<sup>27</sup> For example, recently, we reported an angstrom resolution in differentiating gas molecules.<sup>37</sup> Further advances in pore-size engineering, for example, by developing a self-limiting etching condition, is likely to allow sub-angstrom resolution in molecular differentiation.

For membrane-based separation, graphene is almost always synthesized by the CVD method,<sup>61,79</sup> mainly because the CVD synthesis can be carried out rapidly on the m<sup>2</sup>-length-scale, and is conducive to scale-up. Synthesis of graphene in a roll-to-roll basis by CVD has been already demonstrated.<sup>14,191</sup> For the synthesis of SLG, Cu foil is the preferred catalytic substrate because Cu has a low carbon solubility (<0.001 atomic%) and graphene synthesis proceeds predominantly by nucleation and growth on the Cu surface, which is referred to as the surface-diffusion mechanism.<sup>88</sup> Typical grain growth rate of 1-10  $\mu$ m/min have been reported.<sup>82</sup> Once a polycrystalline film is formed, the growth is somewhat self-limiting with respect to the exposure time of the carbon precursor. In contrast, on metals with high carbon solubility (e.g., Ni), a carbon reservoir is formed at high temperature and a multilayer graphene film is precipitated during the cooling step.<sup>79</sup>

Typically, a small population of intrinsic vacancy-defects is incorporated in the graphene lattice during CVD. These defects have origin in an incomplete intergrowth of misaligned grains<sup>20,21</sup> as well as the etching of graphene lattice in the presence of oxygen leak in the CVD reactor.<sup>18</sup> Nevertheless, the vacancy-defects that have missing 10–16 carbon atoms can be attractive for gas separation by the size-sieving mechanism<sup>22,46</sup>. For example, Huang et al. reported that assynthesized graphene with a low-density (0.025%) of intrinsic defects can separate H<sub>2</sub> from CH<sub>4</sub> with selectivity up to 25.<sup>16</sup> Kidambi et al. showed that by reducing the CVD temperature to 900 °C, the density of intrinsic subnanometer-sized vacancy-defects could be increased.<sup>25</sup>
Yuan et al. investigated gas transport from intrinsic defects in as-synthesized graphene on electropolished Cu foil and reported the evidence of molecular sieving.<sup>187</sup> Khan et al. reported that H<sub>2</sub>-sieving vacancy defects can be incorporated in graphene at lower CVD temperature when benzene is chosen as the carbon precursor.<sup>186</sup> Most of these studies used expensive high-purity Cu foils with prohibitive cost for scaling-up graphene membranes. In fact, as we show here, as-received low-cost, low-purity polycrystalline Cu foils do not lead to high-quality graphene membranes attributing to high surface roughness and mixed crystallographic orientation of the as-received foils. Therefore, optimization of the low-cost Cu foils is crucial to realize a scalable production of the gas-sieving graphene membranes.

Herein, we demonstrate a facile crystallographic and morphological optimization protocol, applied to two different low-cost Cu foils, which successfully transforms them into smooth Cu(111) substrates, resulting in the synthesis of higher-quality single-layer graphene which ultimately led to hydrogen-sieving membranes. Briefly, a slow and controlled annealing close to the melting point of the Cu was carried out which annealed the Cu grains orienting them along the (111) out-of-plane direction. The high-temperature annealing also smoothened the Cu surface, with RMS roughness over a large area down to ca. 100 nm, and on a single Cu step as low as 0.23 nm. This treatment greatly improved the gas separation performance from the intrinsic defects of graphene membranes. For example, before the optimization of Cu foil, gas selectivities were close to those expected from the Knudsen transport, indicating the domination of large non-sieving vacancy-defects in graphene. After the treatment of the Cu foil, attractive H<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> selectivities of 13 and 26, respectively, were achieved along with a H<sub>2</sub> permeance of 1000 GPU (1 GPU =  $3.35 \times 10^{-10}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>). We attribute this to (i) smoothened surface of Cu foil post-annealing, and (ii) crystallographic re-orientation to Cu(111). This is because the smoothened Cu surface facilitates fabrication of high-quality membranes by perhaps avoiding nanoscale cracks during the graphene transfer step. The Cu(111) surface reduces the grain-boundary defects attributing to the fact that there is only a small mismatch (3-4 %) between the lattice constants of the (111) facet of Cu and that of graphene.192,193

### 2.2. Methods

### 2.2.1. Annealing and smoothening of commercial Cu foils

Heat treatment of the commercial Cu foils was carried out in a three-zone high-temperature furnace equipped with a high-purity alumina tube (99.8% purity, diameter: 5 cm, length: 1.2 m, MTI Corp.) housed inside a fused quartz tube (diameter: 6 cm, length: 1.4 m, MTI Corp.) as shown in Figure 2-1. The quartz tube was used for making leak-tight connections with the gas lines and the vacuum source, whereas the alumina tube was used to prevent the silica contamination, originating from quartz tube, onto graphene. In each run, a piece of Cu foil (4  $cm \times 20$  cm) was placed on a high-purity alumina boat (99.8% purity, Almath Crucibles Ltd) and was heated to 1000 °C. The organic contaminants on the foil were removed by treating the sample at 1000 °C and 800 torr in a CO<sub>2</sub> atmosphere for 30 minutes. Then, the system was evacuated and was filled with  $H_2/Ar$  (1:10) to the pressure of 1 bar. After this, annealing was performed by two methods. In the first method, referred to as high-temperature annealing or A<sub>H</sub>, the foil was heated at 1077 °C for 1 hour. After this, the temperature was reduced at a rate of 1 °C/min to 1000 °C. In the second method, referred to as low-temperature annealing or AL, the foil was just annealed at 1000 °C for 1 hour. Post annealing, the foil was either cooled down to room temperature for further characterization or was immediately used to synthesize graphene. Optionally, the foils were also polished to further smoothen their surface. Polishing was carried out using a mechanical polisher (UNIPOL-1210, MTI Corp.) for 10 minutes using a diamond polishing paste (particle size of ca. 0.25 µm, MTI Corp.). After polishing, foils were rinsed by deionized (DI) water and, subsequently, were cleaned by sonication treatment in isopropyl alcohol (4 times for 10 minutes).



Figure 2-1. Photo of the CVD setup for contamination-free graphene growth using an alumina tube inside the quartz tube.

### 2.2.2. Graphene synthesis

SLG was synthesized by the LPCVD<sup>16</sup> process on three separate kinds of 25-µm-thick Cu foils (Figure 2-2a). Two kinds of foil from Alfa Aesar, with purities of 99.8% and 99.999% were used. These are referred to as  $\alpha$  and  $\alpha_{pure}$ , respectively. Another foil with a purity of 99.98% was sourced from Sigma Aldrich and is referred to as  $\sigma$ . Briefly, for LPCVD, a piece of asreceived or annealed Cu foil (2 x 5 cm<sup>2</sup>) was placed inside the reactor and was treated at 1000 °C and 800 Torr in CO<sub>2</sub> atmosphere for 30 minutes to remove the organic contaminations. Then, the reactor was evacuated to 1 mTorr, and subsequently, 8 sccm of H<sub>2</sub> was introduced for 30 minutes, increasing the pressure to 80 mTorr, to anneal the Cu surface and to reduce the surface oxides. Finally, 24 sccm of CH<sub>4</sub> was added for 30 minutes to synthesize a polycrystalline graphene film. In the end, the CH<sub>4</sub> flow was cut off while maintaining the H<sub>2</sub> flow, and the foil was pulled out of the heating zone to stop the crystallization.



Figure 2-2. (a) Schematic of the setup for annealing Cu and LPCVD of graphene. (b) Temperature and pressure profiles as a function of time for the high-temperature annealing of Cu, and subsequent synthesis of graphene. The colored sections refer to the following: I) removal of organic contaminations by CO<sub>2</sub> at 1000 °C, II) heating foil at 1077 °C, III) controlled cooling at 1 °C/min, IV) LPCVD of graphene, and V) rapid cooling to stop crystallization. (c)  $I_D/I_G$  ratio in the Raman spectra of graphene synthesized on as-received as well as thermally-annealed and polished Cu foils. The error bar represents the standard deviation in the  $I_D/I_G$  ratio obtained by mapping (16 spectra or more). SEM images of the graphene grown on commercial Cu inside a quartz reactor (d), and inside the quartz reactor lined with the alumina tube (e). The scale-bar is 2 µm. f) EDX analysis of the particles in (d).

### 2.2.3. Membrane fabrication

The graphene membranes were fabricated using a nanoporous carbon (NPC)-assisted method reported in the previous study (Figure 2-3).<sup>16</sup> Briefly, a solution of 0.1 g block copolymer (poly (styrene-b-4-vinyl pyridine) and 0.2 g turanose in dimethylformamide (DMF) was aged in an autoclave at 180 °C for 3 hours to form a precursor solution. Then, the as-synthesized graphene on Cu was spin-coated (2 min at 2000 rpm) with the precursor solution. The film was pyrolyzed in Ar/H<sub>2</sub> atmosphere at 500 °C for 1 hour, yielding the NPC film. Subsequently, the underlying Cu foil was etched using 0.2 M sodium persulfate solution, and the floating graphene/NPC film was rinsed with DI water several times before transferring it onto a porous tungsten support, fabricated by drilling 2500 5-µm-sized holes in a W foil using a high-energy laser (Potomac Photonics LLC).



Figure 2-3. (a) Schematic of the nanoporous carbon assisted graphene transfer and membrane fabrication. (b) Low-magnification and (c) high-magnification SEM images of the of mechanically polished W support. (d) Low-magnification and (e) high-magnification optical images of the reinforced graphene film transferred on W support.

Two graphene membranes were fabricated using a poly(1-trimethylsilyl-1-propyne) (PTMSP) assisted method reported in the previous study.<sup>194</sup> Briefly, a thin PTMSP film was coated onto the top of graphene on Cu by spin-coating as mechanical support, in order to prevent the graphene film from cracking during the transfer step. For this, a 1.25 wt% of PTMSP solution in toluene was spread on the graphene on Cu, followed by spinning at 1000 rpm for 30 s, and then 2000 rpm for 30 s. The resulting film was dried in ambient conditions for 12 h, and then in a vacuum oven for 12 h at room temperature. Subsequently, the underlying Cu foil was etched using 1 M FeCl<sub>3</sub> solution, and the floating graphene/PTMSP film was rinsed with DI water several times before transferring it onto a porous tungsten support.

### 2.2.4. Characterization

SEM images were acquired by FEI Teneo scanning electron microscope at an operating voltage of 1-2 kV and a working distance of 3-7 mm. Micro-Raman spectroscopy was carried out using Renishaw inVia<sup>TM</sup> instrument equipped with a 457 nm excitation source to directly characterize as-synthesized graphene on Cu. A 100x objective lens yielding a spot size of ca. 1  $\mu$ m was used. The laser power was kept below 1 mW to reduce the localized heating led damages to graphene. Typically, 16 or more spectra were collected for each sample. After the background subtraction, the acquired data were analyzed using MATLAB.

X-ray diffraction (XRD) measurements were carried out in a Bruker D8 Discover X-ray diffractometer equipped with a laser-based alignment system. Surface roughness measurements were performed by Bruker DektaXT stylus profilometer with a 2-µm stylus radius and 3 mg force. The Bruker Vision64 v5.51 software was used for data processing.

The gas permeation tests were performed in a homemade permeation setup (Figure 2-4) consisting of a leak-tight membrane module (details are reported in the previous studies).<sup>16,37</sup> Briefly, the W support was sandwiched between the Swagelok VCR fittings as a gasket. The setup was housed inside a temperature-controlled oven. Ar at 1 bar was used as the sweep gas. The permeation measurements were carried out for H<sub>2</sub>, CH<sub>4</sub>, C<sub>3</sub>H<sub>8</sub>, and SF<sub>6</sub> gases in a single-component mode with a feed pressure of 2 bar. A pre-calibrated mass spectrometer (Hiden Analytical, HPR-20) was used to analyze the permeate stream. Before measurements, membranes were heated to 150 °C to desorb the atmospheric contaminants.



Figure 2-4. Schematic of the membrane permeation measurement setup.

STM was carried out by the Createc low-temperature scanning tunneling microscope at 77 K and  $2x10^{-10}$  mbar. Before imaging, the Cu foil was annealed at 673 K for 30 minutes inside the

STM chamber to clean the surface from contaminations. The image tilt was reduced by flattening in Gwyddion software.

# 2.3. Results and discussion

SLG was synthesized on as-received Cu as well as Cu subjected to various annealing and polishing steps (Figure 2-2a, b). The commercial Cu foil is usually rough hosting several micron-sized grooves attributing to the mechanical rolling process involved in the production of thin foils. Further, the surface of Cu is decorated with surface oxides.<sup>186,195</sup> As a result, thermal annealing of the foil is required to grow high-quality graphene.<sup>196</sup> Extended annealing near or above the melting point of Cu has shown to smoothen the Cu surface which in turn can improve the grain-alignment and reduces the nucleation density, and therefore, can reduce the grain-boundary defects. Further, controlled annealing leads to a reorientation of Cu grains to (111) out-of-plane direction attributing to a lower surface energy of these facets.<sup>197,198</sup> In this work, we investigated the effect of high-temperature annealing on the intrinsic vacancy-defects in CVD graphene and subsequently the gas sieving performance. Two separate as-received low-cost Cu foils ( $\alpha$  and  $\sigma$ ) were studied and contrasted to high-cost, high-purity Cu foil ( $\alpha_{pure}$ with 99.999% purity). When annealing or polishing was carried out, the corresponding sequence is indicated in the nomenclature of the foil. For instance, the high-temperatureannealed  $\alpha$  foil is referred to as  $\alpha$ -A<sub>H</sub>. Similarly, the sequence of high-temperatureannealing/polishing/high-temperature-annealing on the  $\alpha$  foil is referred to as  $\alpha$ -A<sub>H</sub>-P-A<sub>H</sub>.

### 2.3.1. Intrinsic defects in graphene

Graphene was synthesized in the presence of H<sub>2</sub> to minimize the defects caused by the unavoidable leakage of atmospheric O<sub>2</sub> into the evacuated CVD reactor.<sup>18</sup> Raman spectroscopy was used to quantify the density of intrinsic defects and the overall quality of as-synthesized graphene. Consistent with the literature, three characteristic peaks were observed in the Raman spectra: *D* peak near 1350 cm<sup>-1</sup>, *G* peak near 1585 cm<sup>-1</sup>, and 2*D* peak near 2700 cm<sup>-1</sup>. The estimation of defect density was carried out by using the carbon amorphization trajectory,<sup>199,200</sup> by investigating the ratio of the intensities of *D* and *G* peaks, i.e.  $I_D/I_G$ . This is mainly because

the *D* peak is activated in the presence of symmetry-breaking or symmetry-distorting defects such as  $sp^3$ -sites or carbon vacancies.<sup>200</sup>

As-synthesized graphene films with different annealing/polishing history of the Cu foils were analyzed. When the annealing was not carried out, the  $\alpha_{pure}$  foil yielded the lowest  $I_D/I_G$  ratio  $(0.04 \pm 0.01)$ , followed by  $\alpha$  foil  $(0.07 \pm 0.02)$ . The  $\sigma$  foil yielded a much higher  $I_D/I_G$  ratio  $(0.18 \pm 0.02)$ . As we show later, this has roots in the grain-orientation and surface roughness of the Cu foils. When the foils were subjected to annealing/polishing steps, the defect density in graphene could be reduced (Figure 2-2c). The trends were similar for all low-purity Cu foils. After the high-temperature annealing (1077 °C for 1 hour followed by cooling to 1000 °C at 1 °C/min), the  $I_D/I_G$  ratio from the resulting graphene decreased significantly (Figure 2-2c). Polishing the low-purity Cu surface followed by high-temperature annealing further reduced the defect density. Overall, the low-cost foils could be modified by annealing and polishing ( $\alpha$ - $A_H$ -P- $A_H$ ) to yield  $I_D/I_G$  ratio comparable to that from  $\alpha_{pure}$ . To understand the reason behind the obtained results, crystallographic and morphological changes in the Cu foil were studied and are discussed in the next sections.

We would like to note that the Cu annealing was carried in a furnace lined with high-purity alumina tube (Figure 2-1) to prevent build-up of SiO<sub>x</sub> particles on the surface of Cu.<sup>201,202</sup> Briefly, the phase transition ( $\alpha/\beta$ ) of quartz at 573 °C allows Cu atoms and hydrocarbon to diffuse into the quartz tube, leading to the release and the precipitation of the SiO<sub>x</sub> particles onto the Cu foil and graphene. The density of SiO<sub>x</sub> particles on the surface increases by repeated usage of the quartz tube. By adding the high-purity alumina tube inside the quartz tube, the number of particles could be significantly reduced (Figure 2-2d, e, f).

### 2.3.2. The orientation of Cu grains

The in-plane orientation and intergrowth of graphene grain are affected by the arrangement of Cu atoms and grains because graphene growth involves the assembly of the dehydrogenated carbon radicals in energetically-favorable sites on top of the Cu lattice.<sup>185</sup> For example, Murdock *et al.* demonstrated that at LPCVD condition, shape and orientation of graphene grains change conforming to the grain orientation of Cu.<sup>203</sup> Luo *et al.* achieved adlayer-free single-crystal graphene using Cu(111) foil<sup>204</sup> and concluded that the significantly lower carbon content inside the Cu(111) foil compared to the commercially available polycrystalline Cu foils

is the main factor in eliminating the growth of adlayers. It is well-known that the (111) facet promotes an epitaxial-like growth of graphene<sup>205</sup> attributing to an extremely small mismatch in their lattice constants.<sup>192,193</sup> The XRD of as-received Cu foil, before graphene growth, indicated that grains were either completely ( $\alpha$  and  $\alpha_{pure}$ ) or predominantly ( $\sigma$ ) oriented along the (200) direction.  $\sigma$  Cu hosted 31 and 10% of grains oriented along the (111) and (220) direction, respectively (blue trace in Figure 2-5a). The low temperature annealing, 1000 °C for 1 h, similar to the typical Cu annealing during graphene crystallization by LPCVD, does not alter the grain orientation significantly (red traces in Figure 2-5). Therefore, the typical short annealing of Cu foil carried out for the conventional LPCVD synthesis of graphene at 1000 °C is not sufficient to obtain Cu(111). Since the graphene grown on the  $\sigma$  Cu had the highest defect density (Figure 2-2c), we hypothesize that the possible cause could be a less-perfect intergrowth of the graphene grains when the underlying Cu grains have a varying orientation. In other words, a single crystallographic orientation of Cu could improve the intergrowth of graphene grains, lowering the grain-boundary defects. Upon high-temperature annealing, all Cu foils converted to (111) out-of-plane orientation irrespective of their prior orientation (orange traces in Figure 2-5). The top side as well as the bottom side of the annealed Cu foil indicated (111) out-of-plane orientation (Figure 2-6), indicating that the whole Cu foil was transformed by the annealing process.



Figure 2-5. XRD patterns of as-received Cu (blue trace), Cu annealed at 1000 °C during LPCVD (red trace), and Cu exposed to high-temperature annealing (orange trace). The results on  $\sigma$ ,  $\alpha$ , and  $\alpha_{pure}$  samples are shown in (a), (b), and (c), respectively.

During the high-temperature annealing, the Cu foil was heated to 1077 °C, near its melting point of 1083 °C, and was subsequently slowly cooled to 1000 °C to provide enough time for a uniform grain growth and reorientation to Cu(111) attributing to the fact that the (111) facet has the lowest surface energy compared to the other facets.<sup>206,207</sup> Confirming our prior hypothesis, the single crystallographic orientation of annealed low-purity Cu, (111) in this case, significantly reduced the defect density in graphene (Figure 2-2c). We note that there are

several other advantages of synthesizing graphene on the (111) facet of Cu. A lower adsorption and decomposition energy for  $CH_{4}$ ,<sup>208</sup> and a higher rate of carbon diffusion on the Cu surface<sup>192</sup> favors graphene growth. The thermal expansion coefficients of graphene and Cu have the lowest mismatch, and the interfacial interaction is highest when Cu possesses (111) orientation.<sup>209</sup> As a result, the folds and wrinkles in graphene are much reduced on Cu(111).<sup>210</sup> For instance, Ogawa et al.<sup>192</sup> verified that the graphene grains grown on Cu(111) are mostly aligned, yet the graphene grains grown on Cu(100) possess two orientations rotated by 30°, resulting in a higher defect density. We note that the weight loss of Cu foil during the high temperature, ambient-pressure annealing was insignificant (0.21%).



Figure 2-6. XRD patterns of as-received  $\alpha$  Cu (orange trace), front side of the  $\alpha$  Cu exposed to high-temperature annealing (red trace), and back side of the  $\alpha$  Cu exposed to high-temperature annealing (blue trace).

### 2.3.3. Surface morphology of Cu

It is well known that decreasing the surface roughness of Cu reduces the density of graphene nucleation site, subsequently increasing the grain size of graphene.<sup>205,211</sup> Thereby, this can decrease the grain-boundary defects. The as-received commercial Cu foils are rough, attributed to the rolling methods involved in the production of thin foils. Usually, a short annealing of Cu foil is carried out at 1000 °C prior to the graphene growth, however, it does not lead to a significant reduction in the surface roughness. The waviness formed in Cu foil by the rolling process remains intact during the 1000 °C annealing (Figure 2-7). In contrast, the high-temperature annealing process improved the surface roughness significantly (Figure 2-8) with low-purity Cu foils becoming visibly shiny after this step. For example, the surface roughness of the as-received  $\alpha$  and  $\sigma$  foils were 206 and 320 nm, respectively (panel I in Figure 2-8a-d, Table 2-2 in Appendix I). After a single high-temperature annealing step, the corresponding

roughness reduced to 99 and 130 nm, respectively (panel II in Figure 2-8a-d, Table 2-2 in Appendix I). Interestingly, the surface roughness in a single Cu step, decreased considerably, to 0.23 nm, and atomic resolution STM images could be obtained (Figure 2-8c-f). The measured lattice constant, 0.22 nm, agrees well with that from the (111) orientation.<sup>212</sup>



Figure 2-7. SEM images of (a) as-received σ, (b) σ-A<sub>L</sub>, and (c) σ-A<sub>H</sub>-P-A<sub>H</sub>.



Figure 2-8. Profilometer-based surface topography for  $\sigma$  (a) and  $\alpha$  (b) foils. Panels I and II refer to asreceived, and high-temperature annealed foils, respectively. Panel III refers to foil treated to hightemperature annealing, polishing, and high-temperature annealing in a sequential manner. The scalebar is 50 µm. The corresponding SEM images for  $\sigma$  (c) and  $\alpha$  (d) foils with a scale-bar of 3 µm. STM images of the  $\alpha$ - $A_H$  foil displaying the overall smoothness (e), and atomic lattice of Cu (f and g). A bias voltage of 1 V and a tunneling current of 0.2 nA was used for image in panel (e). For images in panels (f) and (g), a bias voltage of 0.1 V and a tunneling current of 0.2 nA was used.

The Cu surface could be further smoothened by mechanical polishing. The treatment was repeated in the following sequence: high-temperature annealing, polishing and finally high-temperature annealing. This led to the complete eradication of the Cu waviness, and the surface

roughness of  $\alpha$  and  $\sigma$  foils reduced to 68 and 79 nm, respectively (Table 2-2 in Appendix I). The size of the Cu grains increased significantly after this treatment, increasing from ca. 100 µm to ca. 340 µm (Figure 2-9). Bigger Cu grains are desired because grain boundaries can obstruct the epitaxial interaction between graphene and Cu(111).<sup>209</sup> However, we observed residues on Cu foil from the polishing step (Figure 2-10). It was not possible to completely remove these residues by washing or sonicating the polished Cu. These residues are detrimental for the application of graphene in membranes especially when the graphene membranes are prepared by reinforcement with the fragile carbon film<sup>16</sup> because the carbon film tends to crack when deposited on top of the residues. We envision that with further development in the residue-free polishing step, the lower surface roughness in the  $\alpha$ -A<sub>H</sub>-P-A<sub>H</sub> or  $\sigma$ -A<sub>H</sub>-P-A<sub>H</sub> foils will be advantageous for the synthesis of graphene membranes. A potential residue-free polishing step is chemical polishing or electropolishing.<sup>196</sup> Here, Cu atoms from the surface are dissolved reducing the surface roughness. However, electropolishing tends to reduce the graphene nucleation density to as low as 1 nuclei/mm<sup>2</sup>. For a short crystallization time, a low nucleation density can lead to imperfect intergrowth of graphene grains, pinholes, etc. On the other hand, for a long crystallization time of graphene, multilayer graphene coverage can increase substantially.



Figure 2-9. Optical images of Cu grains in a)  $\sigma$ -A<sub>L</sub> and b)  $\sigma$ -A<sub>H</sub>.



Figure 2-10. SEM image of the Cu foil after mechanical polishing step where the black particles are the residues from polishing.

### 2.3.4. Gas separation performance from intrinsic vacancy-defects in graphene

We recently demonstrated that the intrinsic defects in LPCVD-derived SLG are composed of subnanometer-sized carbon vacancies or nanopores and can be applied to differentiate gas molecules based on their size.<sup>16</sup> However, the expensive high-purity Cu foil,  $\alpha_{pure}$ , is generally needed to achieve the needed PSD to differentiate molecules based on their size, and the use of other low-purity foils does not result in a good selectivity (Figure 2-11). Here, ideal selectivity between a gas pair is defined as the ratio of gas permeance from the single-component permeance test. Given the reorientation of Cu grains to Cu(111) (Figure 2-5) accompanying a significant improvement in the surface roughness by a single high-temperature annealing step (Figure 2-8), we studied the gas separation performance of graphene derived from all commercial low-purity foils. For this, 2-3 graphene membranes were fabricated from every type of commercial low-purity Cu foil.



Figure 2-11. H<sub>2</sub> permeance (a) and H<sub>2</sub>/CH<sub>4</sub> ideal selectivities (b) at 25 °C from as-synthesized graphene using low-purity and high-purity Cu foils. The data on high-purity Cu,  $\alpha_{pure}$ , is taken from literature.<sup>16</sup>

Overall, the high-temperature annealing of the Cu foil led to graphene membranes with lower  $H_2$  permeance (Figure 2-12a, b) and increased selectivities of  $H_2$  with respect to  $CH_4$  and  $C_3H_8$  (Figure 2-12c-f), indicating that there were fewer nonselective vacancy-defects in graphene

synthesized on the annealed foil. For example, the ideal selectivities obtained from the membrane synthesized on as-received Cu were close to those expected by the Knudsen diffusion mechanism (2.8, 4.7, and 8.0 for H<sub>2</sub>/CH<sub>4</sub>, H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>, and H<sub>2</sub>/SF<sub>6</sub>, respectively, Figure 2-12b, c, e, and f). Knudsen transport is typically observed when a number of nanopores are larger than the size of gas molecules.<sup>101</sup> In turn, larger nanopores have origin in poorly stitched grains of graphene attributing to the non-uniform crystallographic orientation of the Cu grains (Figure 2-5) and the surface roughness of the foil (Figure 2-8). Moreover, the as-received  $\alpha$ -Cu membranes display lower permeance and higher selectivity, and thus higher graphene quality, than that of made by as-received  $\sigma$ -Cu due to a) lower surface roughness of  $\alpha$  Cu foil, and b) single crystallographic orientation (200) of as-received  $\alpha$ -Cu compared to mixed orientation in as-received  $\sigma$ -Cu.

The high-temperature annealing of Cu foil allowed us to realize an attractive combination of H<sub>2</sub> permeance and ideal selectivities from graphene synthesized on low-cost low-purity Cu foils. For example, H<sub>2</sub> permeance above 1000 GPU (1 GPU =  $3.35 \times 10^{-10}$  mol m<sup>-2</sup> s<sup>-1</sup> Pa<sup>-1</sup>) in combination with H<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> selectivities of 12 and 29, respectively, was realized at the permeation temperature of 150 °C for  $\sigma$ -A<sub>H</sub> foil (Table 2-3 in Appendix I). We did not detect the transport of SF<sub>6</sub> (kinetic diameter 5.5 Å) from these membranes. These results were highly reproducible during several membrane fabrication batches.



Figure 2-12.  $H_2$  permeance (a, b) and the ideal selectivities (c, d, e, f) from graphene membranes synthesized using various Cu foils. The horizontal dashed line in panels (c), (d), (e), and (f) correspond to the Knudsen selectivity for a given gas pair. The data marked with '\*' indicate that the SF<sub>6</sub>

# permeance was lower than detection limit of the permeation setup, and the selectivities are calculated based on the detection limit of mass spectrometer.

We note that the ideal selectivity observed here comes from molecular-sized vacancy defects in graphene and not from the NPC film which hosts 20-30 nm sized pores.<sup>16</sup> The observed selectivity does not arise from graphene/NPC interface, otherwise, the selectivity and gas permeance would not be the function of porosity and PSD in graphene.<sup>37</sup> To prove this further, we made two membranes utilizing PTMSP-assisted method from graphene. Permeance and selectivities of these membranes are similar to those made from utilizing the NPC-assisted method (Figure 2-13).



Figure 2-13. Comparison of permeance (a) and ideal selectivities (b, c) of membranes made with PTMSP and NPC supports. The horizontal dashed lines in panels (b) and (c) correspond to the Knudsen selectivity for a given gas pair. The horizontal solid lines in panels (b) and (c) correspond to selectivity for a given gas pair in a membrane made with only PTMSP.<sup>213</sup>

We also note that the graphene defects studied here do not have origin in the pyrolysis to form NPC film (500 °C in the  $H_2$ /Ar atmosphere). Rather, these are intrinsic defects incorporated in the lattice during crystallization at 1000 °C. To prove this, we compared Raman mapping data from as-synthesized graphene to that from graphene placed in the pyrolysis condition for 1 h (Figure 2-14). We did not find any significant change in defect density. The Raman mapping measurements were done on the same area of the sample for all three measurements.



Figure 2-14. Comparison of the defect density of as-synthesized graphene and graphene annealed at the pyrolysis condition for 1 and 24 hours.

The separation of  $H_2$  from hydrocarbons makes these membranes attractive for application in off-gas recovery in the petrochemical industry. The gas transport results are in good agreement with the Raman spectroscopy measurements demonstrating a significant improvement in

graphene quality on par with the previously reported graphene membranes synthesized on expensive high-purity Cu foils.<sup>16</sup> This provides an  $\sim$  80-fold decrease in cost of the Cu foil (Table 2-4 in Appendix I).

The synthesis of high-quality graphene with control over PSD of the intrinsic vacancy defects has a paramount importance to the ongoing efforts on the incorporation of high-density of nanopores in graphene by the postsynthetic etching of graphene lattice to obtain large yet selective gas permeance. Generally, the intrinsic vacancy-defects are expected to expand into large nonselective nanopores during the postsynthetic etching of graphene lattice. However, high selectivity can be obtained by postsynthetic etching if the density of freshly etched nanopores are significantly higher than that of intrinsic vacancy defects.<sup>37,214,215</sup> This study on crystallographic and morphological optimization of Cu foil contributes to this cause by i) reducing the density of the intrinsic vacancy defects (Figure 2-2c; Figure 2-12a and b), and ii) reducing the average size of the intrinsic vacancy defects (Figure 2-12c-f).

To understand the overall effect of high-temperature annealing step which improves the RMS roughness, and orients the Cu foil to (111), leading to improvement in H<sub>2</sub>/CH<sub>4</sub> selectivity, the corresponding data is summarized in Table 2-1. There is a clear correlation of high-temperature annealing with the lowering of defect density ( $I_D/I_G$ ), orientation change of Cu foils to (111), reduction of RMS, reduction of hydrogen permeance, and the increase in H<sub>2</sub>/CH<sub>4</sub> selectivity. The reduction of RMS roughness always lowered down the defect density and improved the membrane performance. However, there is a weak or no correlation of defects and membrane performance with the Cu purity. This could be attributed to the fact that the typical impurities in Cu consist of other metals. During the high-temperature annealing near the melting point of Cu, a liquid Cu layer is present on the surface of the foil which may form a high-purity Cu top-layer. This hypothesis will be confirmed by systematic experiments in future studies. Overall, the most important parameter for the improvement of the graphene membrane on low-cost Cu foil was the improvement of RMS roughness by high-temperature annealing.



Figure 2-15. SEM images of the holes observed in the (a) as-deposited TD-ED Cu and (b,c) after graphene synthesis on the TD-ED Cu.

Table 2-1. Comparisons of the Cu foil and resulting graphene membranes after the annealing step.

Sample	Treatment	Cu crystallographic orientation	Overall RMS (nm)	<i>I</i> <sub>D</sub> / <i>I</i> <sub>G</sub> (graphene)	H <sub>2</sub> permeance (GPU)	H2/CH4 ideal selectivity
α	As-received	(200)	206	$0.07\pm0.02$	2655	5.7
purity = 99.8%	Annealed	(111)	99	$0.06\pm0.01$	925	11.1
σ	As-received	mixed	252	$0.18\pm0.02$	4700	3.3
purity = 99.98%	Annealed	(111)	105	$0.10\pm0.01$	1090	9.5
тс	As-made	mixed	<15	$0.04\pm0.01$	-	-
15	Annealed	(111)	85	$0.04\pm0.01$	-	-
α <sub>pure</sub> purity 99.999%	As-received	(200)	124	$0.04 \pm 0.01$	600	11.3

# 2.4. Conclusions

In conclusion, a facile crystallographic and morphological optimization protocol for commercial low-cost Cu foil is demonstrated which led to the CVD of SLG hosting hydrogensieving intrinsic defects. The slow annealing reported in this study proved much more effective than the usual annealing of Cu foil that invariably takes place during the graphene synthesis. This was evident in the crystallographic changes where the Cu foil orientation changes to (111) only upon the slow-annealing method. The RMS roughness of the high-temperature-annealed Cu foil reduced significantly to ca. 100 nm. The improved smoothness of the Cu foil was the most important factor in achieving better H<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>/SF<sub>6</sub> selectivities. Interestingly, no particular trend was observed with respect to the purity of the Cu foil, which could help to extend the current method to other low-purity foils. We speculate that this could be because of the formation of a high-purity Cu top layer after the high-temperature annealing step. Finally, the ability of carry out atomic-resolution STM imaging on smoothened Cu foils will help future STM studies on understanding the structure of vacancy-defects in graphene.

# **Appendix I**

Sample	RMS (nm)		
α (as-received)	206		
α-A <sub>L</sub>	235		
α-A <sub>H</sub>	99		
α-A <sub>H</sub> -P- α-A <sub>H</sub>	68		
$\sigma$ (as-received)	320		
σ-A <sub>H</sub>	130		
σ-A <sub>H</sub> -P-σ-A <sub>H</sub>	79		
TS (as-synthesized)	<15 (device resolution)		
TS-A <sub>H</sub> (1 $\mu$ m <sup>2</sup> area, measured by STM)	0.25		
$\alpha_{pure}$ (as-received)	124		
$\alpha_{pure}$ - $A_L$	175		

Table 2-2. Surface roughness measurement of various Cu foils and treatments measure by Bruker DektaXT stylus profiler. TS refers to template stripped Cu foils.

Table 2-3. Permeance and ideal selectivity values of the graphene membranes in this study ("ND" indicates that the permeance was lower than MS limit so it was not detected). Data in blue correspond to membranes prepared from as-received Cu foil, whereas the data in red correspond to membranes prepared from high-temperature-annealed Cu foil.

Sample		Permeance (GPU)				Ideal Selectivity			
	T (°C)	$H_2$	CH4	C3H8	SF <sub>6</sub>		H <sub>2</sub> /CH <sub>4</sub>	H2/C3H8	H <sub>2</sub> /SF <sub>6</sub>
- (mombrono #1)	150	2515	867	508	167.1		2.9	5.0	15
6 (memorane #1)	25	1126	340	232	125.4		3.3	4.9	9
- (mombrono #2)	150	6857	1881	989	360		3.6	6.9	19.1
6 (memorane #2)	25	4985	1597	976	335		3.1	5.1	14.9
						•			

σ (membrane #3)	150	4734	1391	832	241		3.4	5.7	19.6	
	25	2172	758	501	120		2.9	4.3	18.2	
a (mombrono #1)	150	2248	442	353	97		5.1	6.4	23.1	
α (membrane #1)	25	660	174	232	65		3.8	2.8	10.2	
a (mombrono #2)	150	3065	489	374	138		6.3	8.2	22.1	
α (membrane #2)	25	992	200	152	73		5.0	6.5	13.6	
- A (mombuono #1)	150	1008	84	34	28.7		11.9	29.3	35.2	
6-AH (memorane #1)	25	393	40	22	28.7		9.9	17.6	13.7	
- A (mombrono #2)	150	827	90	40	28.7		9.1	20.4	28.9	
6-AH (memorane #2)	25	256	42	20	28.7		6.1	12.8	8.9	
$\sigma A_{\rm H}$ (mombrono #3)	150	1442	194	85	28.7		7.4	16.9	50.3	
0-AH (memorane #3)	25	705	116	41	28.7		6.1	17.0	24.6	
g A., (mombrono #1)	150	870	95	43	28.7		9.2	20.4	30.3	
u-A <sub>H</sub> (memorane #1)	25	543	91	38	28.7		6.0	14.3	18.9	
$a_{\rm r} \Lambda_{\rm H}$ (membrono #2)	150	979	76	38	28.7		13.0	25.6	34.2	
	25	403	39	22	28.7		10.4	18.2	14.1	

Table 2-4. Supplier, part number, purity and the price of the Cu foils used in the study.

Supplier	Part number	Purity (%)	Price (USD/cm <sup>2</sup> )		
Sigma Aldrich	349208	99.98	0.56		
Alfa Aesar	Alfa Aesar 46986		0.02		
Alfa Aesar	10950	99.999	1.59		

# **3.** Chapter **3.** Demonstrating and unraveling a controlled nanometer-scale expansion of the vacancy defects in graphene by CO<sub>2</sub>

Adapted with permission from <u>Mojtaba Rezaei</u>, Luis Francisco Villalobos, Kuang-Jung Hsu & Kumar Varoon Agrawal\*, Angewandte Chemie, Accepted manuscript.

## Abstract

A controlled manipulation of graphene edges and vacancies is desired for molecular separation, sensing and electronics applications. Unfortunately, available etching methods always lead to vacancy nucleation making it challenging to control etching. Herein, we report CO<sub>2</sub>-led controlled etching down to 2 - 3 Å per minute while completely avoiding vacancy nucleation. This makes CO<sub>2</sub> a unique etchant for decoupling pore nucleation and expansion. We show that CO<sub>2</sub> expands the steric-hindrance-free edges with an activation energy of 2.71 eV, corresponding to the energy barrier for the dissociative chemisorption of CO<sub>2</sub>. We demonstrate the presence of an additional configurational energy barrier for nanometer-sized vacancies resulting in a significantly slower rate of expansion. Finally, CO<sub>2</sub> etching is applied to map the location of the intrinsic vacancies in the polycrystalline graphene film where we show that the intrinsic vacancy defects manifest mainly as grain boundary defects where intragrain defects from oxidative etching constitute a minor population.

# **3.1.** Introduction

Defect generation in graphene by oxidation has been widely studied due to the inherent uniformity and scalability of the oxidation-based defect generation.<sup>216</sup> Most of the early studies focused on the interaction of graphite with strongly oxidizing agents such as those related to Hummer's method or with gaseous  $O_2$  at high temperatures.<sup>109,114,167</sup> However, under these harsh environments, the oxidation reaction is difficult to control especially when the goal is to control the size of vacancy defects at the nanometer and sub-nanometer length scales or to

precisely shape the graphene edges. Availability of an oxidation method that controllably etches graphene lattice at the rate of a few atoms per second can tune the size of vacancy defects in graphene for molecular separation and sensing. Such methods can also be applied for precisely shaping the width of graphene nanoribbons for band-gap optimization<sup>168,170</sup> with application in electronics and optoelectronics. This would also allow shaping graphene nanomeshes,<sup>141</sup> quantum dots,<sup>169</sup> and nano disks<sup>170</sup> with a high degree of control.

As of now, there is no method to etch graphene edge without nucleating a new vacancy defect in the basal plane of graphene. For example, treatment of graphene with  $O_2^{155}$  and  $O_3^{37}$  results in generation of new vacancy defects. In this context,  $CO_2$  is a promising mild etchant where the energy barrier for the nucleation of single vacancy defect is predicted to be prohibitively large (5.0 eV).<sup>120</sup> In principle, carbon gasification by  $CO_2$  is the Boudouard reaction (C +  $CO_2$  $\leftrightarrow 2CO$ ).<sup>121</sup> Ab-initio calculations have reported energy barrier for the gasification of graphene edge by  $CO_2$  in the range of 2.5-4.6 eV. For example, Zhang et al. reported activation energies for the dissociative chemisorption of  $CO_2$  on single vacancy defect, 55-777 defect, and 555-7777 defect as 2.50, 2.80, and 3.30 eV, respectively.<sup>180</sup> The activation energies for the dissociative chemisorption of  $CO_2$  on zigzag and armchair edges have been estimated to be 2.0 and 4.6 eV, respectively.<sup>184</sup>

The literature probing the mechanism of interaction of  $CO_2$  with defects in graphene suggest the following reaction pathway: (i) physisorption of  $CO_2$  on top of the defective site, (ii) chemisorption of  $CO_2$  on the defective site resulting in the formation of a lactone and/or semiquinone group, and (iii) evolution of the terminal groups followed by the desorption of two CO molecules.<sup>175–178</sup> However, the nature of the  $CO_2$  chemisorption sites (single vacancy, double vacancy, armchair and zigzag edge, etc.), the identity of the intermediate species formed by chemisorption (lactone vs. semiquinone), and the underlying assumptions of the computational methods have resulted in a large discrepancy in the computed energy barrier for the rate-limiting step (1.7 - 4.6 eV) <sup>178,182–184</sup> and there is no clear consensus on the energy barrier.

Experimental studies on probing reaction of  $CO_2$  with graphene edges or vacancies are extremely rare. In fact, currently, there are no systematic studies probing the reaction kinetics of  $CO_2$  with defects in graphene. Recently, Yang et al.<sup>174</sup> reported dependence of the etching rate on the etching temperature and  $CO_2$  flow rate, and demonstrated that  $CO_2$  does not nucleate new defects in the graphene basal plane up to 1000 °C. However, etching kinetics was not

reported because the reaction was not controlled effectively leading to a large heterogeneity in the resulting features, e.g., fully-etched graphene in certain areas, graphene with etched trenches in some areas, and faceted pores in other areas.

Herein, for the first time, we report controlled and uniform etching of graphene with CO<sub>2</sub> at the temperature range of 750 - 1000 °C and extract the energy barrier for the expansion of large edges in graphene as 2.7 eV, corresponding to the chemisorption energy barrier of CO<sub>2</sub> on zigzag edges in graphene. We establish an etching regime that is not limited by the  $CO_2$ mass transfer from the bulk to the graphene edges and study the vacancy expansion rate by adjusting etching temperature and time. We show that nanometer-scale vacancies can be expanded at an attractive rate of 2-3 Å/min making this route highly promising for tuning the pore size in graphene for molecular separation and sensing application. We show the presence of an additional configurational energy barrier for CO<sub>2</sub> to chemisorb at the edge of nanometersized vacancies resulting in an order of magnitude slower rate for the smaller vacancies, with no expansion for defects smaller than 0.15 nm. We demonstrate that CO<sub>2</sub> does not nucleate new vacancy defects resulting in a gaussian PSD of the expanded pores, in sharp contrast to the lognormal PSD typically achieved using oxidative etching methods. Finally, CO<sub>2</sub> etching allows one to map the locations of intrinsic vacancy defects in graphene by transmission electron microscopy, which has been proven a challenging task attributing to their low density. This allows us to establish two distinct origins of the intrinsic vacancy defects: (i) incomplete intergrowth of misaligned graphene grains, and (ii) etching of the lattice in the presence of residual O<sub>2</sub> in the reactor. Our findings demonstrates that CO<sub>2</sub> can be used for structuring graphene films down to the length-scale of a nanometer for various applications such as molecular separation and sensing.

### **3.2.** Methods

### 3.2.1. Graphene synthesis

SLG was synthesized by the LPCVD procedure developed by Li et al.<sup>217</sup>, on 25- $\mu$ m-thick 99.8% purity Cu foil from *Alfa Aesar*. Briefly, a piece of Cu foil (2 × 5 cm<sup>2</sup>) was sonicated for 5 min in Acetone and subsequently for an additional 5 min in isopropyl alcohol (IPA). Then, it was blow-dried by N<sub>2</sub> and placed inside the 1-inch quartz CVD reactor. The Cu foil was treated

at 1000 °C and 800 Torr in a CO<sub>2</sub> atmosphere for 30 min to remove the organic contaminations. Keeping the temperature at 1000 °C for the remaining of the process, the reactor was evacuated to 1 mTorr. Subsequently, 8 sccm of H<sub>2</sub> was introduced for 30 min, increasing the pressure to 80 mTorr, to anneal the Cu surface and reduce the surface oxides. Finally, 24 sccm of CH<sub>4</sub> was added for 30 min to synthesize the polycrystalline SLG film. While maintaining the H<sub>2</sub> flow, the CH<sub>4</sub> flow was cut off to stop the crystallization before further etching experiments were carried out. The Cu foil was not treated with our high temperature annealing method as the subsequent CO<sub>2</sub> etching behavior is independent of the orientation of the Cu substrate.

### **3.2.2.** $CO_2$ etching

 $CO_2$  etching was performed inside the mentioned CVD reactor system. To eliminate the effect of  $O_2$  leak from the atmosphere to the reactor through the quartz tube connections with the gas inlet and the vacuum section, these areas were encapsulated by a pure  $N_2$  gas environment (Figure 3-1). In addition, ultra clean gas filters from *PerkinElmer* were installed on the path of the ultra-pure CH<sub>4</sub> and CO<sub>2</sub> gases to further eliminate the effect of O<sub>2</sub> impurities. H<sub>2</sub> was produced on-site by *NM-500 plus* hydrogen generator and passed through the triple O<sub>2</sub>, H<sub>2</sub>O, and hydrocarbon ultra clean gas filter from *PerkinElmer* before entering the CVD system. CO<sub>2</sub> etching experiments were carried out based on the sample's initial condition:

- a) For freshly synthesized SLG sample that has been kept inside the reactor at  $H_2$  atmosphere, the sample was heated to the desired etching temperature and maintained for 5 min to reach the equilibrium. Next, 500 mTorr CO<sub>2</sub> was introduced to the system via mass flow controller while maintaining the  $H_2$  partial pressure of 300 mTorr. After the desired etching duration, CO<sub>2</sub> flow was cut off, and Cu foil was moved outside the heating zone to cool down the sample and stop the reaction quickly. The sample was taken out of the reactor when the entire system's temperature reached below 30 °C.
- b) For samples that were pretreated outside the CVD reactor, i.e., O<sub>3</sub>-treated and O<sub>2</sub>-treated, the system was evacuated to full vacuum and purged 4 times after the sample was placed inside the reactor. Then, it was heated to the desired etching temperature at 1 atm H<sub>2</sub> before performing the rest of the process as written in section a.
- c) For the suspended SLG sample, a high density of nanopores was etched in a pristine SLG film suspended on the 1  $\mu$ m holes of a holey silicon nitride (Si<sub>3</sub>N<sub>4</sub>) TEM grid using

 $O_3$ .<sup>163</sup> Then, it was exposed to H<sub>2</sub> atmosphere at 900 °C for 1 h to remove adsorbed contaminations and O-containing functional groups from the lattice prior to the CO<sub>2</sub> expansion experiments.<sup>218</sup> The nanopores present in the sample were thoroughly characterized using AC-HRTEM (221 pores from 22000 nm<sup>2</sup>). Using this N-SLG as a starting point, the pores were expanded by CO<sub>2</sub> by following the process written in section b. The N-SLG hosting the expanded pores were thoroughly characterized using AC-HRTEM (381 pores from 40000 nm<sup>2</sup>) without further treatments to eliminate any external factors.



Figure 3-1. Schematic of the CVD system used for graphene synthesis and CO<sub>2</sub> treatment.

### 3.2.3. O<sub>3</sub>-treatment of SLG on Cu

 $O_3$  etching was carried out in a homemade millisecond gasification reactor (MGR) setup.<sup>29</sup> Briefly, as-synthesized SLG on the Cu foil was placed inside the MGR chamber, and the chamber was evacuated by a vacuum pump. A millisecond leak valve (MLV) was used to dose the gases and adjust the chamber pressure. First, the reactor was heated to the etching temperature (250 °C) with a H<sub>2</sub> flow of 20 sccm. Next, H<sub>2</sub> was cut off, and Ar was injected to purge the H<sub>2</sub>. Prior to exposure to O<sub>3</sub>, Ar was cut off to vacuum the chamber. The O<sub>3</sub> etching step was controlled by a LabVIEW program that opens and closes the MLV to deliver the

desired amount of  $O_3/O_2$  mixture (100 ms of the opening time with 9%  $O_3$  on a molar basis) to the MGR chamber. Once the desired amount of  $O_3$  was delivered, Ar was introduced to purge the  $O_3$ . Finally, the system was quickly cooled down to room temperature. The underlying Cu foil became oxidized with higher surface roughness after the  $O_3$  treatment. Prior to characterization and further  $CO_2$  expansion experiments, the sample was annealed at 900 °C in 1 atm H<sub>2</sub> atmosphere for 3 h to reduce the copper oxide and to smoothen the underlying Cu surface to facilitate the STM characterization.

### 3.2.4. O<sub>2</sub>-plasma treatment

 $O_2$ -plasma treatment was done by a 13.56 MHz *MTI EQ-PCE-3* plasma generator at 17 W. The chamber was fully evacuated and purged 3 times before fixing the flow of  $O_2$  to stabilize the system at 50 mTorr. Then, plasma was generated for the desired duration to introduce pores in the sample.

### **3.2.5.** AC-HRTEM sample preparation

As-synthesized SLG was transferred onto a TEM grid using a paraffin reinforcement layer. First, paraffin was melted by heating it to 80 °C and poured on top of the Cu-foil containing the freshly synthesized SLG. The paraffin was spin-coated at 1000 RPM for 30 s with the help of a hot-air gun to maintain the paraffin in liquid state during this process. Then, the Cu-foil was etched using a 1M FeCl<sub>3</sub> solution, and the paraffin-reinforced SLG was washed in a HCl 1 M bath and a DI water bath. Next, the floating paraffin-reinforced SLG was fished with a *PELCO*® *Holey Silicon Nitride* grid with 1 µm holes and dried at 45 °C for two days. Afterward, the paraffin reinforcement layer was removed by immersing the grid for two hours in three consecutive heptane baths. Finally, the resulting grid with a free-standing SLG film covering > 70 % of its 1 µm holes was dried at room temperature for one day before introducing nanopores in it by O<sub>3</sub> treatment.

### 3.2.6. Characterization

SEM images were acquired by *FEI Teneo* at an operating voltage of 1 - 2 kV, an operating current of 13-25 pA, and a working distance of 4 - 7 mm. The in-column (T3) detector was utilized to image the expanded pores in SLG on Cu foil, and the standard secondary-electron Everhart-Thornley detector was used to image the porous SLG sample after being oxidized in air. ImageJ software was used to analyze the pore size and density in each image.

Bright-field and Dark-field TEM (BF-TEM and DF-TEM) images and selected area electron diffraction (SAED) patterns were obtained by *FEI Tecnai G2 Spirit* at the operating voltage of 120 kV. The SLG sample hosting the expanded pores was transferred onto an ultrathin carbon-coated TEM grid via the common wet transfer method.<sup>219</sup> Briefly, 950 PMMA solution in anisole from *Microchem* was spin-coated on the SLG surface at 1000 and 2000 rpm for 1 min each. Then, it was heated at 70 °C for 30 min before etching the underlaying Cu foil by 0.5 M sodium persulfate (Na<sub>2</sub>SO<sub>4</sub>) solution. Next, the PMMA coated SLG was rinsed 3 times with DI water to remove the etching solution. Finally, the floating film was scooped on the ultrathin carbon-coated TEM grid and left to dry overnight. Before imaging the sample, it was placed in Acetone and isopropyl alcohol (IPA) to remove the PMMA layer. ImageJ software was used to analyze the pore size and density in each image.

AC-HRTEM was done with a double-corrected *Titan Themis 60-300 (FEI)* equipped with a Wein-type monochromator using an 80 keV incident electron beam to reduce the electron radiation damage. The electron beam was monochromated to reduce the effects of chromatic aberration, and a negative Cs of ~  $18 - 21 \mu m$  with a slight over-focus was used to give a "bright atom" contrast in the images. Typically, the lattice experienced a total dose of ~  $2 \times 10^5 \text{ e}^- \text{ Å}^{-2}$  during focusing and imaging. The images presented in the manuscript were obtained by integrating the first 5 to 10 frames (each frame corresponds to an exposure time of 200 ms and a dose of ~  $10^3 \text{ e}^- \text{ Å}^{-2}$ ) obtained during imaging of a particular area. When needed, the images were processed with a band-pass filter to make the lattice clearer. ImageJ software was used to analyze the pore size and density in each image.

STM was carried out by the *Createc* low-temperature scanning tunneling microscope (LT-STM) at 4.7 K. Before imaging, the sample was annealed at 873 K for 60 min inside the STM chamber to desorb the surface contaminations. The O<sub>2</sub>- and O<sub>3</sub>-treated SLG samples were measured at 0.2 V bias and 0.5 nA current, and the HOPG sample was measured at 0.15 V bias and 0.5 nA current. The image tilt was reduced by flattening in Gwyddion software.

Raman spectroscopy was carried out using a Renishaw inVia<sup>TM</sup> confocal spectroscope equipped with a 457 nm excitation laser and a 100x objective. The laser power was kept below 1 mW to reduce the localized heating led damages to graphene. Based on the mapped area, 36 to 500 spectra were recorded for different samples. The 2D peak intensity and  $I_D/I_G$  and  $I_{2D}/I_G$  ratios were calculated after background subtraction and curve fitting the 2D, G, and D peaks in MATLAB.

The X-ray photoelectron spectroscopy (XPS) analysis was conducted on the Cu foil using the monochromated K $\alpha$  line of an aluminum X-ray source (1486.6 eV) with the analyzer set at pass energy of 20 eV. The samples were electrically grounded to the XPS sample stage. Shirley's background was used for the peak fitting. The components of the Cu2p were fitted with symmetric line shapes. The following binding energies were used for the Cu2p fitting: Cu2p<sub>1/2</sub>: ~933; Cu2p<sub>3/2</sub>: ~953 eV.

# **3.3. Results and discussion**

Graphene was synthesized on a Cu foil by the CVD approach using CH<sub>4</sub> as the carbon precursor (schematic in Figure 3-1).<sup>61</sup> The synthesized graphene was single-layer with a low density of intrinsic defects as indicated by the mapping data based on Raman spectroscopy ( $I_{2D}/I_G$  of 1.51  $\pm$  0.25;  $I_D/I_G$  of 0.04  $\pm$  0.02, Figure 3-2). These intrinsic defects consist of vacancy defects which are typically formed at grain boundaries or result from the limited oxidation of the lattice with the residual/leaked O<sub>2</sub> in the reactor.<sup>19,20,26,220</sup> The intrinsic defects are composed of vacancy defects which have been argued to form at the grain boundary or to result from a limited oxidation of the lattice in the residual O<sub>2</sub> in the reactor.<sup>19,20,26,220</sup> Based on the carbon amorphization trajectory<sup>200</sup> and gas permeation studies,<sup>16</sup> the density of intrinsic vacancy defects corresponds to ~10<sup>10</sup> cm<sup>-2</sup>. These defects are the starting point for this study. Unless otherwise specified, CO<sub>2</sub> etching was carried out immediately after the graphene synthesis inside the CVD reactor, allowing us to conduct etching studies on contamination-free graphene surface with a CO<sub>2</sub> partial pressure of 500 mTorr, a condition where CO<sub>2</sub> mass transfer from bulk to graphene edges is not rate limiting (see discussion later).



Figure 3-2. Raman spectroscopy analysis of the synthesized pristine SLG.

SEM of graphene etched by CO<sub>2</sub> at 1000 °C for 1.5 min revealed faceted, bright features (Figure 3-3b). These features had a monomodal distribution with a size of 0.45  $\pm$  0.07  $\mu$ m (Figure 3-3c). We assign these features as the expanded intrinsic vacancy defects for the reasons described below. The features are brighter than the surrounding graphene because of the higher yield of secondary electrons from bare Cu (CVD substrate) compared to graphenecovered Cu. When we oxidized the sample in ambient air at 160°C for 60 min, a method that has been used in the past to visualize graphene defects relying on the rapid oxidation of exposed Cu at the defect site,<sup>221,222</sup> the faceted features were severely oxidized whereas the rest of the sample was unaffected (Figure 3-3d). We prepared another sample by CO<sub>2</sub> etching (900 °C for 150 min) and transferred the graphene from Cu foil to SiO<sub>2</sub>/Si wafer. Optical microscopy of the resulting sample revealed the etched features had a contrast that was similar to that of the bare wafer further indicating that the features were holes (Figure 3-3e and Figure 3-4). Raman spectroscopy of one of these features also conclusively confirmed this as the intensity of the Gand 2D peaks dropped to zero inside the faceted feature while typical spectra characterizing high-quality SLG could be readily obtained from the area surrounding the holes (Figure 3-3f).<sup>199</sup> A mapping of the 2D peak intensity also clearly proves this point. The 2D peak intensity remains uniform for the graphene-covered area, and it drops to zero for the pore area (Figure 3-3g and Figure 3-4). The mapping of the surrounding area yielded  $I_D/I_G$  ratio of 0.04  $\pm 0.02$  confirming that graphene domains surrounding the holes are not affected by the hightemperature CO<sub>2</sub> treatment. This indicates that the etching likely takes place only at a defect site (see further discussion later).



Figure 3-3. (a) Schematic representation of  $CO_2$  and a non-selective etchant (e.g.,  $O_2$ ,  $O_3$ ,  $O_3/UV$ , etc.) reacting with SLG. The starting point for both etchants is pristine graphene with intrinsic defects. (b) SEM image of expanded pores (lighter areas) in graphene (darker areas) by 500 mTorr  $CO_2$  on Cu foil at 1000 °C for 1.5 min, and (c) its corresponding pore size distribution. (d) SEM image of the sample shown in panel b after annealing in air at 160 °C for 60 min to oxidize the exposed Cu surface. (e) Optical image of a pore expanded at 900 °C for 150 min after being transferred onto a SiO<sub>2</sub>/Si substrate. Lighter area is the pore, and the darker area is the remaining graphene. (f) Raman spectra of points A and B marked on the optical image shown in panel e. (g) The corresponding Raman spectroscopy mapping of the area marked by the red rectangle in panel e.



Figure 3-4. (a and b) Raman spectroscopy mapping of the SLG hosting expanded pores after transferring onto a SiO<sub>2</sub>/Si substrate.

The size of the expanded defect had a straightforward correlation with the etching time indicating that the etching reaction was not limited by the mass transfer of CO<sub>2</sub> from the bulk to the graphene edge (Figure 3-5 and Figure 3-6a). For example, etching times of 15 and 60 min yielded smaller pores with size distributions of  $0.44 \pm 0.06$  and  $1.80 \pm 0.12 \mu m$ , respectively, compared to that of  $4.87 \pm 0.32 \mu m$  at 150 min at 900°C (Figure 3-6a and Figure 3-5). Again, the size distributions had a gaussian profile at all etching times. A fitting between the pore size and etching time resulted in a straight line passing through the origin corresponding to an etching rate of  $31.40 \pm 1.05$  nm/min (Figure 3-6b). The density and average center to center distance between the pores did not change when the etching time was increased from 15 to 150 min confirming that the nucleation of vacancy defects did not occur with CO<sub>2</sub> (Figure 3-6c,d).

We could controllably expand the intrinsic vacancies using CO<sub>2</sub> with expansion rate increasing from 0.60 to 280 nm/min by increasing the etching temperature from 750 to 1000 °C (Figure 3-7a and Figure 3-8). In fact, the pore expansion rate had an exponential dependence on the CO<sub>2</sub> exposure temperature. An Arrhenius-type dependence of expansion rate on the etching temperature could be fitted with a high goodness of fit ( $R^2 = 0.994$ ) yielding an activation energy of 262 kJ/mole or 2.7 eV (Figure 3-7b). As per the theoretical predictions, CO<sub>2</sub> binding at a defect site in graphene proceeds with a dissociate adsorption which is also the rate-limiting step. For instance, the energy barrier of etching of graphene zigzag and armchair edges have been reported to be 2.6 and 4.6 eV, respectively,<sup>184,223</sup> where the lower barrier for zigzag edge is reasonable given the lower stability of zigzag edges compared to armchair edges.<sup>224</sup> Based on this, we attribute this observed activation energy (2.7 eV) as the energy barrier for the dissociate chemisorption of CO<sub>2</sub> on the zigzag edge of graphene.



Figure 3-5. SEM images of the expanded pores in SLG on Cu foil at 900 °C for (a) 15 min and (b) 60 min. (c) Optical image of the expanded pores in SLG on Cu foil at 900 °C for 150 min after transfer onto a SiO<sub>2</sub>/Si substrate.



Figure 3-6. (a) The histogram of PSD of the expanded pores in samples etched by  $CO_2$  at 900 °C for 15, 60, and 150 min. (b) Expanded pore size versus etching time for the samples shown in panel a, displaying the linear etching behavior of  $CO_2$  regarding etching time. (c) Density of expanded pores as a function of etching time compared to that of intrinsic vacancy defect and (d) average distance between the expanded pores as a function of etching time



Figure 3-7. (a) Etching rate (logarithm scale) of SLG by 500 mTorr  $CO_2$  on Cu foil at 750 – 1000 °C. (b) Linear behavior of the natural logarithm of the etching rate versus the reciprocal of the etching temperature at 500 mTorr  $CO_2$ . (c) Expanded-pore density (natural logarithm scale) versus the reciprocal of the etching temperature at 500 mTorr  $CO_2$ .

We note that the energy barrier for the dissociate chemisorption of CO<sub>2</sub> is expected to be function of the initial defect size where steric hindrance for fitting the CO<sub>2</sub> to the defect site plays an important role especially for nanometer-scale vacancy defects where CO<sub>2</sub> cannot fit inside the defect. Therefore, the estimated energy barrier (2.7 eV) corresponds only for the expansion of larger vacancies (>2 nm in size, also see discussion later) which do not present steric hindrance for CO<sub>2</sub> chemisorption. This is proven by the fact that we observed an exponential dependence of the density of expanded vacancy defects on the etching temperature ( $2.5 \times 10^5$ ,  $1.7 \times 10^6$ ,  $4.3 \times 10^6$ ,  $3.0 \times 10^7$ , and  $1.2 \times 10^8$  cm<sup>-2</sup> at 800, 850, 900, 950, and 1000 °C, respectively) corresponding to an activation energy of 343 kJ/mole or 3.6 eV (Figure 3-7c). The density of expanded defects, even for the case of the highest temperature (1000 °C), remains more than two orders of magnitude lower than the density of intrinsic vacancy defects ( $\sim 10^{10}$  cm<sup>-2</sup>) in the as-synthesized graphene. We note that this does not imply nucleation of a new vacancy defect on basal plane of graphene at higher temperatures. It implies that at higher temperatures, expansion of the smaller defects with steric hindrance for CO<sub>2</sub> chemisorption is activated at higher temperatures.



Figure 3-8. SEM images of expanded pores in SLG by 500 mTorr  $CO_2$  on Cu foil at (a) 1000 °C, (b) 950 °C, (c) 900 °C, (d) 850 °C, and (e) 800 °C.

Recent studies on understanding the origin of intrinsic vacancy defects in as-synthesized CVD graphene using STM, HRTEM, and gas permeation studies point to two separate origins;<sup>16–18</sup> i) an incomplete intergrowth of misaligned graphene grains,<sup>20,21,220</sup> and ii) limited etching of the graphene lattice in the presence of residual/leaked oxygen in the CVD reactor.<sup>19,26</sup> Size and density of these defects are sensitive to the CVD environment (precursor, temperature, pressure, relative concentrations, etc.) and the catalytic substrate.<sup>17,25,26,186,220,225</sup> Given that expansion of vacancy defects makes it much easier to visualize them by electron microscopy, we set out to understand whether intrinsic defects were solely at grain boundaries or inside graphene grains using bright-field and dark-field transmission electron microscopy (BF-TEM and DF-TEM, respectively).



Figure 3-9. Visualization of the location of intrinsic defects with respect to the grain boundaries. (a) BF-TEM image suspended graphene where intrinsic defects are expanded with CO<sub>2</sub> at 950 °C, and corresponding false-colored DF-TEM image (b). White arrows and yellow arrows point out the pores

completely inside a graphene grain and at the grain boundaries, respectively. (c-I) Selected area diffraction pattern (SAED) and corresponding DF-TEM images from the selected diffraction spots (highlighted by red, green and purple circles) differentiated by the matching frame colors (c-II, c-III, and c-IV).

DF-TEM images representing different grain orientations were false-colored and superimposed on top of each other to display the orientation of graphene grains and the location of expanded pores with respect to the grain boundaries (Figure 3-9 and Figure 3-10). The pores appear black due to lack of diffraction from porous domains and were not false-colored (Figure 3-9b and Figure 3-10b). White and yellow arrows point out pores located completely inside a graphene grain and at grain boundaries, respectively. Visualization in this straightforward manner confirms that the intrinsic defects were present at the grain boundaries as well inside the grain without touching the grain boundary (Figure 3-9b), indicating both abovementioned origins contribute to intrinsic defects in graphene.



Figure 3-10. (a) BF-TEM image of SLG hosting expanded pores at 950 °C and (b) the false-colored DF-TEM image of the same area displaying the location of pores (dark areas) with respect to the three different graphene grain orientations. White arrows and yellow arrows point out the pores inside the graphene grain and at the graphene grain boundary, respectively. (c-I) SAED pattern and (c-II, c-III, and c-IV) the corresponding DF-TEM images of the selected diffraction spot differentiated by the matching frame colors.

The presence of higher energy barrier for nanometer-scale vacancies manifested in a slower expansion of these defects. We used high-resolution transmission electron microscopy (HRTEM) and scanning transmission microscopy (STM) in combination with SEM to probe small defects. For larger defects, we observed an expansion rate of ~ 3.5 nm/min, independent of the size of the defect (160-1000 nm, Figure 3-11a), consistent with our previous observation of the rate of expansion under these expansion conditions. For 20 – 80 nm sized defects, we observed a slight drop in the expansion rate, i.e., ~  $3.1 \pm 0.8$ ,  $2.7 \pm 0.2$ , and  $2.5 \pm 0.2$  nm/min for 80, 40, and 20 nm defects, respectively (Figure 3-11b). The progressively decreasing rate can be well described by much smaller rate for expansion of vacancies with steric hindrance which reduces the overall rate of expansion as per Equation 3.1:

Overall rate = 
$$\frac{\sum_{d_i}^{d_f} r_{\nu_i} \Delta t_i}{\sum_{d_i}^{d_f} \Delta t_i}$$
 Equation 3.1

where  $r_{v_i}$  and  $\Delta t_i$  correspond to size-dependent expansion rate and time duration of expansion, respectively, for a given size interval to arrive to the next size.  $d_i$  and  $d_f$  refer to the initial and final sizes of the pore, respectively.



Figure 3-11. Effect of pore size on expansion kinetics in the presence of 500 mTorr of CO<sub>2</sub> at 800 °C. (a) SEM images of expanded pores at progressively increasing etching times of 25, 45, 80, 120, 150, and 240 min. (b) TEM images of expanded pores at 8 and 15 min. (c) AC-HRTEM image of the expanded pore at 3 min. (d) STM image of an expanded pore on Cu foil after exposure to CO<sub>2</sub> for 3 min. (e) STM image of expanded pores on HOPG after exposure to CO<sub>2</sub> for 3 min.



Figure 3-12. Effect of pore size on expansion kinetics in the presence of 500 mTorr of CO<sub>2</sub> at 800 °C. (a-I) Evolution of the etching rate versus pore size. (a-II) The magnified plot of the yellow-colored area in panel a-I. (a-III) The magnified plot of the green-colored area in panel a-II. (b) PSD corresponding to expanded pores in suspended SLG before and after exposure to CO<sub>2</sub> for 3 min.

To probe the size-dependent etching, we turned towards expansion behavior of sub-nanometersized vacancies (expansion condition identical as above) by imaging their structure and size distribution by an AC-HRTEM. Imaging was carried out under exposure conditions which do not expand the defects during the image acquisition. To improve the pore sampling for the statistical accuracy, one requires a pore density that is much higher than intrinsic vacancy defects. Therefore, we deliberately introduced sub-nanometer-sized pores (mean pore size of  $0.31 \pm 0.25$  nm, where pore-size is defined as the diameter of the biggest circle that fits inside the pore) in suspended graphene resting on a TEM grid by O<sub>3</sub> treatment yielding defect density of  $10^{12}$  cm<sup>-2</sup> (Figure 3-13).<sup>163</sup> We make the following observations by comparing the PSD before and after CO<sub>2</sub> expansion (Figure 3-11c, Figure 3-12, Figure 3-13, Figure 3-14, and Figure 3-15):

Pores with size up to 0.15 nm were not affected by the CO<sub>2</sub> and did not expand (Figure 3-12). This is consistent with the fact that CO<sub>2</sub> cannot fit inside these pores, therefore, the in-plane configuration needed for the dissociative chemisorption of CO<sub>2</sub> is not achieved. In contrast, we observed almost complete decline in the population of pores with size of 0.30 nm where CO<sub>2</sub> does fit (Figure 3-12b).

- Mean pore size shifted from 0.30 ± 0.25 nm to 1.05 ± 0.29 nm after 3 min of etching (Figure 3-11c and Figure 3-12), which corresponds to an effective etching rate of ~ 0.25 nm/min, more than 10-fold lower than that for the larger pores.
- Another 3 minutes of etching resulted in coalescence of nearby pores resulting in a larger pore (Figure 3-15). Based on the average distance between the pores before the etching and the size of the coalesced pore, an etching rate of 0.25 ± 0.12 nm/min could be estimated, consistent with the above observation.
- CO<sub>2</sub> only expanded the existing pores without nucleating new defects (constant pore density of  $\sim 10^{12}$  cm<sup>-2</sup> before and after exposure to CO<sub>2</sub>) consistent with our previous conclusion.



Figure 3-13. AC-HRTEM images of the initial O<sub>3</sub>-treated SLG before exposure to CO<sub>2</sub>.



Figure 3-14. AC-HRTEM images of the O<sub>3</sub>-treated SLG sample shown in Figure 3-13 after exposure to 500 mTorr CO<sub>2</sub> at 800 °C for 3 min.


Figure 3-15. AC-HRTEM images of the O<sub>3</sub>-treated SLG sample shown in Figure 3-14 after exposure to 500 mTorr CO<sub>2</sub> at 800 °C for 3 min.

The above HRTEM based results were obtained on suspended graphene while our SEM observation for larger pores were based on graphene resting on Cu foil. To understand whether or not the Cu foil contributed to the observed differences, we carried out STM of CO<sub>2</sub>-expanded pores in graphene resting on a Cu foil where pores were incorporated using the same conditions as those in the TEM study. We observed similar slow expansion rate for nanometer-sized vacancies (0.27 nm/min), which rules out any significant effect of Cu foil (Figure 3-16). This was further confirmed by another experiment using freshly-cleaved HOPG where 0.8 nm pores expanded to 1.7 nm with a similar etching rate (0.30 nm/min; Figure 3-17). The pore size is defined as the diameter of the biggest circle that fits inside the pore. These sets of experiments validate the slower etching kinetics in nanometer-scale pores.



Figure 3-16. STM images of a typical O<sub>3</sub>-induced pore in SLG on Cu foil (a) before and (b) after exposure to 500 mTorr CO<sub>2</sub> at 800 °C for 3 min.



Figure 3-17. STM images of the 2s O<sub>2</sub>-plasma treated HOPG after exposure to to 500 mTorr CO<sub>2</sub> at 800 °C for 3 min.

# 3.4. Conclusion

This study establishes  $CO_2$  as a highly promising etchant for controlled manipulation of graphene edges and vacancy defects down to a rate of a few Å per minute. The theoretical literature predicts that  $CO_2$  should not nucleate pores in graphene because of an extremely high energy barrier for its chemisorption on the basal plane of graphene. This systematic pore expansion study, tracking the density of expanded pores as a function of etching condition, not only confirms the theoretical prediction but also reveals that only vacancy defects larger than 0.30 nm can be expanded by  $CO_2$ . So far, the energetics for  $CO_2$  led etching of graphene edges were only studied by computational calculations and no experimental data was available. This study, for the first time, validates that  $CO_2$  expands graphene edges with an energy barrier is 2.7 eV, close to that predicted for the dissociative chemisorption of  $CO_2$  on the zigzag edges.

Two pieces of evidence are presented to reveal another finding.  $CO_2$  experiences an additional energy barrier for expanding the nanometer-scale vacancies compared to the pore that are several nanometers in size. The evidences are: (i) the density of expanded pores increases exponentially as a function of the etching temperature resulting from the activation of small vacancy defects at high temperature, and (ii) a much-reduced rate of expansion for nanometerscale pores compared to larger pores.

These results present a novel tool for the manipulation of vacancy defects in graphene with an added advantage of highly controlled size manipulation decoupling pore nucleation from pore expansion. This will inspire and aid future studies aiming to tune the PSD in graphene for molecular separation and sensing studies. It will also aid efforts to manipulate the width of graphene nanoribbons to control their electronic properties. Finally, CO<sub>2</sub> etching will also find application in the mapping of the intrinsic vacancy defect with respect to grain boundaries, a

method which can be extremely useful for researchers looking to control or manipulate the intrinsic defects.

# Appendix I

### Effect of Cu crystallographic grain orientation on CO2 etching of SLG

Surveying a large area, ~ 2 mm<sup>2</sup>, of expanded pores in SLG on Cu foil revealed that mean pore size and density of the expanded pores do not depend on the Cu grain orientation (Figure 3-18). Yang et al. reported a similar behavior after exposing graphene to  $CO_2$  and analyzing the density of the etched trenches and areas.<sup>174</sup>



Figure 3-18. A typical SEM image of pore size and pore density distributions in SLG on different Cu grain orientations.

#### Shape of the expanded pores

Analysis of the SEM images of the expanded pores in SLG on Cu foil revealed that all expanded pores were faceted. Being faceted or not depends on the initial structure of the pore before exposure to CO<sub>2</sub>. In our study, etching was originated from the intrinsic defects and resulted in faceted expanded pores, validating the conclusion of the previous reports on graphite and other carbon substrates, and expanding it to SLG. Two main explanations have been suggested for a similar observation in reaction of CO<sub>2</sub> with graphite: steric hindrance and etching mechanism. The first argument suggests that the pore's initial structure determines the shape of the expanded pore.<sup>126,147</sup> In case of a pore constructed from few missing atoms, resembling SLG intrinsic defects<sup>16</sup>, the dimension of the pore is smaller than the collision diameter of the etching gas molecules in the early stages of the expansion. Hence, the corner atoms have a lower probability of interaction with CO<sub>2</sub> and the subsequent etching due to steric hindrance. In case of a larger circular pore, no such restriction is present, and CO<sub>2</sub> can access all edge atoms. The second argument is based on the proposed mechanism of carbon gasification by CO<sub>2</sub>. After physical adsorption of the CO<sub>2</sub> molecule on the defective site, simultaneous chemical adsorption and breakage of the first C=O bond occur. This step is widely known as dissociative chemisorption and is believed to be the rate-limiting step. A DFT study by Zhu et al. argues that dissociative chemisorption of CO<sub>2</sub> can only occur on two consecutive edge sites, thus preventing the reaction of corner atoms with CO<sub>2</sub>.<sup>178</sup> Figure 3-19 visualizes the evolution of pore expansion for several relevant initial pore structures.



Figure 3-19. Schematic of the evolution of pore expansion based on its initial structure for single vacancy, double vacancy, triple vacancy, slit-shaped, and 5-atom missing pores.

#### Non-oxidative interaction of CO2 and SLG on Cu foil

XPS analysis of the Cu foil exposed to Cu at 1000 °C for 1 h demonstrated that  $CO_2$  does not oxidize the Cu substrate (Figure 3-20), making pore expansion by  $CO_2$  a suitable method to etch graphene where Cu substrate needs to remain active and/or smooth for further processing (e.g., utilizing the catalytic property of exposed Cu substrate) or characterization (e.g., STM analysis). In contrast,  $O_2$  and  $O_3$  rapidly oxidize the Cu foil at elevated temperatures, increasing its surface roughness and reducing its catalytic activity due to the formation of a copper oxide layer on the surface of the Cu foil.<sup>29,226</sup> Moreover, Yang et al., utilizing XPS, demonstrated that amount of C=O groups does not change after exposing graphene to CO<sub>2</sub> at 1000 °C, and thus it does not oxidize graphene either.<sup>174</sup>



Figure 3-20. XPS Cu 2p profiles of Cu foil (a) before and (b) after exposure to CO<sub>2</sub> at 1000 °C for 1 h.

# 4. Chapter 4. Competitive etching and growth of singlelayer graphene for molecular sieving

Adapted with permission from <u>Mojtaba Rezaei</u>, Luis Francisco Villalobos & Kumar Varoon Agrawal\*, manuscript in preparation for submission to a journal.

# Abstract

SLG is predicted to play a major role in shaping the future of membrane separation due to its ultimate thinness, flexibility, mechanical strength, and chemical stability. Recent efforts in introducing gas sieving nanopores in graphene have led to either wide PSD or low density of pores, attributing to simultaneous pore nucleation and expansion of the existing pores hindering the true potential of this material. Herein, we develop a method to tune the PSD of N-SLG film and fabricate graphene membranes with a high pore-density while maintaining a narrow PSD. We exposed highly porous graphene (SLG treated by  $O_2$  plasma) with a broad PSD to graphene synthesis CVD condition in the presence of both CH<sub>4</sub> and CO<sub>2</sub>. It seemed that the pore expansion (as a result of etching) and shrinkage (as a result of growth) reached a comparable rate. Additionally, CO<sub>2</sub> suppressed nucleation of graphene grain and enabled the synthesis of high-quality graphene at temperatures below 800 °C by further removing the imperfect graphene lattice and carbon contaminations during the synthesis process. The CH<sub>4</sub>/CO<sub>2</sub> ratio was optimized at 800 °C yielding membranes with H<sub>2</sub> permeance reaching 10000 GPU in combination with an attractive H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> selectivity of 26.

# 4.1. Introduction

A thorough understanding of graphene growth and etching interplay during the CVD process is imperative to synthesizing high-quality SLG and modifying SLG properties to realize its potential in various applications.<sup>83</sup> Choubak et al. was one of the first to systematically investigate the interplay of CH<sub>4</sub> (as the C precursor) and O<sub>2</sub> (as the etching agent) and proved that minuscule amount of O<sub>2</sub> in the CVD system (due to air leakage from the atmosphere into the CVD reactor) leads to etching of graphene when the CH<sub>4</sub> flow is cut off and an adequate amount of H<sub>2</sub> flow is not provided to counterbalance the etching effect of O<sub>2</sub>.<sup>87,227</sup> Moreover, our previous study on the defect formation during CVD synthesis of SLG demonstrated that higher O<sub>2</sub> leak into the CVD system leads to the synthesis of SLG with higher defect density, which can be used in gas-sieving membrane fabrication.<sup>18</sup> Furthermore, O<sub>2</sub> leak into the CVD reactor introduces atomic O on the Cu surface, leading to a higher graphene growth rate by lowering the energy barrier of CH<sub>4</sub> decomposition and passivating the Cu surface active sites.<sup>82,195</sup>

To the best of our knowledge, the only study on CH<sub>4</sub>-CO<sub>2</sub> interplay in SLG synthesis was published by Strudwick et al. in 2015.<sup>228</sup> They investigated the effect of CO<sub>2</sub> in graphene synthesis and reported that presence of CO<sub>2</sub> during the Cu foil annealing and the graphene crystallization enhances the SLG quality by removing the existing and emerging carbon contaminations and etching the imperfect graphene deposited during the crystallization step. They suggested a novel SLG synthesis method based on pulsed CH<sub>4</sub> and CH<sub>4</sub>-CO<sub>2</sub> gas mixture flow during the graphene growth process. However, several critical aspects of the CH<sub>4</sub>-CO<sub>2</sub> interplay during the SLG crystallization are still unexplored: a) CO<sub>2</sub> impact on SLG crystallization kinetics, b) effect of temperature in CH<sub>4</sub>-CO<sub>2</sub> CVD chemistry, c) CH<sub>4</sub>-CO<sub>2</sub> interplay in nanometer-size pores of N-SLG, and d) definitive role of CO<sub>2</sub> in SLG crystallization.

Elucidating the above-mentioned elements could significantly benefit the 2D membrane community. In particular, SLG is predicted to play a significant role in shaping the future of membrane separation due to its ultimate thinness, flexibility, mechanical strength, and chemical stability.<sup>7,8</sup> However, pristine SLG is inherently impermeable even to He.<sup>15</sup> Thus, incorporating a high density of pores with narrow PSD in SLG is crucial for membrane fabrication. Common methods of graphene perforation fell short in fabricating a high density of uniformly-sized nanopores pores as the existing pores continue to expand while new pores are introduced in the graphene lattice.<sup>37,136</sup> It is reported that presence of an insignificant fraction of large nanopores will deteriorate the membrane selectivity.<sup>47</sup> The majority of the gas flux will pass through the larger pores due to their lower energy barrier. Hence, tuning the pore size in graphene is of utmost importance to effectuate various separation applications.

Recent efforts in SLG membrane development have been focused on eliminating the trade-off between pore-density and PSD by decoupling the pore nucleation and expansion. In the bottom-up approach, the density of the sub-nanometer size pores was increased by tuning the CVD parameters, mainly by decreasing the CVD temperature.<sup>25,26</sup> Moreover, various top-down approaches were explored to obtain greater control over the PSD. O'Hern et al. and Cheng et al. utilized ion bombardment to nucleate high density of vacancy defects in SLG film and subsequently expanded them by oxidative etching in an acidic potassium permanganate solution.<sup>27,28</sup> These resulted in N-SLG membranes suitable for ion separation and nanofiltration as the membranes' mean pore size were larger than what is required in gas-sieving applications. Recently, our group demonstrated a two-regime etching method utilizing multipulse millisecond O<sub>3</sub> treatment to decouple the pore nucleation and expansion for gas-sieving membrane fabrication.<sup>29</sup> Pore nucleation and expansion regimes were regulated by tuning the  $O_3$  pressure, and membranes with a permeance of up to 8730 GPU and attractive  $CO_2/N_2$ selectivity of 33.4 were reported. An alternative method could further the proficiency of the decoupling method by providing control over a broader PSD range and avoiding oxidation of the Cu substrate due to the O<sub>3</sub> treatment, thus broadening the N-SLG membrane applications. The oxidizing the Cu surface increases its surface roughness (making it impractical to be used for studying the nature and structure of the defects introduced in graphene via scanning probe microscopy techniques) and decreases the Cu catalytic activity for further graphene crystallization efforts.

Our previous report on kinetic Monte-Carlo (kMC) simulation of N-SLG synthesis in presence of CH<sub>4</sub> and CO<sub>2</sub> disclosed that the interplay between the competitive etching and growth modulates the PSD while maintaining a high pore-density.<sup>185</sup> Here, we investigate the effect of CH<sub>4</sub> and CO<sub>2</sub> flow during the SLG synthesis at the micrometer and nanometer scales and propose an alternative method to tune the PSD in N-SLG that can be applied in a simple, clean way inside the CVD reactor.

### 4.2. Methods

#### 4.2.1. Graphene synthesis

SLG on 25-µm-thick 99.8% purity Cu foil from *Alfa Aesar* was synthesized utilizing the LPCVD method developed by Li et al.<sup>217</sup> The polycrystalline Cu foil with mixed crystallographic orientation was transformed to Cu(111) with a lower surface roughness utilizing our high-temperature annealing method prior to the synthesis process.<sup>17</sup> Enclosures

filled with pure N<sub>2</sub> gas were placed around the quartz tube connections with the vacuum and gas inlet systems to suppress the effect of O<sub>2</sub> leak from the atmosphere (Figure 4-1). Moreover, ultrapure H<sub>2</sub>, CH<sub>4</sub>, and CO<sub>2</sub> gases were passed through gas purification filters to further eliminate the effect of these impurities. Briefly, a piece of Cu foil ( $2 \times 4 \text{ cm}^2$ ) was sonicated for 5 min in acetone and IPA subsequently. Next, it was placed inside a 1-inch quartz CVD reactor. 760 Torr CO<sub>2</sub> for 30 min at 1000 °C was used to remove the organic contaminations<sup>228</sup> before filling the reactor with 760 Torr H<sub>2</sub>/Ar (1:10) mixture. The sample was heated to and maintained at 1075 °C for 1 h before slowly cooling it down to 1000 °C for the subsequent 30 min of H<sub>2</sub> annealing at 80 mTorr (8 sccm of H<sub>2</sub>). Then, 24 sccm of CH<sub>4</sub> was added for 30 min to synthesize the SLG film. Finally, while maintaining the H<sub>2</sub> flow, the sample was quickly cooled down to room temperature before taking it out of the reactor.



Figure 4-1. Schematic of the homemade CVD system.

#### 4.2.2. CO<sub>2</sub> etching

 $CO_2$  etching was performed inside the same CVD reactor used for SLG synthesis. The connections of the quartz tube with the vacuum and gas inlet systems were enclosed inside cylinders with pure N<sub>2</sub> flow to eliminate the effect of O<sub>2</sub> leak from the environment to the CVD reactor (Figure 4-1). In addition, both CH<sub>4</sub> and CO<sub>2</sub> gases passed through the ultraclean gas

filters from *PerkinElmer* to further eliminate the effect of O<sub>2</sub> impurities. H<sub>2</sub> was produced onsite by *NM-500 plus* hydrogen generator and passed through the triple O<sub>2</sub>, H<sub>2</sub>O, and hydrocarbon ultra-clean gas filter from *PerkinElmer* before entering the CVD system. The micrometer size pores in SLG were created utilizing the CO<sub>2</sub> etching method described in chapter 3. Briefly, after cutting off the CH<sub>4</sub> flow at the end of the SLG synthesis, the sample was kept in an H<sub>2</sub> environment at 1000 °C for 3 min to stop the crystallization and reach equilibrium. Next, 500 mTorr CO<sub>2</sub> was introduced to the system while retaining 300 mTorr H<sub>2</sub> partial pressure. Finally, the sample was moved outside the heating zone to stop the reaction after the desired etching duration.

#### 4.2.3. Regrowth by CH<sub>4</sub>-CO<sub>2</sub>

CH<sub>4</sub>-CO<sub>2</sub> regrowth process was performed inside the same CVD reactor used for both SLG synthesis and CO<sub>2</sub> etching. The regrowth process followed one of the below procedures based on the initial condition of the sample.

- a) For samples hosting micrometer size pores: after creating the pores by CO<sub>2</sub> etching, they were cooled down to and kept at 800 °C for 3 min in an H<sub>2</sub> environment to let the system reaches a uniform temperature profile. Next, various ratios of methane to carbon dioxide along with 185 mTorr H<sub>2</sub> were introduced to the system for the desired duration before moving the samples outside the heating zone to stop the reaction.
- b) For O<sub>2</sub> plasma-treated N-SLG samples: the system was evacuated to  $< 10^{-3}$  Torr and purged with H<sub>2</sub> four times after placing the samples inside the CVD reactor. Next, the samples were heated to and maintained at 600 °C for 30 min in 760 Torr H<sub>2</sub> to desorb the surface contaminations coming from the environment during the plasma treatment step. Then, the system was heated to and kept at 800 °C for 3 min to reach a uniform temperature profile before performing the rest of the process as written in section a.

#### 4.2.4. O<sub>2</sub> plasma treatment

O<sub>2</sub>-plasma treatment was carried out by a 13.56 MHz *MTI EQ-PCE-3* plasma generator at 17 W. The chamber was fully evacuated and purged with O<sub>2</sub> three times before stabilizing the

system at 50 mTorr by controlling the  $O_2$  flow. Then, plasma was generated for the desired duration to introduce pores in the SLG sample.

#### 4.2.5. Membrane fabrication

N-SLG membranes were fabricated using a PTMSP-assisted method reported in our previous study.<sup>194</sup> Briefly, a thin layer of PTMSP was coated on top of N-SLG on Cu by spin-coating. This layer supports the membrane and prevents crack formation in N-SLG film during the transfer steps. For this, graphene on Cu was covered with 1.25 wt% PTMSP solution in toluene, followed by spinning at 1000 rpm for 30 s, and then 2000 rpm for an additional 30 s. Next, the sample was dried in ambient conditions for 12 h, and then in a vacuum environment for an additional 12 h at 30 °C. Then, the underlying Cu foil was etched by 1 M FeCl<sub>3</sub> solution. Afterward, the PTMSP/N-SLG film was transferred to a 10 wt% HCl bath to remove the remaining FeCl<sub>3</sub> molecules. Finally, the film was repeatedly rinsed with deionized (DI) water before transferring it onto a porous tungsten support. SEM images of the W support and optical image of a N-SLG membrane on W support are shown in Figure 4-2.



Figure 4-2. (a) Low and (b) high magnification SEM images of the polished porous W support. (c) Optical image of the PTMSP-supported N-SLG membrane on the W support.

#### 4.2.6. AC-HRTEM sample preparation

N-SLG samples for AC-HRTEM analysis were prepared using our recently published strategy that uses a lacey carbon film assisted transfer to minimize transfer-related contaminations and a 900 °C cleaning step in a reducing atmosphere inside an activated carbon bed to remove atmospheric and synthesis-related contaminations.<sup>218</sup> Briefly, a lacey polybenzimidazole copolymer film (*Fumion*® *AM* provided by *FUMATECH BWT GmbH*, *Germany*) was fabricated on top of a sacrificial Cu foil using non-solvent induced phase separation. Then, the

Cu foil was etched using a 1 M FeCl<sub>3</sub> solution, and the floating lacey copolymer film was washed with 1M HCl and DI water, respectively. Next, the floating film was fished with the Cu foil containing the targeted N-SLG sample. The lacey copolymer film on top of the N-SLG was dried overnight at room temperature. Afterward, the sample was treated at 500 °C in a reducing atmosphere to convert the lacey film into an amorphous carbon lacey film. The resulting lacey carbon interacts strongly with the N-SLG and is ideal for HRTEM imaging as it conducts heat efficiently. Subsequently, the Cu foil was etched, and the floating lacey carbon-supported N-SLG was washed with DI water and transferred to a 400-mesh TEM grid. Finally, the TEM grid containing the lacey carbon-supported N-SLG was treated at 900 °C for 1 h in a reducing atmosphere inside an activated carbon bed (800 Torr of H<sub>2</sub>; the overpressure during this step prevents O<sub>2</sub> molecules from leaking into the system).

#### 4.2.7. Characterization

SEM images were acquired by *FEI Teneo* scanning electron microscope at an operating voltage of 1 - 2 kV, an operating current of 25 pA, and a working distance of 5 - 7 mm. In-column T3 secondary-electron detector was used to take the high-contrast graphene-Cu surface images. ImageJ was used to analyze the SEM images and measure the graphene growth rates.

Raman spectroscopy was done by *Renishaw inVia*<sup>TM</sup> confocal spectroscope equipped with a 457 nm excitation laser and *ZEISS Plan-Apochromat 63X/1.4 Oil DIC* objective. The combination of 457 nm laser and *ZEISS Plan-Apochromat 63X/1.4 Oil DIC* objective resulted in a spatial resolution of 200 nm, calculated by the  $0.61\lambda$ /NA equation. Where  $\lambda$  is the wavelength of the laser, and NA is the numerical aperture of the objective. The laser power was kept below 1 mW to prevent damaging the samples due to localized heating. Samples were first transferred onto SiO<sub>2</sub>/Si substrates using the common PMMA transfer method.<sup>219</sup> Briefly, 950 PMMA solution in anisole from *Microchem* was spin-coated on the sample at 1000 and 2000 rpm for 1 min each. Then, it was heated at 70 °C for 30 min. After etching the Cu foil by 0.5 M Na<sub>2</sub>SO<sub>4</sub> solution and rinsing the PMMA/graphene film with DI water, the floating film was picked up by an O<sub>2</sub>-plasma-treated SiO<sub>2</sub>/Si substrate. The sample was dried in air overnight, and it was heated at 150 °C and 190 °C for 10 min each map. The 2D peak intensity and  $I_{D}/I_G$  and  $I_{2D}/I_G$  ratios were calculated by subtracting the background and curve fitting the 2D, G, and D peaks in MATLAB.

AC-HRTEM was carried out with a double-corrected *Titan Themis 60-300 (FEI)* equipped with a Wein-type monochromator using an 80 keV incident electron beam to reduce the electron radiation damage. The electron beam was monochromated to reduce the effects of chromatic aberration, and a negative Cs of ~18–21 µm with a slight over-focus was used to give a "bright atom" contrast in the images. Typically, the lattice experienced a total dose of ~  $2 \times 10^5$  e<sup>-</sup> Å<sup>-2</sup> during focusing and imaging. When needed, the images were processed with a band-pass filter to make the lattice clearer. ImageJ was used to analyze AC-HRTEM images and measure the pore size and density.

Gas permeation tests were performed in a homemade permeation setup consisting of a leaktight membrane module (details are available in our previous report<sup>16</sup>). A schematic of the membrane testing setup is shown in Figure 4-3. Briefly, the porous W supporting the graphene membrane acted as a gasket between *Swagelok* VCR fittings, and the setup was kept inside a temperature-controlled oven. Ar at 1 bar was used as the sweep gas, and the feed gas was kept at 2 bar. The single-gas permeation measurements were carried out for H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub>, and C<sub>3</sub>H<sub>8</sub> gases. A pre-calibrated *Hiden Analytical HPR-20* mass spectrometer was used to analyze the permeate stream. Membranes were heated to and maintained at 150 °C to desorb the atmospheric surface contaminants before measuring their permeance.



Figure 4-3. A schematic of the membrane testing setup.

### 4.3. Results and discussion

The SLG on polycrystalline Cu foil was synthesized by the CVD method developed by Li et al.<sup>61</sup> Although CO<sub>2</sub> etching rate is not dependent on the Cu crystallographic orientation, a preferential crystallographic orientation is a must to achieve a uniform graphene growth rate on the Cu substrate as the diffusion rate of the carbon species on the Cu surface and the CH<sub>4</sub> adsorption energy and its subsequent decomposition vary on different Cu crystallographic orientations.<sup>192,208</sup> Thus, Cu foil was treated by our high-temperature annealing method prior to SLG synthesis to transform the rough mixed-oriented Cu foil to (111) orientation with a lower surface roughness.<sup>17</sup> The SLG synthesis and the subsequent regrowth experiments were done on Cu foils inside the same homemade CVD system, thus simplifying the process and preventing complications arising from sample mishandling between various equipment and transferring graphene to another substrate. The schematic of the CVD system is shown in Figure 4-1.

The SLG net growth rate strongly depended on the methane to carbon dioxide ratio (denoted by  $M_xC_y$  where x/y indicates methane to carbon dioxide ratio). The interplay of growth and etching at various  $M_xC_y$  conditions at 1000°C are presented in Figure 4-4. After annealing the Cu foil in H<sub>2</sub>, Cu foil was exposed to CH<sub>4</sub> and H<sub>2</sub> for 10 s at the typical LPCVD condition to crystallize graphene domains before introducing CO<sub>2</sub>. It was followed by 30 min of exposure to CH<sub>4</sub>, CO<sub>2</sub>, and H<sub>2</sub> at M<sub>1</sub>C<sub>1</sub>, M<sub>1</sub>C<sub>3</sub>, and M<sub>1</sub>C<sub>5</sub> conditions while maintaining the same H<sub>2</sub> and CH<sub>4</sub> partial pressures. M<sub>1</sub>C<sub>1</sub> resulted in a continuous graphene film, and M<sub>1</sub>C<sub>3</sub> and M<sub>1</sub>C<sub>5</sub> resulted in graphene grains with a mean size of  $1.39 \pm 0.08 \ \mu m$  and  $1.32 \pm 0.08 \ \mu m$ , respectively. Unless otherwise specified, all further regrowth experiments were carried out at 800 °C to find a balance between growth and etching rates while slowing down the reactions to control the outcome better and investigate the effects of x/y ratio and reaction duration. Both graphene growth and CO<sub>2</sub> etching kinetics strongly depend on the temperature, accelerating at higher temperatures.<sup>174,229</sup>



Figure 4-4. SEM images of the graphene grown by 10 s LPCVD condition  $(M_1C_0)$  at 1000 °C followed by 30 min of exposure to (a)  $M_1C_1$ , (b)  $M_1C_3$ , and (c)  $M_1C_5$  ratio at 1000 °C. (d) Optical image of the sample shown in panel (b) after annealing at 200 °C for 2 min in air. Bright spots are the graphene grains, and the darker area is oxidized Cu foil.

SEM of regrown SLG on Cu foil at various  $M_xC_y$  conditions at 800 °C revealed a similar graphene net growth rate dependence. First, micron-sized faceted pores were etched at 950 °C in freshly synthesized SLG utilizing the method described in chapter 3 (Figure 4-5a). This was done by exposing the SLG film on Cu foil to CO<sub>2</sub> to expand the graphene intrinsic defects immediately after synthesis. Next, the temperature was quickly lowered to 800 °C in the H<sub>2</sub> atmosphere before introducing various  $M_xC_y$  condition to start the reaction. The reaction was maintained for 15 min before cooling down the sample rapidly to terminate the synthesis. In the absence of CO<sub>2</sub> (M<sub>1</sub>C<sub>0</sub>), crystallization occurred at the edges of the previously etched pores and new graphene grains were nucleated inside the etched pores, where bare Cu surface was exposed (Figure 4-5b). We observed that the number of new nuclei depended on the available bare Cu surface, resulting in more nucleation events inside the bigger pores (Figure 4-6).



Figure 4-5. SEM images of the etched pores in freshly synthesized SLG (a) before regrowth and after 15 min regrowth at (b)  $M_1C_0$ , (c)  $M_1C_{0.2}$ , (d)  $M_1C_{0.3}$ , (e)  $M_1C_{0.5}$ , (f)  $M_1C_1$ , and (g)  $M_1C_2$  conditions. h) The observed net crystallization rate in various  $M_xC_y$  conditions.

On the contrary, introducing CO<sub>2</sub> during the regrowth process suppressed graphene nucleation (Figure 4-5c-g). This was observed in all conditions with net positive CO<sub>2</sub> partial pressure. The carbon-etching nature of CO<sub>2</sub> prevented localized precursor supersaturation and the subsequent graphene nucleation. Generally, nucleation occurs as a result of active carbon supersaturation on the Cu surface.<sup>81</sup> Graphene nucleation and its suppression is a well-studied subject. Researchers demonstrated that presence of atomic oxygen on the surface of the Cu substrate suppresses the nucleation.<sup>19,82</sup> However, previous XPS reports on Cu surface before and after exposure to CO<sub>2</sub> at up to the tested temperature of 1060 °C illustrated that CO<sub>2</sub> does not oxidize the Cu surface, thus, dismissing this explanation in our case.<sup>174</sup> The extent of existing carbon

contamination on the Cu surface is another factor that affects the nucleation rate.<sup>83</sup> In our case, all samples were kept inside the CVD system during the whole process, from the initial SLG film synthesis to the pore expansion by  $CO_2$  exposure and the subsequent regrowth process. In addition,  $CO_2$  was used to clean the Cu surface before the initial SLG film synthesis and etch the faceted pores before the regrowth process, further eliminating the effect of the existing carbon contamination. The third reported reason is the difference in surface roughness of the Cu surface. A smoother Cu surface leads to a lower nucleation density.<sup>84</sup> This does not concern our experiments as all samples were treated in the same manner during the entire study. Lastly, faster growth rate is known to decrease the nucleation rate by decreasing the duration of the crystallization and consequently lowering the possibility of nucleation.<sup>195</sup> Nonetheless, we observed similar and lower growth rate in presence of  $CO_2$  compared to  $M_1C_0$  condition, nullifying this explanation in our experimental condition.



Figure 4-6. SEM image of the SLG on the Cu foil after exposing to the  $M_1C_0$  regrowth condition at 800 °C for 15 min, showcasing exposed-Cu-area dependent graphene nucleation.

The net crystallization rate decreased by increasing the CO<sub>2</sub> partial pressure (from  $M_1C_0$  to  $M_1C_2$ ), as shown in Figure 4-5h. No significant change in size of the etched pores before and after regrowth at  $M_1C_2$  condition was observed (Figure 4-5g), suggesting a balance between growth and etching rates. Additionally, the pores remained faceted, indicating no noticeable growth from the pore edges.



Figure 4-7. Typical Raman spectra of SLG grown from <sup>12</sup>CH<sub>4</sub> and <sup>13</sup>CH<sub>4</sub>.

The combination of carbon isotope labeling and Raman spectroscopy mapping was used to elucidate the regrowth process and to better understand the roles of CH<sub>4</sub> and CO<sub>2</sub>. First, micronsized pores were created in freshly synthesized SLG (from <sup>12</sup>CH<sub>4</sub> precursor). Next, <sup>13</sup>CH<sub>4</sub> was used to regrow the pores at 800 °C. The M<sub>1</sub>C<sub>0</sub> and M<sub>1</sub>C<sub>0.5</sub> conditions were used to compare the outcome and isolate the role of CO<sub>2</sub> in the regrowth process. Typical Raman spectra of SLG grown from <sup>12</sup>CH<sub>4</sub> and <sup>13</sup>CH<sub>4</sub> are presented in Figure 4-7. A downshift of ~100 cm<sup>-1</sup> in the 2D peak position was observed, corresponding to the inverse relation of the Raman mode frequency with the atomic mass.<sup>230</sup> More information on the combination of Raman spectroscopy and carbon isotope labeling is presented in Note 1 in Appendix I. Additionally, *I*<sub>2D</sub>/*I*<sub>G</sub> ratio of all recorded spectra of the mapped area were significantly higher than 1, confirming the single-layer nature of the synthesized graphene. SEM images of the M<sub>1</sub>C<sub>0</sub> and M<sub>1</sub>C<sub>0.5</sub> samples are shown in Figure 4-8.





The 2D peak intensity mappings of the samples after the regrowth process revealed that the carbon precursor for the  $M_1C_0$  (in the absence of  $CO_2$ ) regrowth process only came from the <sup>13</sup>CH<sub>4</sub> in the feed and not from any other carbon contamination in the reactor. Samples were treated by the regrowth process and were transferred onto a SiO<sub>2</sub>/Si substrate prior to Raman mapping. The 2D peak intensity of the samples exposed to  $M_1C_0$  condition are presented in

Figure 4-9a. The panels a-I and a-III are the Raman intensity maps of 2D<sup>12</sup>, and a-II and a-IV are the corresponding maps of 2D<sup>13</sup>. The panels a-I and a-II correspond to a short regrowth duration, and the panels a-III and a-IV correspond to a longer regrowth duration. The SLG area around the pore exhibited 2D peak position of pure <sup>12</sup>C, while the newly grown graphene domains inside the pore were characterized as pure <sup>13</sup>C. Recorded spectra at the pore edges possessed both  $2D^{12}$  and  $2D^{13}$  peaks as the laser spot size of ~200 nm limits the resolution of the mapping and probes the area consisting of both <sup>12</sup>C and <sup>13</sup>C from before and after the regrowth process, respectively. The intensity of each peak,  $2D^{12}$  and  $2D^{13}$ , is proportional to the laser spot area populated by each carbon isotope.<sup>79</sup> Confirming the SEM analysis, distinct growth of new graphene domains and crystallization of graphene from the pore edges were observed. Figure 4-9c shows the acquired spectra from various points (marked by the numbers 1 - 6 on Figure 4-9b) outside, at the edge, and inside the pore after the regrowth process. Yaxis scale for left (containing D and G peaks) and right (containing 2D peak) halves of the figure are different for better readability. Each side of the figure is normalized by the highest observed intensity (belonging to spectrum 6). Spectrum 1 was acquired from the new graphene domain grown by the regrowth process and matched the Raman spectrum of the pure <sup>13</sup>Cgrown SLG. On the contrary, spectrum 6 that was acquired from outside the pore displayed the pure  ${}^{12}$ C-grown SLG characteristics. Spectra 2 – 5 were collected at the pore edges and exhibited a mixture of <sup>12</sup>C and <sup>13</sup>C isotopes.



Figure 4-9. (a) Raman map of 2D peak intensity in  $M_1C_0$  condition for  ${}^{12}C$  and  ${}^{13}C$  presented in panels I,III and II,IV, respectively. (b) Enlarged Raman map of  $2D^{13}$  peak intensity in  $M_1C_0$  condition and (c) the corresponding Raman spectra of the points marked by numbers 1 - 6 in panel b.

Likewise, the 2D peak intensity mappings of samples after the  $M_1C_{0.5}$  (presence of  $CO_2$  in the feed) regrowth process revealed that  $CO_2$  does not contribute C to the crystallization and the

carbon precursor for the  $M_1C_{0.5}$  condition only came from the <sup>13</sup>CH<sub>4</sub> in the feed. The 2D peak intensity mappings of two pores after the regrowth process with  $M_1C_{0.5}$  condition are presented in Figure 4-10a. The panels a-I and a-III are the Raman intensity maps of  $2D^{12}$ , and a-II and a-IV are the corresponding maps of  $2D^{13}$ . Analogous to the  $M_1C_0$  condition, the 2D peak position of the SLG area surrounding the pore matched that of the SLG grown with pure <sup>12</sup>C. However, no nucleation inside the pore was observed. Graphene only grew from the pore edges, and the bare Cu was exposed in the center of the pore. Like the  $M_1C_0$  condition, the y-axis scale for left (containing D and G peaks) and right (containing 2D peak) halves of the figure are different for better readability. Each side of the figure is normalized by the highest observed intensity (belonging to spectrum 6). The presence of the pure <sup>13</sup>C-grown SLG areas inside the pore (spectra from this area matched spectrum 1) further illuminated the role of CO<sub>2</sub> in the regrowth process. Contrary to the previous report on CO<sub>2</sub> enhanced crystallization of multilayer graphene on Si nanoparticles,<sup>231</sup> CO<sub>2</sub> did not act as a growth precursor in our experiments.

Careful analysis of the six spectra (Figure 4-10c) collected from various points (marked by the numbers 1 - 6 on Figure 4-10b) outside, at the edge, and inside the pore and comparing them to the six spectra collected from M<sub>1</sub>C<sub>0</sub> condition revealed the crystallization of higher-quality SLG with lower defect-density in the presence of CO<sub>2</sub>. Analyzing 15 points inside the pores for each condition led to  $I_D/I_G$  ratio of  $0.22 \pm 0.06$  and  $0.10 \pm 0.04$  for M<sub>1</sub>C<sub>0</sub> and M<sub>1</sub>C<sub>0.5</sub> conditions, respectively.  $I_D/I_G$  ratio in graphene's Raman spectrum is a precise measure of the defect density in SLG; this ratio is proportional to the number of defects and imperfections in the graphene lattice.<sup>199</sup> It is reported that CO<sub>2</sub> selectively etches the defective graphene and amorphous carbon due to their lower reaction barrier than pristine graphene.<sup>174,180,228</sup> Thus, CO<sub>2</sub> not only suppressed graphene nucleation but also etched the imperfect graphene at the edges during the regrowth process, leading to the synthesis of higher quality graphene. This is visible by comparing spectrum 1 of both conditions shown in panel c of Figure 4-9 and Figure 4-10.



Figure 4-10. (a) Raman map of 2D peak intensity in  $M_1C_{0.5}$  condition for  $^{12}C$  and  $^{13}C$  presented in panels I,III and II,IV, respectively. (b) Enlarged Raman map of  $2D^{13}$  peak intensity in  $M_1C_{0.5}$  condition and (c) the corresponding Raman spectra of the points marked by numbers 1 - 6 in panel b.

Understanding the interaction of  $CH_4$  and  $CO_2$  in the micrometer scale provides us with valuable insight into the potential applications of this method. One such potential is the

fabrication of N-SLG membranes for various separation applications. As mentioned, N-SLG membranes, owing to their one atom thickness, can potentially surpass the performance of existing gas separation membranes.<sup>8</sup> However, almost all published methods of pore nucleation in SLG suffer from a relation between pore density and PSD because of the simultaneous pore nucleation and expansion of the existing pores.

Understanding the interplay of graphene growth and etching can help us bring forward a new method to overcome this issue. However, the growth rate in nanometer-scale pores is of orders of magnitude slower than that of micrometer size pores due to the lower catalytic Cu surface availability to decompose CH<sub>4</sub> and provide carbon precursor for graphene growth.<sup>81</sup> In addition, the CO<sub>2</sub> etching rate of the nanometer-size pores is an order of magnitude slower than that of the larger pores. Hence, an investigation into CH<sub>4</sub>-CO<sub>2</sub> interaction within nanometer-size pores is essential.

The regrowth process proved to be an effective method to tune the PSD in SLG, leading to gassieving membrane fabrication. Several membranes from N-SLG films exposed to the regrowth method with various M<sub>x</sub>C<sub>y</sub> conditions were made and tested. A schematic of the membrane testing setup is shown in Figure 4-3. First, highly porous graphene was fabricated by exposing the SLG to 6 s O<sub>2</sub> plasma to achieve a high porosity at the expense of losing the gas-sieving capability.<sup>194,214</sup> Next, the sample was placed back inside the CVD environment to regrow the larger nanopores in the presence of both CH<sub>4</sub> and CO<sub>2</sub> at 800 °C. Finally, a thin layer of PTMSP was used to mechanically reinforce the membrane before transferring it to a porous W substrate. SEM images of the W support and optical image of the N-SLG membrane on W support are shown in Figure 4-2. A schematic of the evolution of the PSD before and after regrowth treatment is presented in Figure 4-11. As the benchmark, several membranes consisting of solely PTMSP layer were made (denotes as "PTMSP" in Figure 4-12). In addition, 6 s plasma-treated SLG before the regrowth process was used to fabricate additional membranes to isolate the effect of the regrowth method (denoted as "6s plasma" in Figure 4-12). In all tested temperatures,  $M_1C_0$  (in the absence of  $CO_2$ ) membranes exhibited a similar selectivity to that of the PTMSP and 6 s plasma control samples, indicating the presence of large pores in the N-SLG that dominate the gas transport (Figure 4-12a-c). However, a significant decrease in H<sub>2</sub> permeance from PTMSP to 6s plasma membranes was observed, highlighting the role of the nonporous area of SLG as an impenetrable barrier (Figure 4-12d). Introducing a specific amount of CO<sub>2</sub> during the regrowth process increased the ideal

selectivities, reaching selectivities of ~ 7 and ~ 28 at the  $M_1C_{0.5}$  condition for  $H_2/CH_4$  and  $H_2/C_3H_8$ , respectively.



Figure 4-11. Schematic of the PSD in regrowth process in the presence of both CH<sub>4</sub> and CO<sub>2</sub>

An optimum  $M_xC_y$  condition was required to benefit from the CO<sub>2</sub> presence in the system without expanding the pores or reaching equilibrium at a larger pore size than the kinetic diameter of C<sub>3</sub>H<sub>8</sub>. A lower x/y ratio expanded the pores (or did not shrink the pores enough), resulting in membranes with similar selectivities to that of the PTMSP and 6s plasma control samples. An analogous trend was observed in micrometer-sized pores, although at a lower x/y ratio (M<sub>1</sub>C<sub>2</sub> in micrometer-sized pores compared to M<sub>1</sub>C<sub>1</sub> in nanometer-size pores). Similar behavior in H<sub>2</sub> permeance can be seen in Figure 4-12d. The minor H<sub>2</sub> permeance disparity in M<sub>1</sub>C<sub>0.2</sub>, M<sub>1</sub>C<sub>0.3</sub>, and M<sub>1</sub>C<sub>0.5</sub> samples is believed to be due to the plasma-induced defect density fluctuations at the step prior to the regrowth process. The permeance and ideal selectivity of these membranes are available in tabular format in Table 4-1 in Appendix I. Moreover, regrowth in the presence of CO<sub>2</sub> lowered the defect density of the samples compared to that of the M<sub>1</sub>C<sub>0</sub> condition and plasma-treated samples and improved the graphene crystallinity (Figure 4-12e). These results are based on the single component permeance through the membranes, representing their ideal selectivity. Mixture separation tests could be performed to investigate the effect of component adsorption on the graphene surface.<sup>16</sup>



Figure 4-12. Gas pair ideal selectivity of various samples at (a) 25 °C, (b) 100 °C, and (c) 150 °C. (d) The corresponding H<sub>2</sub> permeance of the presented samples in panels a-c at 25, 100, and 150 °C. (e) The corresponding Raman spectroscopy analysis of the samples mentioned in the panels a-d.

We chose the  $M_1C_{0.5}$  regrowth condition, which resulted in the highest  $H_2/C_3H_8$  selectivity, to investigate the evolution of the mean pore size by time. Two to three membranes were made for each condition by varying the regrowth duration from 3 to 30 min (Figure 4-13). In all tested temperatures, selectivity was increased by prolonging the regrowth process, reaching its highest value in the 10 min sample and remaining comparable for the longer treatment. It seemed that the pore shrinkage (as a result of growth) and pore expansion (as a result of etching) reached a balance by 10 min. The permeance and ideal selectivity of these membranes are available in tabular format in Table 4-2 in Appendix I. Furthermore, the H<sub>2</sub> permeance decreased significantly from 10 min- to 30 min-treated membranes (Table 4-2 in Appendix I). We believe this could be due to amorphous carbon deposition on the N-SLG surface, thus increasing the resistance in the path of the H<sub>2</sub> molecules. More discussion on the amorphous carbon deposition is provided below.



Figure 4-13. Gas pair ideal selectivity of the  $M_1C_{0.5}$  samples with various regrowth duration (a) 25 °C, (b) 100 °C, and (c) 150 °C.

AC-HRTEM imaging revealed a clear shift in PSD of the regrown samples, indicating successful shrinking of the pores. Three conditions (6 s plasma and 3 and 8 min  $M_1C_{0.5}$  regrowth) were chosen to image and analyze (Figure 4-14). Analysis of the AC-HRTEM images of the control sample, 6 s plasma or 0 min regrowth, revealed a lognormal PSD with a mean pore size (arithmetic average of the pore diameters) of  $2.4 \pm 1.7$  nm (Figure 4-14a). Several large nanopores up to ~ 10 nm were observed. Samples treated by  $M_1C_{0.5}$  regrowth process for 3 and 8 min had progressively smaller pores with mean pore sizes of  $2.0 \pm 1.8$  nm and  $1.1 \pm 1.5$  nm, respectively (Figure 4-14b and Figure 4-14c, respectively).



Figure 4-14. TEM images of the 6 s plasma-treated SLG before the regrowth process and the corresponding PSD. TEM images of the 3 min and 8 min  $M_1C_{0.5}$  regrowth processes and their corresponding PSD shown in (b) and (c), respectively.

The larger pores at the tail of the PSD curve were eliminated after the regrowth process, resulting in a narrower PSD. The AC-HRTEM observations corroborated the previously presented membranes' performances, in which  $H_2/CH_4$  and  $H_2/C_3H_8$  selectivities rose after 8 min  $M_1C_{0.5}$  regrowth process and reached their maximum in the 10 min sample. Recent works illustrated that presence of a small fraction of large pores eradicates the membrane

performance, and the majority of the gas molecules flow through these large pores.<sup>47,188</sup> Consequently, eliminating the big pores at the tail of the PSD curve is of utmost importance.

Furthermore, graphene crystallization at the pore edges followed the same grain orientation as their surroundings, and the graphene lattice was as perfect as the graphene grown at 1000 °C. As discussed,  $CO_2$  can etch the defective and imperfect graphene at the edges, leading to the crystallization of high-quality SLG even at temperatures below 1000 °C.

Comparing the growth rate in nanometer-sized pores (obtained from AC-HRTEM images) to the growth rate in micrometer-sized pores (obtained from SEM images) revealed ~200-fold slower rate for smaller pores (0.15 nm/min and 30 nm/min for nanometer and micrometer size pores, respectively). This is expected as both graphene growth and etching are expected to have much lower rates in nanometer-size pores (refer to the previous discussion for details).



Figure 4-15. AC-HRTEM images of the regrown SLG at  $M_1C_{0.5}$  condition at 800 °C for (a) 3 min and (b) 10 min, displaying the higher amount of the amorphous carbon on the graphene surface.

Further analysis of the AC-HRTEM images of the 3 and 8 min  $M_1C_{0.5}$  samples unveiled a higher level of amorphous carbon contamination on the surface of the longer treated sample (Figure 4-15). A combination of lower than typical CVD temperature<sup>81</sup> and limited available catalytic Cu surface could have led to the amorphous carbon deposition on the graphene surface. It is reported that amorphous carbon can form on the graphene surface during the CVD process via gas-phase reaction of carbon species and adsorption of the gas phase formed clusters on the Cu and graphene surface.<sup>232</sup> Amorphous carbon progressively captures the available carbon species during the CVD process, thus increasing its surface coverage. In addition, decreasing the catalytic activity of the Cu substrate is reported to increase the amorphous carbon deposition by insufficient decomposition of the carbon species.<sup>233</sup>

## 4.4. Conclusion

This study establishes a novel method to tune the PSD of the nanopores in SLG using the competitive nature of graphene growth and etching. Exposing a highly porous SLG film with a broad PSD to our regrowth process (in the presence of  $CH_4$  as the growth agent and  $CO_2$  as the etching agent) revealed that the graphene net crystallization rate is strongly dependent on the methane to carbon dioxide ratio. At a certain temperature, an optimum  $M_xC_y$  condition to achieve the desired pore size with the narrowest PSD exists, and it represents the equilibrium between growth and etching at a particular pore size.

 $CO_2$  suppresses the graphene nucleation by preventing the localized supersaturation of C species while increasing the quality of the synthesized graphene film by etching away the imperfect graphene edges and carbon contaminations during the synthesis process. In addition, utilizing carbon isotope labeling and Raman spectroscopy, we demonstrated that the C precursor for the graphene crystallization only comes from the CH<sub>4</sub> in the feed and not from the CO<sub>2</sub> or the existing carbon species on the surface of the graphene or inside the CVD reactor.

This method could solve the longstanding issue of decoupling the pore nucleation and expansion in large-scale N-SLG membrane fabrication, advancing these membranes one step closer to their scale-up and commercialization.

# **Appendix I**

#### Note 1. Carbon isotope labeling and Raman spectroscopy analysis

The combination of carbon isotope labeling and Raman spectroscopy mapping is a powerful tool to study the graphene growth process by analyzing the spatial distribution of methane precursors (<sup>12</sup>CH<sub>4</sub> and <sup>13</sup>CH<sub>4</sub>).<sup>230,234</sup> The Raman mode frequency of a mixture of <sup>12</sup>C and <sup>13</sup>C can be calculated using the following equation.<sup>235</sup>

$$\omega = \omega_{12} \sqrt{\frac{m_{12}}{n_{12}m_{12} + n_{13}m_{13}}}$$
 Equation 4.1

where  $\omega$  is the Raman mode frequency of mixed isotopes,  $\omega_{12}$  is the Raman mode frequency of <sup>12</sup>C,  $m_{12}$  and  $m_{13}$  are the atomic masses of <sup>12</sup>C and <sup>13</sup>C, respectively; and  $n_{12}$  and  $n_{13}$  are the atomic fractions of <sup>12</sup>C and <sup>13</sup>C, respectively. Utilizing the inverse relation of the frequencies of the Raman modes with the atomic mass, a downshift of  $\sqrt{12/13}$  for the Raman spectrum of <sup>13</sup>C compared to that of <sup>12</sup>C can be observed, which results in ~100 cm<sup>-1</sup> downshift in 2D peak position.

		Permeance (GPU)					Idea selectivity		
Sample	T (°C)	H <sub>2</sub>	CH4	CO <sub>2</sub>	N2	C3H8	H <sub>2</sub> /CH <sub>4</sub>	H <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	CO <sub>2</sub> /N <sub>2</sub>
PTMSP 1	150	78932	35903	54916	14859	22288	2.2	3.5	3.7
	100	76146	40789	73207	14429	22599	1.9	3.4	5.1
	25	64152	45654	125958	13125	17845	1.4	3.6	9.6
	150	72835	34235	52792	14092	21395	2.1	3.4	3.7
PTMSP 2	100	70053	38390	70827	13632	20910	1.8	3.4	5.2
	25	58912	43130	124496	13382	16903	1.4	3.5	9.3
	150	68701	29043	56678	16086	27387	2.4	2.5	3.5
PTMSP 3	100	65827	30024	73986	15912	27326	2.2	2.4	4.6
	25	49331	29718	113893	12779	27227	1.7	1.8	8.9
	150	39658	15520	27787	7923	9786	2.6	4.1	3.5
6s plasma 1	100	37035	15838	40664	7624	9730	2.3	3.8	5.3
	25	29500	17107	62394	7235	9028	1.7	3.3	8.6
	150	30190	12271	20191	5721	7728	2.5	3.9	3.5
6s plasma 2	100	29158	12471	26943	5580	7452	2.3	3.9	4.8
	25	24619	13845	41403	5344	7054	1.8	3.5	7.7
	150	27905	13217	18944	6364	8158	2.1	3.4	3.0
M1C0 1	100	27166	14995	25306	6696	8496	1.8	3.2	3.8
	25	25637	19778	47766	7413	8971	1.3	2.9	6.4
	150	29980	13034	17534	6833	7820	2.3	3.8	2.6
M1C0 2	100	29410	14779	22633	7276	8356	2.0	3.5	3.1
	25	28416	18887	41405	7804	8709	1.5	3.3	5.3

Table 4-1. Permeance and ideal selectivity of the membranes made in this study.

	150	25961	10241	19652	5835	9175	2.5	2.8	3.4
M1C0 3	100	24666	11636	26573	6113	8987	2.1	2.7	4.3
	25	21155	13354	46327	5969	8307	1.6	2.5	7.8
	150	8342	2085	4741	1020	998	4.0	8.4	4.6
M1C0.2 1	100	6422	1630	4985	740	709	3.9	9.1	6.7
	25	3138	737	5000	451	353	4.3	8.9	11.1
	150	3528	1493	2009	610	965	2.4	3.7	3.3
M1C0.2 2	100	3425	1664	2617	628	910	2.1	3.8	4.2
	25	3191	2143	4805	686	799	1.5	4.0	7.0
	150	11599	3913	6822	1531	2208	3.0	5.3	4.5
M1C0.3 1	100	9503	3616	7876	1279	1785	2.6	5.3	6.2
	25	6259	3200	11238	1083	1104	2.0	5.7	10.4
M <sub>1</sub> C <sub>0.3</sub> 2	150	8709	2316	4403	1113	944	3.8	9.2	4.0
	100	6876	1824	4549	920	728	3.8	9.4	4.9
	25	3463	950	4655	590	377	3.6	9.2	7.9
	150	10174	1569	3336	792	380	6.5	26.8	4.2
M1C0.5 1	100	8686	1498	4017	698	379	5.8	22.9	5.8
	25	5873	1095	5229	448	228	5.4	25.8	11.7
	150	15292	3080	5455	1685	849	5.0	18.0	3.2
M1C0.5 2	100	14141	3400	7219	1715	1036	4.2	13.6	4.2
	25	13501	4463	14233	1853	1049	3.0	12.9	7.7
	150	10829	1617	3441	890	1174	6.7	9.2	3.9
M1C0.5 3	100	9217	1548	4041	777	940	6.0	9.8	5.2
	25	6166	1149	5670	532	393	5.4	15.7	10.7
	150	30931	14642	25093	7155	6837	2.1	4.5	3.5
M1C1 1	100	27477	14755	30091	6593	5927	1.9	4.6	4.6
	25	19431	12594	47653	4645	3133	1.5	6.2	10.3
	150	33907	10970	23501	5556	9025	3.1	3.8	4.2
M <sub>1</sub> C <sub>1</sub> 2	100	28452	10980	28875	5381	8369	2.6	3.4	5.4
	25	21466	10754	46034	4354	5176	2.0	4.1	10.6

		Permeance (GPU)					Idea selectivity		
Sample	T (°C)	$H_2$	CH4	CO <sub>2</sub>	<b>N</b> 2	C3H8	H <sub>2</sub> /CH <sub>4</sub>	H <sub>2</sub> /C <sub>3</sub> H <sub>8</sub>	CO <sub>2</sub> /N <sub>2</sub>
	150	32485	14089	24442	7197	8284	2.3	3.9	3.4
3 min 1	100	31359	14525	31247	6755	7304	2.2	4.3	4.6
	25	24995	14377	49986	5470	6428	1.7	3.9	9.1
	150	31348	12953	23231	6747	7153	2.4	4.4	3.4
3 min 2	100	30372	13301	29651	6295	6099	2.3	5.0	4.7
	25	24823	14230	51850	6432	5583	1.7	4.4	8.1
	150	21181	8896	14692	3966	6249	2.4	3.4	3.7
3 min 3	100	20978	10198	19942	4086	6010	2.1	3.5	4.9
	25	19210	12428	36081	3966	5051	1.5	3.8	9.1
	150	5750	1601	3505	735	750	3.6	7.7	4.8
5 min 1	100	4687	1327	3944	530	519	3.5	9.0	7.4
	25	3236	923	5448	322	293	3.5	11.0	16.9
5 min 2	150	8903	2943	5730	1341	1584	3.0	5.6	4.3
	100	8046	2885	5103	1179	1306	2.8	6.2	4.3
	25	6502	2827	12280	837	948	2.3	6.9	14.7
	150	13359	5484	9474	2461	3019	2.4	4.4	3.8
5 min 3	100	13099	6091	12825	2358	2553	2.2	5.1	5.4
	25	12722	7941	24593	2290	2081	1.6	6.1	10.7
	150	14691	3578	6911	1726	1604	4.1	9.2	4.0
8 min 1	100	13880	3390	6848	1025	1276	4.1	10.9	6.7
	25	10320	3159	6263	436	760	3.3	13.6	14.4
	150	18428	4661	9987	2290	1971	4.0	9.3	4.4
8 min 2	100	17472	4314	9652	1452	1534	4.0	11.4	6.6
	25	11854	3736	8814	606	834	3.2	14.2	14.5
	150	10174	1569	3336	792	380	6.5	26.8	4.2
10 min 1	100	8686	1498	4017	698	379	5.8	22.9	5.8
	25	5873	1095	5229	448	228	5.4	25.8	11.7

Table 4-2. Permeance and ideal selectivity of the membranes made from N-SLG treated by  $M_1C_{0.5}$  condition for various durations.

10 min 2	150	15292	3080	5455	1685	849	5.0	18.0	3.2
	100	14141	3400	7219	1715	1036	4.2	13.6	4.2
	25	13501	4463	14233	1853	1049	3.0	12.9	7.7
10 min 3	150	10829	1617	3441	890	1174	6.7	9.2	3.9
	100	9217	1548	4041	777	940	6.0	9.8	5.2
	25	6166	1149	5670	532	393	5.4	15.7	10.7
30 min 1	150	1604	321	552	160	111	5.0	14.4	3.4
	100	1058	256	568	117	92	4.1	11.5	4.8
	25	707	178	605	49	58	4.0	12.2	12.2
	150	1168	147	327	90	71	8.0	16.3	3.6
30 min 2	100	893	129	353	67	51	6.9	17.6	5.3
	25	338	88	362	27	16	3.8	20.7	13.7
30 min 3	150	1343	281	475	168	101	4.8	13.3	2.8
	100	1161	246	483	148	86	4.7	13.6	3.3
	25	805	192	439	42	42	4.2	19.0	10.3

# 5. Chapter 5. Summary and perspective

## 5.1. Summary of the thesis

Graphene's one-atom-thickness, high mechanical strength, chemical stability, and flexibility establish it as a compelling material for gas separation membrane fabrication. Its 2D structure provides the least resistance towards the permeating molecules leading to the highest estimated achievable permeance and its physical and chemical stability enables its operation in a broad spectrum of separation applications at harsh conditions, including high temperature and transmembrane pressure ranges. In addition, membrane processes can be conveniently retrofitted to existing infrastructures due to their simple design and steady-state operation. The development of a robust CVD-based graphene synthesis method in 2009, and more recently its roll-to-roll synthesis for high-capacity production, further cemented graphene's place as the star material for membrane fabrication. However, incorporating a high density of pores with precise, narrow PSD in SLG is essential to realize the true potential of this material due to its inherent impermeability to even the small gases such as He.

There are three primary bottlenecks in manufacturing large-scale, market-ready graphene membranes: a) reproducible, cost-effective synthesis of high-quality SLG on commercial Cu foil; b) perforation of the SLG film with a high density of nanopores with narrow PSD; and c) development of a support layer for large-scale membrane fabrication to provide mechanical support during the transfer and pressurized operation. This work focuses on solving the first two issues, advancing the graphene membranes one step closer to the industrial market.

First, we developed a straightforward crystallographic and morphological optimization method to synthesize H<sub>2</sub>-sieving high-quality SLG on low-cost commercial Cu foils consistently. This was achieved by replacing the usual annealing step in the typical CVD graphene synthesis process with a facile slow high-temperature annealing step. Membranes with reproducible attractive H<sub>2</sub>/CH<sub>4</sub>, H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub>, and H<sub>2</sub>/SF<sub>6</sub> selectivities were fabricated using the graphene film grown on the treated Cu foils. Generally, expensive high-purity Cu foils were used for gassieving-capable graphene film synthesis, hindering the graphene membranes' eventual scale-up goal due to their prohibitively high cost (16000 /m<sup>2</sup>). Our optimized graphene synthesis recipe lowered the cost of the Cu substrate down to 200 /m<sup>2</sup>. The proposed annealing process smoothened the surface of the Cu foil, decreasing its RMS roughness down to 100 nm. The

improved surface smoothness was the most influencing factor in growth of the high-quality SLG films. In addition, the Cu foils were transformed to Cu(111) after our annealing process regardless of their initial crystallographic orientation. Interestingly, no significant trend with respect to the purity of the Cu substrates was detected, suggesting further possible cost savings in the future using lower-cost Cu foils. We suspect that this could be due to the formation of a high-purity top Cu layer during the high-temperature annealing process. Finally, the ultrasmooth surface (RMS = 0.23 nm) of the single Cu step enabled us to obtain atomic-resolution STM images of the Cu surface, providing a convenient substrate to study the structure of the vacancy defects in graphene in the future.

Next, we demonstrated a controlled etching of CVD-grown SLG with CO<sub>2</sub> at various temperatures (750 – 1000 °C) and extracted the kinetics of etching, including the activation energy of the expansion of pores for the first time. We showed an etching regime that is not limited by the CO<sub>2</sub> mass transfer from bulk to the reaction sites and tuned the etching rate by adjusting the temperature and exposure duration. We proved that etching initiates from the existing defects in the graphene lattice and CO<sub>2</sub> does not nucleate new defects in the graphene basal plane (up to the tested temperature of 1000 °C) resulting in a monomodal PSD of the expanded pores, in contrast to the typical lognormal PSD achieved using common oxidative etching methods such as O<sub>2</sub>, O<sub>3</sub>, O<sub>3</sub>/UV, and H<sub>2</sub>O. Afterward, we revealed the effect of initial pore size on etching rate and energy barrier by investigating the reaction rate and CO<sub>2</sub> etching behavior at various temperatures and initial pore sizes: a) higher temperature overcomes the higher activation energy of pore expansion in smaller pores, and b) etching rate of the pores below  $\sim 2$  nm is an order of magnitude slower than that of the larger pores at the same etching condition. By visualizing the expanded pores, we displayed the origin of graphene intrinsic defects indicating that these defects were conceived by both incomplete intergrowth of misaligned graphene grains and the limited etching due to the presence of residual/leaked  $O_2$ in the reactor. Moreover, we proved that the Cu foil does not play a significant role in the CO<sub>2</sub> etching of graphene and is not essential for the etching reaction. Our findings concluded that CO<sub>2</sub> etching grants a methodology for the precision fabrication of nanostructured graphene films for various applications such as sieving membranes, sensors, and electronics.

Finally, we demonstrated a new concept of modulating the pore size in graphene by adding an etchant in the CVD reactor. We exposed a highly porous graphene film, with a wide PSD as a result of  $O_2$  plasma treatment, to the CVD environment in the presence of both growth (CH<sub>4</sub>)

and mild etching (CO<sub>2</sub>) agents. Optimizing the temperature and the partial pressures of CH<sub>4</sub> and CO<sub>2</sub> led to an equilibrium between growth and etching of the graphene edge atoms resulting in a narrow PSD while maintaining the initial high pore-density. CO<sub>2</sub> as a mild etchant was chosen as it only reacts with the existing edge atoms without nucleating new defects in the graphene basal plane. Moreover, introducing CO<sub>2</sub> during the regrowth process suppressed the graphene nucleation by preventing localized carbon supersaturation. Carbon isotope labeling revealed that the growth precursor only comes from the CH<sub>4</sub>, and CO<sub>2</sub> does not act as the C donner for the crystallization process. Furthermore, we fabricated several membranes using the graphene treated with this method and observed an optimum ratio of CH<sub>4</sub> to CO<sub>2</sub> to achieve a high H<sub>2</sub> permeance of 10000 GPU with high gas pair selectivities (H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> = 27 and H<sub>2</sub>/CH<sub>4</sub> = 6). Moreover, our regrowth method improved the graphene crystallinity by etching away the imperfect graphene during the crystallization and decreasing the graphene grain boundaries by increasing the size of the graphene domains.

In this thesis, we demonstrated a precise, controlled etching of graphene with CO<sub>2</sub> for the first time and utilized this knowledge to develop a unique regrowth CVD method to tune the PSD of the N-SLG films by competitive growth and etching of the graphene edge atoms. This method along with the proposed catalytic Cu foil optimization protocol are an important step towards reaching the eventual goal of the N-SLG membranes: reaching their true place in the gas separation field as the ultimate gas-sieving membranes.

# 5.2. Perspective

As discussed in the previous chapters, N-SLG membranes have a unique potential to become the ultimate gas sieving membranes. All the membranes presented in this dissertation were at the millimeter scale. Recently, our group demonstrated a method to fabricate centimeter-scale N-SLG membranes capable of gas-sieving.<sup>188</sup> However, there is a long road to achieve the meter-scale membranes required for industrial applications. Two major obstacles need to be addressed to obtain the final meter-scale gas-sieving membranes: a) development of a method to utilize even lower cost Cu foils for SLG synthesis without being dependent on a specific supplier, and b) development of a support layer to mechanically strengthen the membrane during the transfer process as well as operation at high transmembrane pressures differences. Here, we present the preliminary findings to address the first matter.
Even though we showed that purity of the Cu foil does not have a significant impact on the quality of the synthesized graphene via our high-temperature annealing method, big contamination particles (due to the Cu foil manufacturing processes) which might exist on the surface of these foils can have a detrimental effect on the overall membrane fabrication process.<sup>236</sup> These  $\mu$ m-size particles crack the graphene's supporting layer, consequently deteriorating the gas-pair selectivity. The density and size of these particles depend on the properties of the initial Cu source and the foil manufacturing process, varying from a vendor to another. These features are observed with higher frequency in lower-cost commercial Cu foils. Thus, developing a strategy to remove these surface contaminations prior to the synthesis process is a must to diversify the potential Cu foils suppliers and enable us to exploit the cheaper available commercial foils.

We explored several methods to tackle the contaminations including acid treatment, electropolishing, and mechanical polishing followed by acid treatment. A low-cost Cu foil from *Carl Roth AG* costing ~ 90 /m<sup>2</sup> was chosen for these experiments due to its extremely low price and availability in large size. For the acid-treated sample, the Cu foil piece was floated on a 4 wt% nitric acid bath for 10 min followed by washing with DI water. The electropolished sample was prepared by electropolishing the Cu foil for 1 min, similar to the method described here.<sup>18</sup> The last sample was prepared by first mechanically polishing the Cu surface (as described in chapter 2) and then floating the sample on the 4 wt% nitric acid bath for 10 min. All samples were placed inside the CVD reactor simultaneously and were washed by acetone and IPA prior to graphene synthesis. The SEM images of the SLG grown on these Cu foils are shown in Figure 5-1.

We observed that all treatments eliminated the large contamination particles, contrary to the graphene grown on the as-received Cu foil. We ceased further investigating the mechanical polishing followed by the acid treatment process as it was the most complex option and required new equipment for its eventual scale-up. The other samples we analyzed by probing a randomly chosen ~ 0.5 mm<sup>2</sup> area by SEM to quantify the density and size of the surface particles. The result is summarized in Table 5-1. The as-received sample contained 60 and 92 particles bigger than 2  $\mu$ m and 1  $\mu$ m, respectively. Both acid treatment and electropolishing eliminated all particles in this range. The smaller particles do not play a significant role in the performance of the fabricated membranes, as seen in our previous works.<sup>16,17,188</sup> Acid treatment

was chosen for further investigation as it was the simplest and most cost-effective option, providing a straightforward process requiring no additional equipment.



Figure 5-1. SEM images of the (a) as-received Cu foil, and graphene grown on the (b) as-received, (c) acid-treated, (d) electropolished, and (e) mechanically polished followed by acid treatment Cu foils.

Table 5-1. Quantitative analysis of the particle size distribution and density of the surface particles after graphene growth.

Sample	No. of particles per 1 mm <sup>2</sup>			
	$> 2 \ \mu m$	> 1 µm	$> 0.5 \ \mu m$	
As-received	60	92	392	
Acid-treated	0	0	126	

	Electropolished	0	0	146
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Probing the effect of each treatment on the surface roughness revealed that all treated samples displayed a lower surface roughness compared to that of the as-received sample. As discussed, surface roughness is the most influential factor (among factors related to the Cu foil) in CVDgrown graphene quality.<sup>17</sup> Result of the surface profilometry of the samples mentioned in Figure 5-1 is visualized in Figure 5-2. All samples are characterized after going through a typical graphene synthesis process to represent the actual condition used to fabricate a membrane. A  $300 \times 300 \ \mu\text{m}^2$  area was probed for each sample to properly examine its global surface roughness by inspecting the Cu foil alleys and peaks caused by the rolling process during its manufacturing. Even though annealing is proficient in smoothening the Cu foil in nm- and µm-scale, it is not enough to provide a globally smooth surface in tens or hundreds micron scale; the RMS surface roughness slightly decreased from 293 to 261 nm by annealing the Cu foil during the typical graphene synthesis condition. The RMS of the acid-treated, electropolished, and mechanically polished followed by acid treatment samples were 150, 82, and 62 nm, respectively. As discussed above, the acid treatment was chosen as the preferred option due to its simplicity and scalability. In addition, RMS of 150 nm is sufficient for highquality graphene growth suitable for H<sub>2</sub>-sieving membrane fabrication.<sup>17</sup>

Next, we explored the effect of acid treatment duration on surface roughness. The duration of the acid treatment was varied from 1 to 60 min while maintaining the other parameters fixed. Afterward, all samples were placed inside the CVD reactor simultaneously to synthesis graphene. Next, the topography and surface roughness of these samples were measured by surface profilometry similar to the above-mentioned samples. The surface roughness did not significantly differ between the 1, 5, and 10 min samples (Figure 5-3a-c). However,  $\mu$ m-sized holes appeared on the surface of the Cu foil after 20 min or longer acid treatment, increasing the global surface roughness (Figure 5-3d-f). These holes were 20 – 30  $\mu$ m wide and 0.4 – 1.45  $\mu$ m deep, thus rendering the corresponding graphene samples unacceptable for membrane fabrication. Based on these observations, we suggest the 10 min acid treatment process as the preferred option to remove all large surface particles and smoothen the Cu foil surface to obtain the optimum graphene quality for large-scale N-SLG membrane fabrication. The development of a proper support layer is needed to definitively determine the performance of the membranes derived from this treatment.



Figure 5-2. Topography and surface roughness of the (a) as-received Cu foil, and graphene grown on the (b) as-received, (c) acid-treated, (d) electropolished, and (e) mechanically polished followed by acid treatment Cu foils.



Figure 5-3. Topography and surface roughness of the CVD-grown graphene on Cu foils treated by nitric acid for (a) 1 min, (b) 5 min, (c) 10 min, (d) 20 min, (e) 30 min, and (f) 60 min.

Another path to lower the surface roughness of the Cu substrate, and thus improve the graphene quality used for fundamental research is template-stripping strategy. We prepared Cu foil by the template-stripping (TS) process.<sup>205,237</sup> For this, ca. 1- $\mu$ m-thick Cu film was deposited on a Si/SiO<sub>2</sub> wafer by a thermal evaporator (Figure 5-5a, d). Next, a 25- $\mu$ m-thick Cu film was electrodeposited (ED) on top of the thermally-deposited (TD) Cu film to improve the mechanical robustness of the film for the subsequent graphene synthesis step (Figure 5-4 and Figure 5-5b, e). An extremely smooth and shiny surface, with a local surface roughness of 0.19 Å, on a single Cu step measured by STM, was obtained by peeling off the Cu foil (Figure 5-5c,

f, and g). The grains in the as-synthesized foils were not uniformly oriented, however, they had a preference towards the (111) facet, in agreement with the literature (Figure 5-5h). The grain orientation was more or less maintained during the graphene synthesis where the foil is annealed at 1000 °C. However, similar to the observation with the commercial foils, the grain orientation converted entirely to (111) after the high-temperature annealing. Even after annealing, the foil retained its local smoothness and atomic-resolution images could be obtained (Figure 5-5i, j). Consistent with the prior observations, the combination of (111) grain orientation and extremely smooth surface led to the lowest defect-density in graphene ( $I_D/I_G =$  $0.04 \pm 0.01$ ) among all the samples in this study. These homemade foils will be highly attractive for the synthesis of graphene membranes.



Figure 5-4. Photos of the Cu electrodeposition setup.



Figure 5-5. Optical and SEM images of the thermally deposited (TD) Cu film on SiO<sub>2</sub>/Si wafer (a and d), electrodeposited (ED) Cu film on TD Cu film (b and e), and peeled-off TD-ED Cu facing the SiO<sub>2</sub>/Si wafer (c and f). g) Surface roughness measurement of the peeled-off TD-ED Cu film. (h) XRD patterns of as-synthesized, annealed at 1000 °C, and exposed to high-temperature annealing template-stripping (TS) Cu foil. (i, j) Atomic resolution STM images (bias voltage of 0.1V and tunneling current of 0.2nA) of the ultra-flat TS exposed to high-temperature annealing.

Another future direction in N-SLG membranes is further investigating the regrowth process at various temperatures to tune the PSD in a wider range with more precision, reaching attractive selectivities for various desired separations. The goal would be to find a correlation based on the operating conditions (T, P<sub>CH4</sub>, P<sub>CO2</sub>, etc.) to achieve the desired PSD. This could finally realize the true potential of the SLG as the ultimate material for membrane fabrication due to its ability to be tuned to separate any desired gas pairs while maintaining a high permeance.

Increasing the temperature of the regrowth process not only accelerates the growth and etching rates, but also allows  $CO_2$  to overcome the higher energy barrier of certain defect

configurations that was not possible to manipulate at 800 °C (refer to section 3.3 for further discussion). We have already shown that the graphene PSD can be tuned by varying the CH<sub>4</sub>:CO<sub>2</sub> ratio during the regrowth process at 800 °C. H<sub>2</sub> permeance reaching 10000 GPU in combination with the H<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> selectivity of 26 was achieved by optimizing the CH<sub>4</sub>:CO<sub>2</sub> ratio at 800 °C. Moreover, CH<sub>4</sub> can dehydrogenate faster on the Cu surface at higher temperatures and the probability of graphene growth in smaller nanopores increases leading to a smaller mean pore size suitable for H<sub>2</sub>-sieving separations or carbon capture applications. This could make N-SLG membranes an attractive option for post-combustion carbon capture (CO<sub>2</sub>/N<sub>2</sub> separation).

Indeed, the most promising option to reduce the CO<sub>2</sub> emission in Switzerland (46 million ton<sub>CO2</sub> emission in 2019 accounting for 1.6% of the European Union and 0.1% of global emissions)<sup>238</sup> is utilization of post-combustion carbon capture units that can be retrofitted to the existing facilities with possibility of treating decentralized small-scale CO<sub>2</sub> sources.<sup>2,239</sup> N-SLG membranes satisfy these criteria completely.<sup>240</sup> A recent techno-economic analysis of the post-combustion carbon capture by N-SLG membranes from flue gas (10 – 13.5% CO<sub>2</sub>) by two-stage N-SLG membranes revealed a competitive capture penalty of 30 – 40 \$/ton<sub>CO2</sub> and energy penalty of ~ 1.5 MJ/kg<sub>CO2</sub>, based on conservative membrane cost of 500 \$/m<sup>2,241</sup> Capture penalty of 28 – 46 \$/ton<sub>CO2</sub> for steel and cement industries (CO<sub>2</sub> concentration of 25%) were estimated assuming a higher electricity cost (0.20 \$/kWh) compared to the power plant (0.06 \$/kWh). In comparison, the amine-based separation processes (the current dominant technology in the CO<sub>2</sub> separation industry) possess a high capture penalty of 50 – 110 \$/ton<sub>CO2</sub><sup>239</sup> and a high required thermal energy of 3 – 4 MJ/kg<sub>CO2</sub><sup>2</sup>. In addition, these processes are not suitable for decentralized applications and suffer from amine loss and degradation.<sup>242,243</sup>

In conclusion, the two main future paths for N-SLG membranes are development towards their scale-up (Cu foil optimization and support layer development) and further tunning the PSD with more precision to cover a broad range of separations while maintaining their high permeance and selectivity.

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# **Curriculum Vitae**

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## SKILLS

Membranes, Gas Separation, CVD, Characterization techniques (SEM, STM, TEM, AFM, XRD, MS, surface profilometry), UHV, Clean room

### **EDUCATION**

**École polytechnique fédérale de Lausanne (EPFL)**, Valais, Switzerland Doctoral Assistant in **Chemistry and Chemical Engineering**, 2017-Present Thesis: Crystallization of size-selective nanopores in graphene for gas separation

**Eindhoven University of Technology (TU/e)**, Eindhoven, Netherlands Master of Science in **Chemical and Process Technology**, 2014-2016, GPA: 8.54/10 Thesis: Kinetic investigation of methanol to DME over ZSM-5 and γ-Al<sub>2</sub>O<sub>3</sub> Catalysts

University of Tehran, Tehran, Iran

Bachelor of Science in **Chemical Engineering**, 2007-2011, GPA: 17.38/20 Thesis: Modeling, simulation, and optimization of C<sub>3</sub>MR LNG Process

## ACADEMIC EXPERIENCES

École polytechnique fédérale de Lausanne (EPFL), Basic Science Department, Lausanne campus, Switzerland

• *Teaching Assistant*, 2017 -2020: Process Development I&II (4 Semesters), Equilibrium-stage Separation Processes (1 Semester)

University of Tehran, Chemical Engineering Department, Tehran, Iran

- *B.Sc. Theses Assistant Supervisor*, 2013–2014: Counseling several B.Sc. theses in Natural Gas Processing Area
- *Invited Lecturer*, 2012: Teaching a 12-hour short course on "LNG and NGL Recovery Technologies Selection"
- *Teaching Assistant*, 2011-2014: Processes of Gas Industries (4 Semesters), Application of Math in Chem. Eng. (1 Semester), Computer aided Process Simulation (1 Semester), Unit Operation II (1 Semester), Gas Transmission & Distribution (1 Semester)

## **PUBLICATIONS**

- 1. **M. Rezaei**, L. F. Villalobos, K. V. Agrawal, Competitive Etching and Growth of Graphene for Molecular Sieving, In preparation.
- 2. **M. Rezaei**, L. F. Villalobos. K-J. Hsu, K. V. Agrawal, Demonstrating and Unraveling a Controlled Nanometer-Scale Expansion of the Vacancy Defects in Graphene by CO<sub>2</sub>, Angewandte Chemie, Accepted.
- 3. **M. Rezaei**, S. Li, S. Huang, K. V. Agrawal, Crystallographic and morphological optimization of catalytic copper foil for high-quality single-layer graphene membranes, Journal of Membrane Science, 2020, 612, 118406.

- 4. S. Li, M. T. Vahdat, S. Huang, K-J. Hsu, **M. Rezaei**, M. Mounir, N. Marzari, K. V. Agrawal, Structure Evolution of Graphitic Surface Upon Oxidation: Insights by Scanning Tunneling Microscopy, JACS Au, 2022, jacsau.1c00570.
- 5. M. Dakhchoune, L. F. Villalobos, R. Semino, L. Liu, **M. Rezaei**, P. Schouwink, CD. E. Avalos, P. Baade, V. Wood, Y. Han, M. Ceriotti, K. V. Agrawal, Gas sieving zeolitic membranes fabricated by condensation of precursor nanosheets, Nature Materials, 2021, 20 (3), 262-369.
- 6. G. He, S. Huang, L. F. Villalobos, J. Zhao, M. Mensi, E. Oveisi, **M. Rezaei**, K. V. Agrawal, Highpermeance polymer-functionalized single-layer graphene membranes that surpass the postcombustion carbon capture target, Energy & Environmental Sciences, 2019, 12-16.
- 7. M. H. Khan, M. Dakhchoune, **M. Rezaei**, S. Huang, J. Zhao, K. V. Agrawal, Hydrogen Sieving from Intrinsic Defects of Benzene-Derived Single-Layer Graphene, Carbon, 2019, 153, 458-456.
- 8. S. Dutta, M. T. Vahdat, M. Rezaei, K. V. Agrawal, Crystallization of gas-selective nanoporous graphene by competitive etching and growth: a modeling study, Scientific Reports, 2019, 9, 5202.
- 9. S. Huang, M. Dakhchoune, W. Luo, E. Oveisi, G. He, **M. Rezaei**, J. Zhao, A. Züttel, M. S. Strano, K. V. Agrawal, Large-area single-layer graphene membranes by crack-free transfer for gas mixture separation, Nature Communications, 2018, 9, 2632.
- C. Ortega, M. Rezaei, V. Hessel, G. Kolb, Methanol to dimethyl ether conversion over a ZSM-5 catalyst: Intrinsic kinetic study on an external recycle reactor, Chemical Engineering Journal, 2018, 347, 741-753.

#### **CONFERENCES**

- 1. M. Rezaei, K. V. Agrawal, Swiss Chemical Society (SCS) Meeting, 2019, 2020, 2021, Switzerland
- 2. M. Rezaei, K. V. Agrawal, North American Membrane Society (NAMS), May 18-21st, 2020, Arizona, USA (Online)
- 3. S. Huang, M. Rezaei, K. V. Agrawal, et al., Euromembrane 2018, July 9-13, 2018, Valencia, Spain
- 4. C. Ortega, M. Rezaei, V. Hessel, G. Kolb, 18th Netherlands' Catalysis and Chemistry Conference (NCCC XVIII), March 3-8th, 2017, Noordwijkerhout, The Netherlands
- 5. A. Vatani, M. Rezaei, S. Mokhatab, 1st Iran LNG Conf., October 2011, Tehran, Iran

#### AWARDS

- Editor's choice article for June 2020, Journal of Membrane Science, paper entitled: Crystallographic and morphological optimization of catalytic copper foil for high-quality singlelayer graphene membranes
- Graduated "With Great Appreciation" with M.Sc. in Chemical and Process Technology, Eindhoven University of Technology, The Netherlands, 2016
- ALSP full scholarship (tuition and living fees) for MSc studies at TU/e, The Netherlands, 2014-2016
- Accepted for M.Sc. program as a Talented Student Awardee with full scholarship (declined), University of Tehran, Iran, 2011
- Ranked 1st among over 100 students in Chemical Engineering Department of University of Tehran at 4th year (GPA: 19.00/20) [4-years overall rank: 8th]
- Top 1% in Iran National Universities Entrance Examination (Admitted for B.Sc. with a full scholarship)

## PROFESSIONAL EXPERIENCES

#### Arman Energy Maad (ARENMAAD) LLC, Tehran, Iran

Process Engineer, 2011-2014 (Part-time)

• Responsibilities: Equipment design, Preparation of technical documents and reports, Process simulation

### Oil Turbo Compressor (OTC) Group, Tehran, Iran

Technical Advisor, Research and Training Center, 2012-2015

- Responsibilities: Provision of counsel in the area of courses, their syllabuses, and their requirements
- Project Engineer, 2012-2013 (part-time)

• Responsibilities: Preparing Closeout Report & Lesson Learned

## Industrial Internship, 2011

• Function manager for educational project management app development team