

# **Fabrication and Applications of Graphene Hollow Fibre Membranes**

By

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## Declaration of Originality

I hereby declare that this thesis and the work reported herein was composed by and originated entirely from me. Information derived from the published and unpublished work of others has been acknowledged in the text and the relevant references are included in this thesis.

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## Abstract

Graphene has attracted vast amount of research in the last decade. Attributed to its  $sp^2$  hybridisation, graphene is chemically inert, making it an ideal material to be used in extremely harsh conditions. Graphene's ultra-thin property also makes it an ideal material for membrane separation because permeation is inversely proportional to membrane thickness. While many studies have been carried out on graphene membranes, scaling up remains a key challenge, designing graphene membrane in a geometry which favours module assembly is strongly desired. Furthermore, chemical resistance of metallic membrane can be improved by integrating graphene as a protective barrier. In this thesis, the fabrication and applications of the prepared graphene hollow fibre membranes are explored.

Firstly, graphene protected nickel hollow fibre membrane was developed and demonstrated improved chemical resistance compared to the non-protected membrane. Its application was further explored in the production of nanoparticles. Pristine graphene membranes supported on porous ceramic hollow fibre was successfully prepared via the sacrificial layer assisted chemical vapour deposition (CVD) approach. A dense metal sacrificial layer was deposited on the hollow fibre support using electroless plating. After successful graphene growth, this sacrificial layer was removed while the ceramic hollow fibre remained intact to act as the support. Both copper and nickel sacrificial layers were explored. When copper was used, copper dewetting on ceramic surface was observed during high temperature synthesis, which hindered good quality graphene growth. The membrane showed compaction where the permeation flux declined during filtration. Nickel was then investigated to prevent metal dewetting. A dense and continuous nickel sacrificial layer was formed, which was suitable for high-quality CVD graphene synthesis. Finally, pristine graphene membrane supported on ceramic hollow fibre was realised after metal etching, demonstrating reasonable flux and rejection. This study thus presents the successful engineering of graphene hollow fibre membranes suitable for industry scale-up.

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# Table of Content

|                                                                                           |           |
|-------------------------------------------------------------------------------------------|-----------|
| <b>Abstract.....</b>                                                                      | <b>2</b>  |
| <b>Acknowledgement .....</b>                                                              | <b>3</b>  |
| <b>Table of Content .....</b>                                                             | <b>4</b>  |
| <b>List of Figures.....</b>                                                               | <b>8</b>  |
| <b>List of Tables.....</b>                                                                | <b>10</b> |
| <b>Chapter 1: Introduction.....</b>                                                       | <b>11</b> |
| 1.1 Background .....                                                                      | 11        |
| 1.2 Research objectives .....                                                             | 13        |
| 1.3 Thesis scope .....                                                                    | 15        |
| References .....                                                                          | 16        |
| <b>Chapter 2: Literature review.....</b>                                                  | <b>17</b> |
| 2.1 Graphene and its properties .....                                                     | 17        |
| 2.2 Graphene synthesis.....                                                               | 17        |
| 2.3 Graphene growth via chemical vapour deposition.....                                   | 19        |
| 2.3.1 Substrates .....                                                                    | 20        |
| 2.3.1.1 Transition metal substrates .....                                                 | 20        |
| 2.3.1.2 Porous Substrates .....                                                           | 22        |
| 2.3.1.3 Non-metal substrates .....                                                        | 22        |
| 2.3.2 CVD Parameters .....                                                                | 25        |
| 2.3.2.1 Carbon precursors.....                                                            | 25        |
| 2.3.2.2 Temperature .....                                                                 | 26        |
| 2.3.2.3 Role of Hydrogen .....                                                            | 27        |
| 2.4 Graphene and its potential applications.....                                          | 28        |
| 2.4.1 Graphene protective coating .....                                                   | 28        |
| 2.4.2 Graphene and graphene-based membranes .....                                         | 32        |
| 2.4.2.1 Theoretical and simulation studies on nanoporous graphene membranes.....          | 33        |
| 2.4.2.2 Preparation of nanoporous graphene membranes .....                                | 35        |
| 2.4.2.3 Applications of nanoporous graphene membranes .....                               | 37        |
| 2.4.2.3.1 Liquid separation and performance.....                                          | 37        |
| 2.4.2.3.2 Gas separation and performance .....                                            | 42        |
| 2.4.2.4 Graphene-based membrane performance.....                                          | 44        |
| 2.5 Potential micro-tubular substrates for graphene hollow fibre membranes synthesis..... | 45        |
| 2.5.1 Metallic hollow fibre membranes.....                                                | 46        |
| 2.5.1.1 Pristine metallic hollow fibre membranes.....                                     | 46        |

|                                                                                                                                                                  |           |
|------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------|
| 2.5.1.2 Deposition of metallic layer on hollow fibre supports .....                                                                                              | 49        |
| 2.5.1.2.1 Electroless plating .....                                                                                                                              | 49        |
| 2.6 Summary, challenges & research motivations.....                                                                                                              | 53        |
| References .....                                                                                                                                                 | 55        |
| <b>Chapter 3: Experimental.....</b>                                                                                                                              | <b>65</b> |
| 3.1 Phase-inversion.....                                                                                                                                         | 65        |
| 3.2 Electroless plating .....                                                                                                                                    | 67        |
| 3.2.1 Sensitisation and activation of YSZ hollow fibres .....                                                                                                    | 67        |
| 3.2.2 Electroless plating .....                                                                                                                                  | 68        |
| 3.3 Sintering and annealing of hollow fibre membranes .....                                                                                                      | 68        |
| 3.3.1 Sintering of YSZ hollow fibres .....                                                                                                                       | 68        |
| 3.3.2 Annealing of metallic hollow fibre membranes.....                                                                                                          | 69        |
| 3.4 Graphene synthesis via CVD growth.....                                                                                                                       | 70        |
| 3.5 Etching of the metal sacrificial layer .....                                                                                                                 | 70        |
| 3.6 Post-etching defect-patching treatment .....                                                                                                                 | 70        |
| 3.7 Characterisation .....                                                                                                                                       | 72        |
| 3.7.1 Scanning Electron Microscopy .....                                                                                                                         | 72        |
| 3.7.2 Raman spectroscopy .....                                                                                                                                   | 72        |
| 3.7.3 Mechanical strength .....                                                                                                                                  | 73        |
| 3.7.4 Pore size and pore size distribution .....                                                                                                                 | 73        |
| 3.7.5 Porosity .....                                                                                                                                             | 73        |
| 3.8 Performance .....                                                                                                                                            | 74        |
| 3.8.1 Liquid Permeation.....                                                                                                                                     | 74        |
| 3.8.2 Rejection tests.....                                                                                                                                       | 74        |
| 3.8.3 Gas-tightness test .....                                                                                                                                   | 75        |
| References .....                                                                                                                                                 | 76        |
| <b>Chapter 4: Graphene-protected nickel hollow fibre membrane and its application in the<br/>production of nanoparticles for high-performance catalysts.....</b> | <b>77</b> |
| Abstract.....                                                                                                                                                    | 77        |
| 4.1 Introduction .....                                                                                                                                           | 77        |
| 4.2. Experimental .....                                                                                                                                          | 79        |
| 4.2.1 Fabrication of graphene-protected nickel hollow fibre membranes.....                                                                                       | 79        |
| 4.2.2 Preparation of TiO <sub>2</sub> microspheres using G-Ni-HF membranes .....                                                                                 | 80        |
| 4.2.3 Characterisations .....                                                                                                                                    | 81        |
| 4.3 Results and discussion .....                                                                                                                                 | 81        |
| 4.3.1 Graphene protected nickel hollow fibre membranes.....                                                                                                      | 81        |

|                                                                                                                                                     |            |
|-----------------------------------------------------------------------------------------------------------------------------------------------------|------------|
| 4.3.2 Properties of G-Ni-HF membranes.....                                                                                                          | 84         |
| 4.3.3 Corrosion Tests .....                                                                                                                         | 85         |
| 4.3.4 Synthesis of TiO <sub>2</sub> microspheres using G-Ni-HF membrane.....                                                                        | 87         |
| 4.3.4.1 High-performance catalysts based on the microspheres prepared by the G-Ni-HF.....                                                           | 89         |
| 4.4. Conclusion.....                                                                                                                                | 90         |
| Additional Information A .....                                                                                                                      | 92         |
| References .....                                                                                                                                    | 99         |
| <b>Chapter 5: Pristine graphene membranes supported on ceramic hollow fibre prepared via a copper sacrificial layer assisted CVD approach .....</b> | <b>102</b> |
| Abstract.....                                                                                                                                       | 102        |
| 5.1 Introduction .....                                                                                                                              | 102        |
| 5.2 Experimental .....                                                                                                                              | 105        |
| 5.2.1 Preparation of copper plated YSZ hollow fibre.....                                                                                            | 105        |
| 5.2.2 Annealing and graphene growth via CVD .....                                                                                                   | 105        |
| 5.2.3 Etching of copper sacrificial layer and post-etching defect-patching treatment .....                                                          | 106        |
| 5.2.4 Characterisation and performance tests .....                                                                                                  | 106        |
| 5.3 Results and discussions.....                                                                                                                    | 107        |
| 5.3.1 Formation of copper sacrificial layer on YSZ hollow fibre .....                                                                               | 107        |
| 5.3.2 Graphene growth via CVD on Cu-YSZ-HF .....                                                                                                    | 111        |
| 5.3.3 Etching of copper sacrificial layer .....                                                                                                     | 114        |
| 5.3.4 Post-etching defect-patching treatment .....                                                                                                  | 116        |
| 5.3.5 Performance of graphene membrane supported on YSZ hollow fibre.....                                                                           | 117        |
| 5.4 Conclusion.....                                                                                                                                 | 119        |
| Additional Information B .....                                                                                                                      | 119        |
| References .....                                                                                                                                    | 124        |
| <b>Chapter 6: Pristine graphene membranes supported on ceramic hollow fibre prepared via a nickel sacrificial layer assisted CVD approach .....</b> | <b>127</b> |
| Abstract.....                                                                                                                                       | 127        |
| 6.1 Introduction .....                                                                                                                              | 127        |
| 6.2 Experimental .....                                                                                                                              | 129        |
| 6.2.1 Electroless nickel plating on YSZ hollow fibre.....                                                                                           | 129        |
| 6.2.2 Annealing and CVD graphene growth on Ni-YSZ-HF .....                                                                                          | 130        |
| 6.2.3 Etching of nickel sacrificial layer and post-etching defect-patching treatment .....                                                          | 130        |
| 6.2.4 Characterisation and performance tests .....                                                                                                  | 131        |
| 6.3 Results and discussions.....                                                                                                                    | 132        |
| 6.3.1 Formation of nickel sacrificial layer on YSZ hollow fibre .....                                                                               | 132        |

|                                                                           |            |
|---------------------------------------------------------------------------|------------|
| 6.3.2 Graphene synthesis on Ni-YSZ-HF .....                               | 134        |
| 6.3.3 Etching of nickel sacrificial layer .....                           | 135        |
| 6.3.4 Post-etching defect-patching treatment .....                        | 138        |
| 6.3.5 Performance of graphene membrane supported on YSZ hollow fibre..... | 138        |
| 6.4 Conclusion.....                                                       | 139        |
| Additional Information C .....                                            | 140        |
| References .....                                                          | 144        |
| <b>Chapter 7: Conclusion and future work.....</b>                         | <b>146</b> |
| 7.1 Overall conclusion.....                                               | 146        |
| 7.2 Future work.....                                                      | 148        |
| 7.2.1 Graphene protected porous nickel hollow fibre membranes .....       | 148        |
| 7.2.2 Pristine graphene hollow fibre membranes .....                      | 148        |
| References .....                                                          | 150        |
| <b>List of Publications .....</b>                                         | <b>152</b> |
| <b>List of Conference Presentations .....</b>                             | <b>153</b> |
| <b>Permissions for third party copyright works.....</b>                   | <b>154</b> |

## List of Figures

|                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                     |    |
|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|----|
| Figure 2.1. Graphene structure. Reproduced from Ref [3] with permission from Elsevier.....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                          | 17 |
| Figure 2.2. Various graphene synthesis methods compared in terms of size, quality and price for mass production. Reproduced from Ref [5] with permission from Springer Nature. ....                                                                                                                                                                                                                                                                                                                                                                                                 | 19 |
| Figure 2.3. Schematic of graphene growth mechanism of methane on Ni and Cu. Reproduced from Ref [6] with permission from John Wiley Sons. ....                                                                                                                                                                                                                                                                                                                                                                                                                                      | 21 |
| Figure 2.4. a) Graphene synthesis on SiO <sub>2</sub> substrate using polymers or SAMs. Reproduced from Ref [30] with permission from American Chemical Society; b) Direct graphene synthesis on quartz by evaporating off copper. Reproduced from Ref [33] with permission from American Chemical Society. C) Graphene formation on di-electric substrates by removing the top graphene layer and leaving the bottom graphene layer on substrate. Reproduced from Ref [36] with permission from Elsevier.....                                                                      | 24 |
| Figure 2.5. a) Schematic of graphene acting as protection barrier; b) Copper penny w and w/o graphene after 2 mins in H <sub>2</sub> O <sub>2</sub> ; c) Photographs of graphene protected or non-protected Cu and Ni/Cu alloy after annealing in air for 4h. Reproduced from Ref [57] with permission from American Chemical Society.....                                                                                                                                                                                                                                          | 29 |
| Figure 2.6. Schematic demonstrating the diffusion paths of molecules through monolayer (a) and multilayer (b) graphene. Reproduced from Ref [75] with permission from Elsevier. ....                                                                                                                                                                                                                                                                                                                                                                                                | 31 |
| Figure 2.7. Nanoporous graphene membranes with nanopores. Reproduced from Ref [78] permission from Royal Society of Chemistry.....                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 32 |
| Figure 2.8. Bilayer graphene membrane with nanopore radius R, separation layer H and pore offset O. (Red-white molecules representing water and large green molecules representing salt-NaCl). Reproduced from Ref [86] from American Chemical Society.....                                                                                                                                                                                                                                                                                                                         | 34 |
| Figure 2.9. a) Schematic of the graphene transfer process onto a target substrate using PMMA. Reproduced from Ref [89] with permission from IOP Publishing; b) Schematic of the direct pressing method. Reproduced from Ref [90] with permission from American Chemical Society, c) Schematic of the graphene membrane formation using support created from the phase inversion process. Reproduced from Ref [63] with permission from American Chemical Society; d) Graphene transfer on target substrate using nanoporous carbon film. Reproduced from Ref [92], Open Source..... | 36 |
| Figure 2.10. Pores generated by (a) ion bombardment. Reproduced from Ref [63] with permission from American Chemical Society or (b) by O <sub>2</sub> plasma treatment. Reproduced from Ref [61] with permission from Springer Nature. ....                                                                                                                                                                                                                                                                                                                                         | 37 |
| Figure 2.11. Graphene oxide structure. Reproduced from Ref [99] with permission from John Wiley Sons.....                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 44 |
| Figure 3.1. Schematic of the spinning process.....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                  | 65 |
| Figure 3.2. Schematic of the sensitisation and activation step on YSZ hollow fibres.....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 67 |
| Figure 3.3. Schematic of the electroless plating process.....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 68 |
| Figure 3.4. Schematic of the annealing & CVD set-up.....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                            | 69 |
| Figure 3.5. Schematic of the dead-end filtration set-up.....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                        | 71 |
| Figure 3.6. Schematic of the gas-tightness set-up.....                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                                              | 76 |
| Figure 4.1. a) Membrane emulsification using G-Ni-HF membrane; b) Conventional emulsification method.....                                                                                                                                                                                                                                                                                                                                                                                                                                                                           | 81 |
| Figure 4.2. Photographs of pristine nickel (top) and graphene protected nickel (bottom) hollow fibres membranes (bottom).....                                                                                                                                                                                                                                                                                                                                                                                                                                                       | 81 |

|                                                                                                                                                                                                                                                                                                                |     |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----|
| Figure 4.3. SEM images of a) cross-sectional surface of the hollow fibre; b&c) pristine Ni-HF membrane surface; d&e) G-Ni-HF membrane surface; f) Raman spectra of G-Ni-HF membrane; g) 2D:G ratio distribution in a 25 $\mu\text{m}$ ×25 $\mu\text{m}$ scanned area (inset-Raman mapping of 2D:G ratio) ..... | 83  |
| Figure 4.4. a) Pore size distribution of G-Ni-HF membrane; b) Load Vs Extension for G-Ni-HF and YSZ hollow fibres .....                                                                                                                                                                                        | 85  |
| Figure 4.5. Images of the G-Ni-HF before (a&c); and after (b&d) immersing in 0.5M nitric acid for 3 hours; e&f) SEM images of the G-Ni-HF after 3 hours immersion in 0.5 M nitric acid.....                                                                                                                    | 86  |
| Figure 4.6. Morphology of TiO <sub>2</sub> microspheres; a-c) Asymmetric egg-white TiO <sub>2</sub> microspheres prepared using G-Ni-HF membrane; d-f) Symmetric homogeneous TiO <sub>2</sub> microspheres prepared using the traditional emulsification method. ....                                          | 88  |
| Figure 4.7. Catalytic activity of asymmetric & symmetric TiO <sub>2</sub> -Pd catalysts for CO oxidation as a function of weight hourly space velocity (WHSV) .....                                                                                                                                            | 90  |
| Figure 5.1. Illustration of preparation procedure for obtaining graphene hollow fibre membranes                                                                                                                                                                                                                | 105 |
| Figure 5.2. SEM images of a& b) cross-sectional image of YSZ hollow fibre; c) plain YSZ outer surface, (inset- photograph of plain YSZ hollow fibre, 1cm scale); d) Pd seeded YSZ outer surface, (inset- photograph of Pd seeded YSZ, 1cm scale) .....                                                         | 108 |
| Figure 5.3. a) SEM image of plated Cu-YSZ-HF; b&c) copper dewetting on YSZ surface; d) SEM image of Cu-YSZ-HF after annealing; e) Photograph of Cu-YSZ-HF after annealing (1cm scale); d) cross-sectional image of Cu-YSZ-HF .....                                                                             | 110 |
| Figure 5.4. a) Cross sectional view of G-Cu-YSZ-HF under TEM (Inset- photograph of G-Cu-YSZ-HF); b&c) SEM images of G-Cu-YSZ-HF surface; d) copper dewetting on G-Cu-YSZ-HF.....                                                                                                                               | 113 |
| Figure 5.5. a) Photograph of the copper sacrificial layer removed using ferric chloride; b) SEM image of G-YSZ-HF; c) Raman spectra of G-YSZ-HF; d) Distribution of 2D:G ratio (inset-Raman mapping of 2D:G ratio).....                                                                                        | 115 |
| Figure 5.6. a) Cross-sectional & b) Outer surface of G-YSZ-HF post defect-patching treatment; c) Cross-sectional & d) Outer surface of direct deposition of graphene flakes on plain YSZ hollow fibre.....                                                                                                     | 116 |
| Figure 6.1. Illustration of the preparation procedure for obtaining graphene hollow fibre membrane using nickel.....                                                                                                                                                                                           | 129 |
| Figure 6.2. Schematic of the various etching methods used to leach away the nickel sacrificial layer, a) cotton bud method; b) oxygen plasma method; c) thermal oxygen method, followed by immersing in 8 M HNO <sub>3</sub> .....                                                                             | 131 |
| Figure 6.3. SEM images of a) plated nickel surface on YSZ hollow fibre; b) annealed nickel surface on YSZ hollow fibre; c) cross-sectional area of the annealed nickel on YSZ hollow fibre; d) gas tightness test .....                                                                                        | 133 |
| Figure 6.4. a) SEM image of G-Ni-YSZ hollow fibre surface (inset-photograph of G-Ni-YSZ, 1 cm scale); b) Raman spectra; c) Raman mapping of 2D:G ratio; d) 2D:G ratio distribution.....                                                                                                                        | 135 |
| Figure 6.5. a) SEM image of G-YSZ-HF; b) Raman spectra (inset- Raman mapping of 2D:G ratio).....                                                                                                                                                                                                               | 137 |
| Figure 6.6. SEM images of a&b) Cross sectional view & surface of G-YSZ-HF post graphene flakes treatment.....                                                                                                                                                                                                  | 138 |
| Figure 6.7. a) SEM image of G-YSZ-HF after rejection tests; b) 2D:G ratio distribution (inset- Raman mapping of 2D:G ratio) of G-YSZ-HF after rejection tests.....                                                                                                                                             | 139 |

## List of Tables

|                                                                                       |     |
|---------------------------------------------------------------------------------------|-----|
| Table 2.1. Liquid separation performance of various prepared graphene membranes ..... | 41  |
| Table 3.1. Dope suspension compositions.....                                          | 66  |
| Table 4.1. Breaking load and bending stress of hollow fibre membranes .....           | 85  |
| Table 5.1. Composition of electroless copper plating studied .....                    | 105 |
| Table 5.2. Electroless copper plating composition .....                               | 109 |
| Table 6.1. Composition of electroless nickel plating studied .....                    | 129 |
| Table 6.2. Electroless nickel plating composition .....                               | 132 |

# Chapter 1: Introduction

## 1.1 Background

Graphene is an ultra-thin two-dimensional material that was first successfully isolated in 2004 by Geim and Novoselov using the traditional scotch tape method [1]. Since then the global demand of graphene has risen rapidly with the global graphene market estimated at USD 42.8 million in 2017 [2] and according to the Grand View Research Inc., this market is going to expand significantly potentially reaching USD 552.3 million by 2025 [3]. This increase mainly arise from research and development and particularly, in the field of semiconductor, electronics, battery energy and more. All these advancements are attributed to the superior properties possess by graphene. Besides the ultra-thin property, graphene is also chemically inert and revealed to be one of the strongest materials in the world, possessing a Young's modulus of 1 TPa [4]. It also has excellent thermal and electrical properties attributed to the  $sp^2$  hybridisation in which  $\pi$  electron clouds are delocalised above and below the graphene plane. Techniques in fabricating graphene films are readily available and large area of high-quality graphene can be fabricated using chemical vapour deposition (CVD) [5]. Under CVD, the carbon precursors are decomposed, diffused or adsorbed on the transition metal substrates subject to the substrate's characteristics and finally the graphene layers are formed upon synthesis. In terms of graphene applications, many research and development carried out so far have focused on semiconductors and energy storage systems. However, explorations have also been carried out on other types of non-electronic applications, such as protective coating and membrane applications.

Membrane technology is an energy efficient, environmentally friendly process that can be used in either separation or reaction. It is a low energy-intensive method to achieve the desired separation instead of the conventional high energy-intensive distillation process. It can also be used as a reactor or disperser to facilitate the formation of the desired products. One of the most important uses of membranes is in water treatment, which mainly includes desalination, wastewater treatment and the production of drinking water. With the increasing pressure on global water shortage, the world's

demand for membranes is forecasted to rise 8.5 % annually to USD 26.3 billion in 2019 [6]. Other markets such as the food and beverage are also projected to grow. The pharmaceutical and medical markets are also fast-growing markets for membrane because of the increasing stringent standards for medical applications [6].

Performance of membrane is strongly dependent on the geometry and materials. In terms of configuration, disk and plate membranes have been widely used in research works because of the ease of fabrication. However, membrane of this geometry poses low separation-area-to-volume ratios, which makes it undesirable for large scale production. So far, the most advanced structural design in terms of permeation rate has been the hollow fibre configuration. Hollow fibre membranes exhibit high membrane-area-to-volume ratio and can potentially reach up to 8,000-10,000 m<sup>2</sup> m<sup>-3</sup> [7]. For hollow fibre membrane, a thin selective layer can be supported on a macro porous hollow fibre substrate. This is to achieve an effective membrane performance whilst not sacrificing the robustness of the membrane.

Choosing the desired membrane selective layer is also crucially important. Due to the inverse relationship between flux and membrane thickness, the ultra-thin property possess by graphene is strongly desired. This means that the permeation flux can be significantly improved, in which ultimate permeation can be achieved [8]. The graphene layer can also act as a protective coating for metallic membranes, enabling the improved chemical resistant membrane to be used in a variety of applications, especially when harsh conditions is required [9].

So far graphene membranes are mostly prepared in flat sheet geometry. To expand the versatility of graphene membranes, commercialization is a key challenge to be tackled. Scalability of graphene membranes can be enhanced by developing graphene in hollow fibre geometry. This allows ease of module assembly which is vital for module design and commercialization. In this thesis, cutting-edge technologies have been developed to synthesise pristine graphene membranes in hollow fibre

geometry. Since graphene can be readily grown on metal, the use of metallic hollow fibre membranes to facilitate the preparation of graphene hollow fibre membranes is explored.

## **1.2 Research objectives**

The main objectives of this PhD project are to develop graphene membranes in the hollow fibre geometry. This study also explores the applications of graphene as a protective coating for hollow fibre membranes and its separation performance in liquid separation. This study looks to investigate the following areas:

### **(i) To develop pristine graphene-metallic porous hollow fibre membranes**

Dense and porous metallic hollow fibre membranes have demonstrated uses in microfiltration and gas separation. Metallic material is generally susceptible to harsh and corrosive environments. By integrating graphene as a protective coating on metallic hollow fibre membranes, the applications in which metallic hollow fibre membranes can be used are increased. Phase inversion and sintering process are employed to produce porous metallic-nickel hollow fibre membrane. Hereafter, CVD is used to synthesise high quality continuous multilayer graphene on the metallic hollow fibre membrane. Imaging technologies such as scanning electron microscopy (SEM) is used to study the membrane surface, morphology and pore size. Raman spectroscopy is used to characterise the graphene quality of the prepared pristine graphene-metallic hollow fibre membrane. Graphene acting as a protective coating is investigated by immersing in highly acidic acid and the rates in which graphene protected and non-protected hollow fibre membranes dissolve are explored. The application of this improved chemical resistant graphene protected porous metallic hollow fibre membrane is also studied.

**(ii) To improve the scalability of pristine graphene membrane by developing in the hollow fibre geometry**

Currently, continuous graphene membranes can only be made on flat sheet which limit mass production because of the low surface-area-to-volume ratio. To improve the scalability, an unprecedented method is developed to fabricate graphene membrane in the hollow fibre geometry. Firstly, a dense metal sacrificial layer is deposited on a porous ceramic hollow fibre support via electroless plating. Chemical vapour deposition is then carried out for graphene formation. Hereafter, the metal layer is removed leaving the continuous ultra-thin graphene layer enclosed around the ceramic hollow fibre.

**(iii) To investigate the best approach in fabricating graphene hollow fibre membranes**

The mechanism of graphene formation is different dependent on the metallic substrate used. Furthermore, the interaction between metallic sacrificial layer and ceramic hollow fibre support during high temperature synthesis is also different. A suitable sacrificial layer for the formation of pristine graphene hollow fibre membrane is investigated. Copper and nickel are the most commonly used substrates for CVD synthesis. Both materials can also be deposited on ceramic hollow fibre via electroless plating. Therefore, the resultant graphene hollow fibre membranes prepared from the 2 metals are studied and the most suitable material used as the sacrificial layer in achieving high performing pristine graphene hollow fibre membrane is realised.

**(iv) To investigate the characteristics and liquid separation performance of graphene hollow fibre membranes**

Characterisation and liquid separation performance are conducted to investigate the quality of the obtained graphene hollow fibre membranes. Imaging technologies such as SEM is used to study the membrane surface and the underlying support morphology. Raman spectroscopy

is used to characterise the continuity and homogenous distribution of graphene across the complex hollow fibre geometry. Any large defects induced during the etching process are sealed with graphene flakes. Performance of the obtained graphene hollow fibre membranes is characterised using solvent filtration and rejection tests.

### **1.3 Thesis scope**

This PhD thesis consists of 7 chapters in total studying the fabrication and applications of graphene hollow fibre membranes. Chapter 1 introduces the background of graphene and membrane technology, and the research objectives in developing graphene membrane in the hollow fibre geometry utilising metallic hollow fibre membranes. Chapter 2 provides an in-depth review on the literatures available on graphene, graphene synthesis, applications of graphene as protective coating and membrane applications. The review also looks into the literatures of metallic hollow fibre membranes to enable the exploration of suitable micro-tubular substrates for graphene hollow fibre membrane synthesis. Chapter 3 outlines the key experimental procedures used in the preparation and characterisation of the graphene hollow fibre membranes.

Chapter 4-6 present the experimental work conducted in obtaining graphene hollow fibre membranes. Chapter 4 describes the preparation of graphene protected nickel hollow fibre membrane and the potential applications of the improved chemical resistant nickel membrane in the field of nanoparticles production. Chapter 5 focuses on improving the scalability of the graphene membrane by developing it in the hollow fibre geometry. This chapter reveals the use of a copper as the sacrificial layer for the graphene synthesis, followed by etching of the copper layer to obtain the pristine graphene membrane supported on hollow fibres. Chapter 6 follows from Chapter 5's study by looking into the use of nickel sacrificial layer to rectify problems arose from the use of copper sacrificial layer. A high performing graphene hollow fibre membrane is realised using nickel, demonstrating reasonable flux and dye rejection.

Finally, Chapter 7 concludes the findings from the PhD studies, outlining key findings from each of the research areas. Recommendations of future work are also provided to assist with future exploration in the area of graphene hollow fibre membranes and the use in large scale operation.

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## Chapter 2: Literature review

### 2.1 Graphene and its properties

Graphene is a two dimensional, one-atom thick material that is packed in the form of a honeycomb lattice, shown in Figure 2.1 [1-3]. It has excellent electrical conductivities attributed to its  $sp^2$  orbital hybridisation, here  $\pi$  electrons are delocalised above and below the graphene plane due to the p-orbitals overlap [2]. Atoms and molecules are repelled away when passing through this high density electron cloud, making defect-free graphene impermeable to all gases and liquids and chemically inert [4]. Graphene is also the strongest material ever measured, with an intrinsic tensile strength of approximately 130 GPa [5]. Within its structure, each carbon atom is bonded to three neighbouring carbon atoms, consisting of 3  $\sigma$ -bonds and 1  $\pi$ -bond and the strength comes from the  $\sigma$  carbon-carbon bond with the length of 1.42 Å. Moreover graphene is elastic and can be formed as a conformal layer on most metal surfaces with the most complexing topographies [5]. Since its discovery and successful isolation in 2004, the superior thermal, electrical and mechanical properties that graphene exhibits have attracted widespread of interests [1, 2].

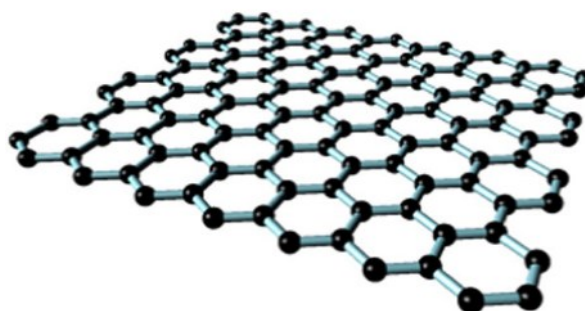


Figure 2.1. Graphene structure. Reproduced from Ref [3] with permission from Elsevier.

### 2.2 Graphene synthesis

Many efforts have been focused on the synthesis method in producing high quality, large area graphene. It was first successfully isolated in 2004 by Geim and Novoselov using the scotch tape method, where graphene was exfoliated from highly ordered pyrolytic graphite [1]. Although this

method is easy and reliably produces high quality graphene, this method is not suitable for large scale production because only graphene flakes in the size of tens of micrometres are produced and the number of exfoliated layer is not easily controlled [6]. Other methods such as the reduction of graphene oxide (GO) [7], liquid phase exfoliation of graphite [8] and synthesis on SiC [9] have been demonstrated. Reduction of graphene oxide involves removal of the oxygen-containing group, however, complete reduction of GO is difficult to achieve [7]. Liquid exfoliation involves exposing the graphite in solvent, upon sonication, individual flakes are extracted and are enriched through centrifugation. Selection of solvent is important because the solvent-graphene interaction needs to balance the inter-sheet attractive forces for a stable dispersion to form [10]. After exfoliation, the dispersion can then be deposited as a thin film on any surfaces. This method, however, has low yield efficiency and requires long period of time since numerous steps of mixing, exfoliating and vacuum filtrations are involved. Graphene can also be obtained through thermal decomposition of SiC. During high temperature annealing, silicon sublimate leaving behind the carbon atoms, which subsequently rearrange and form the graphitic layer [9]. This method is desired for electronic applications because graphene is obtained directly on commercially available semiconducting substrate and silicon carbide is a material commonly used for high power electronics [9]. However, the drawback associated with this method is the high cost of the SiC wafers. Large-area of polycrystalline graphene film have been produced using chemical vapour deposition (CVD) on transition metals [11, 12], showing promising and high quality graphene for many applications. This process can be energy intensive because high temperature synthesis is needed. However, this method allows growth on different types of transition metal substrates and conformal growth of graphene on metal surfaces can be carried out on the most complex topographies [13, 14]. Amongst these synthesis methods, CVD has shown to be the most promising route in producing large area and high-quality graphene. As demonstrated by Novoselov et al., shown in Figure 2.2, CVD is the optimum approach to produce graphene in terms of quality, price for mass production and scalability when comparing to other methods [5].

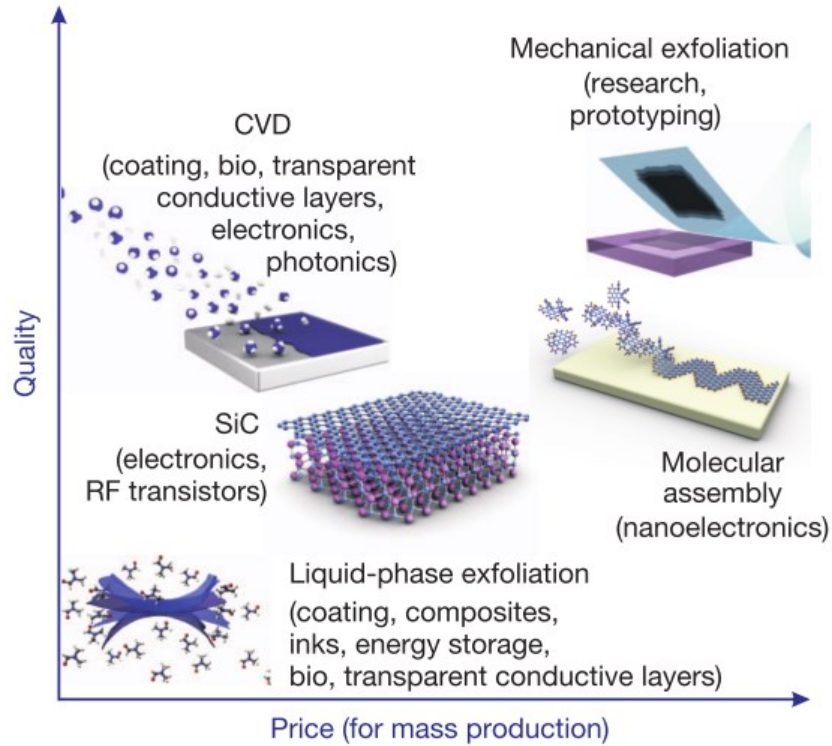


Figure 2.2. Various graphene synthesis methods compared in terms of size, quality and price for mass production. Reproduced from Ref [5] with permission from Springer Nature.

## 2.3 Graphene growth via chemical vapour deposition

Chemical vapour deposition has emerged as the promising synthesis method in the aspects of controllability, scalability, and feasibility for the fabrication of high-quality and large scale graphene using transition metals [6, 11, 12]. In general, chemical vapour deposition consists of the following steps. Carbon precursor is first fed into the reactor containing the metal catalyst substrate. Energy is then supplied to the reaction zone to decompose the carbon precursor into active carbon species. During the synthesis, carbon radicals adsorb or diffuse into the substrate governed by the solubility of carbon in the substrate, resulting in different growth mechanism for different substrates. The energy that the chemical reaction demands can be supplied with the aid of various sources, such as heat, light, or from electric discharge in thermal, laser-assisted, or plasma-assisted CVD [6].

### **2.3.1 Substrates**

#### **2.3.1.1 Transition metal substrates**

Transition metals are commonly used substrates for CVD because their ability to lower activation energy and catalytically enhance the growth process [6, 15]. Graphene synthesis on ruthenium, platinum, stainless steel, copper and nickel have been demonstrated [11, 12, 16-19]. However, the cost of platinum and ruthenium is high therefore graphene growth on these substrates would not be cost-effective. Stainless steel is considered relatively cheaper compared to the other two, however, high quality graphene growth on stainless steel is difficult to achieve. Copper was coated on stainless steel surface to enhance the quality of graphene growth in the study by Ghaemi et al. [20]

Copper (Cu) and nickel (Ni) have been the most commonly used substrates because they are relatively low cost and have demonstrated to produce high quality graphene [11, 12]. Growth mechanism associated with these two metals, however, are markedly different, where one is by surface adsorption and the other is by precipitation process. Using carbon-isotope labelling technique, Li and his co-workers successfully demonstrated the different kinetic behaviour of CVD graphene growth on Ni and Cu [21]. The difference is attributed to the difference in carbon solubility. At 900 °C the solubility of carbon in Ni is ~0.9 at.% [21], whereas copper is close to being negligible at ~0.00048 at. % at 870 °C [22]. Graphene growth on copper is generally formed by the surface adsorption method, the decomposed carbon radicals adsorb and migrate on the surface, resulting in the formation of monolayer graphene. Due to the low carbon solubility, negligible amount of carbon diffuses into the substrate and precipitate to the surface. In 2009, Li and his co-workers demonstrated one of the first CVD graphene growth on copper substrate with 95 % monolayer graphene coverage at 1000 °C [11]. Here, they also explained that the graphene growth on copper is a self-limited process, once the copper surface is fully covered by carbon atoms, its catalytic activity to decompose carbon precursors stops, thus terminating the growth process [11]. It was also found that the thickness of the copper catalyst does not influence the graphene growth, indicating the growth mechanism of copper is by the surface catalysed process. However, later research studies have shown that multilayer graphene can

also be synthesised on copper under certain CVD conditions and parameters. Surface roughness, density of defects and impurities on the copper surface can all play a role in the formation of multilayer graphene [23-25]. In particular, studies have revealed that impurity such as silicon oxide nanoparticles can act as catalyst for graphene growth, where they can decompose carbon precursors and become nucleation sites for the growth of successive graphene layers [23].

On the other hand, graphene growth on nickel substrate is by the precipitation method and multilayer graphene is generally formed because of the high carbon solubility. Carbon radicals diffuse into the nickel bulk, and after the carbon in nickel reaches supersaturation, an equilibrium monolayer graphite phase forms on the surface. Upon rapid cooling, the dissolved carbon atoms precipitate out to the surface forming multilayer graphene layers, carbon solubility decreases at decreasing temperature [12]. Here, large area of continuous graphene film was grown on polycrystalline Ni. Since solubility decreases at decreasing temperature, the effect of cooling rate was found to have a large influence on the graphene thickness [26]. Low cooling rate ( $0.1\text{ }^{\circ}\text{C per sec}$ ) were not sufficient to cause carbon segregation at the surface and if the cooling rate ( $20\text{ }^{\circ}\text{C per sec}$ ) is too rapid, significant amount of carbon segregates at the surface but does not have enough time to have a good crystallinity, medium cooling rate of  $10\text{ }^{\circ}\text{C per sec}$  produces few layers graphene. As a result, graphene quality and thickness can be controlled through the cooling rate. A schematic of graphene growth mechanism using methane as the carbon precursor on Ni and Cu can be seen in Figure 2.3.

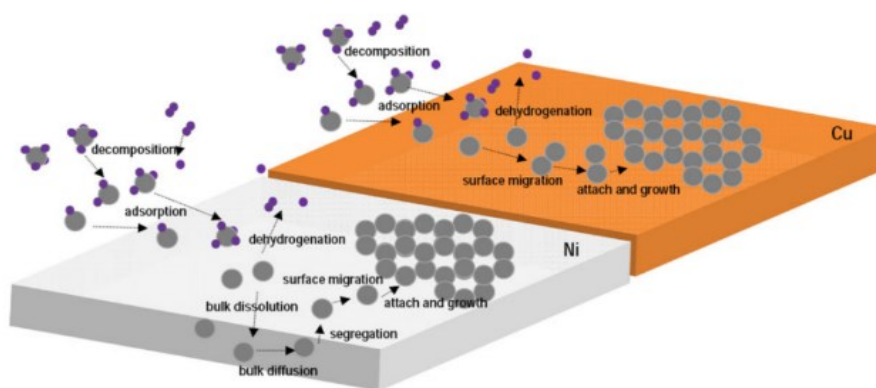


Figure 2.3. Schematic of graphene growth mechanism of methane on Ni and Cu. Reproduced from Ref [6] with permission from John Wiley Sons.

### **2.3.1.2 Porous Substrates**

Studies reported so far have been growth on dense Ni or Cu films. Since graphene can form a conformal layer on metal surfaces, growth can happen even at the most complex topographies, such as porous substrates [13, 14, 27-29].

3D graphene porous networks have been fabricated and have been used as a support to produce graphene-based metal-oxide composite for supercapacitors applications and flow distributor in proton exchange membrane (PEM) fuel cells [13, 14, 27]. Cao et al. and Dong et al. have demonstrated the synthesis of 3D graphene network with a skeleton type of structure by growing graphene on a Ni foam [13, 14]. A free-standing 3D network structure can be obtained if the nickel foam was removed [13]. These networks can be used as templates for the construction of graphene/metal oxide composite-based supercapacitor electrodes. Lee et al. have demonstrated graphene growth on nickel foam for the use in PEM fuel cells as flow distributor [27].

Graphene growth on porous metallic micro-tubes have been shown by Werner et al. and Chong et al. [28, 29] Werner et al. have synthesised graphene-nickel micro-tubular membrane to act as the cathode for Anaerobic Electrochemical Membrane Bioreactors. Graphene was successfully grown on Cu/Cu-Fe micro-tube by Chong et al., where they synthesised high surface-area-to-volume ratio graphene micro-tubes that can be useful as catalytic reactors and heat exchangers. As a result, different networks and porous structures can be used for graphene growth and freestanding 3D graphene network can be produced by etching away the metal substrate.

### **2.3.1.3 Non-metal substrates**

Graphene growth on non-metal insulating or dielectric substrates have also been investigated widely. Unlike metal, these substrates generally possess low surface energy and have weak catalysis function for hydrocarbon decomposition. Nevertheless, much efforts have been proposed to synthesise high

quality graphene on these substrates. These syntheses can be classified into two major categories, one involves the assistance from transition metal, and another is direct metal-free growth.

There are many approaches for the metal-assisted growth. One involves depositing a layer of solid carbon source such as, polymer film, amorphous carbon or self-assembled monolayers (SAMs) on the dielectric substrates ( $\text{SiO}_2$ , Si, Quartz or sapphire) followed by the deposition of a capping metal which serve as the metal catalyst. During high temperature synthesis, the carbon source transforms into the graphene film and grown on the dielectric/metal surfaces, the metal layer is then removed by dissolution or evaporation [30, 31], an example of this work is indicated in Figure 2.4a. In another instance, copper is sandwiched between two patterned sapphire substrates with an extremely small gap distance for direct CVD graphene growth using methane as the carbon precursor [32]. Ismach et al. have demonstrated the direct growth on dielectric substrate by first depositing the copper layer on quartz and following graphene growth using methane, the graphene layer is transferred/grown directly onto the underlying quartz surface through dewetting and evaporation of the copper layer at high temperature, shown in Figure 2.4b [33]. For Su et al., Peng et al. and Chen et al., they have deposited copper or nickel layer on the dielectric substrates, following CVD and tuning the synthetic parameters. Su et al. reported the synthesis of graphene on both top Cu surfaces and the interface between Cu and the underlying dielectrics, where dissociated carbon atoms not only migrated on copper surfaces, but also diffused to the interface between Cu and underlying dielectrics through the grain boundaries between copper grains. By removing the top layer graphene, the underlying graphene is formed on the dielectric surface [34]. Similar method was conducted using nickel by Chen et al. and Peng et al. where graphene layers were formed above and in between the nickel and dielectric surfaces, following removal of the nickel, graphene layers are formed on the dielectric surface (Figure 2.4c) [35, 36]. Metal has also been introduced in the vapour phase for the assisted growth on dielectric substrates. Copper film was placed in the upstream of the reactor. During high temperature synthesis, copper sublimates and enters the reaction zone as vapour surrounding the dielectric substrate, enhancing the decomposition of hydrocarbons and assisting the nucleation of

graphene on the substrates [37-39]. However, here, graphene quality is hindered, and defects were present, which could be caused by the random nucleation and poor surface migration of the carbon atoms.

In the second strategy metal-free direct graphene growth is tested on dielectric substrates. Sun et al. have demonstrated direct growth on glass, borosilicate glass and sapphire glass under atmospheric pressure at 1000 °C [40]. Large area of mono layer, bi-layer and few layers graphene have been synthesised. However, the presence of defects on the graphene film are noticeable from Raman spectroscopy. Since the non-metal substrates have low catalytic activity, plasma assisted CVD was proposed to enhance the decomposition of hydrocarbon using energetic plasma electrons to promote the ionization, excitation and dissociation of the carbon precursors at relatively low temperatures [41]. Crystalline monolayer graphene was achieved but defects are also obtained using this method.

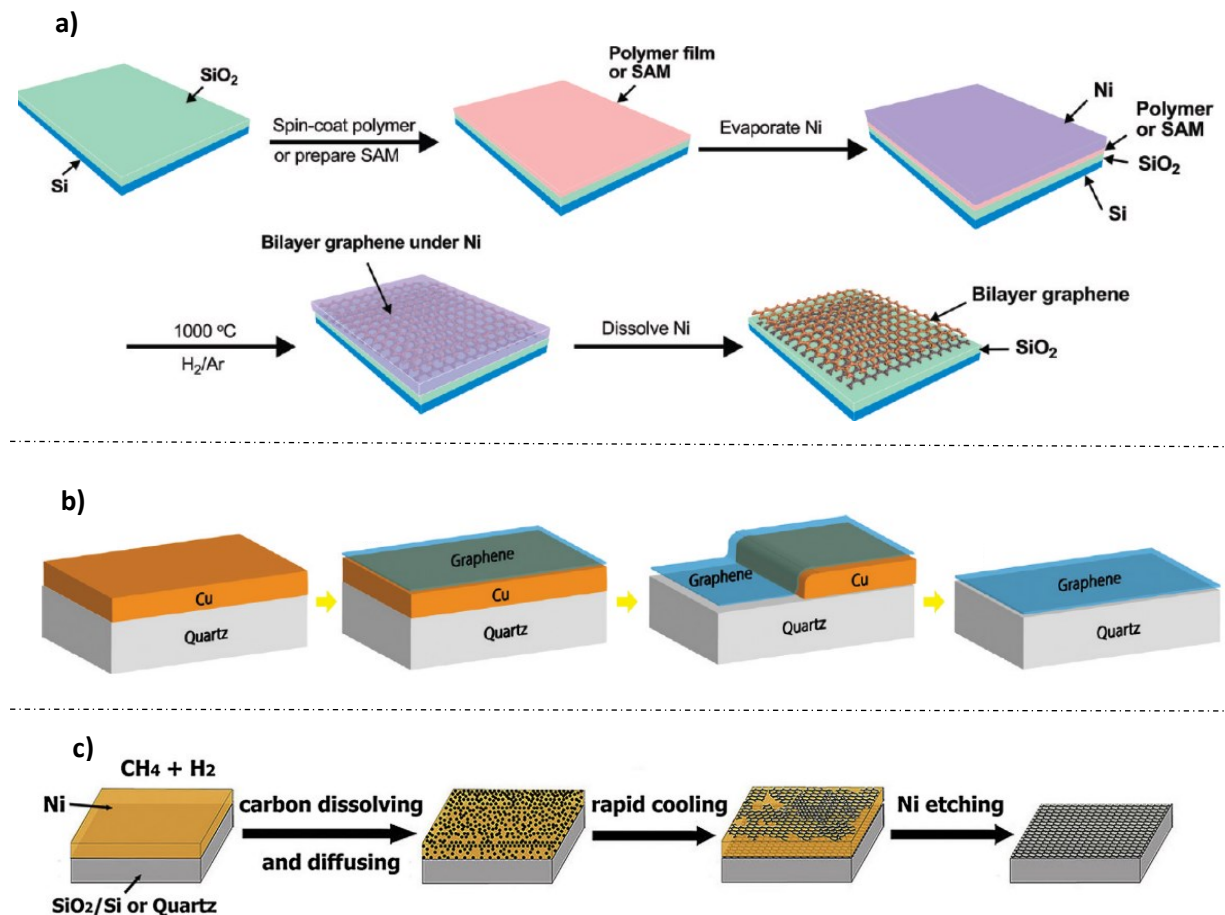


Figure 2.4. a) Graphene synthesis on SiO<sub>2</sub> substrate using polymers or SAMs. Reproduced from Ref [30] with permission from American Chemical Society; b) Direct graphene synthesis on quartz by evaporating off copper. Reproduced from Ref [33] with permission from American Chemical Society. c) Graphene formation on di-electric substrates by removing the top graphene layer and leaving the bottom graphene layer on substrate. Reproduced from Ref [36] with permission from Elsevier.

As demonstrated above, many techniques have been studied synthesising graphene on dielectric substrates. So far, graphene grown directly on dielectric substrate is of low quality and metal assisted approach provides better synthesis. Effective graphene growth on dielectric substrates is viable and dependent on the applications required, different routes and substrates are chosen for the synthesis.

## **2.3.2 CVD Parameters**

### **2.3.2.1 Carbon precursors**

In addition to the substrate used for graphene growth, other parameters such as the carbon precursor has a large influence on the quality of the graphene growth. So far, gas, liquid and solid carbon precursors have been studied. Selecting the right type of precursor is largely influenced by the energy required to break the C-H bond. Hydrocarbon such as methane has been the mostly commonly used precursor for CVD, it has dehydrogenation energies of  $410 \text{ kJ mol}^{-1}$  [42] and is highly stable, it has a good thermal stability which prevent pyrolysis at high temperature [43]. Growth using other hydrocarbon such as ethane and propane have been attempted [44]. Ethane and propane have weaker C-H and C-C bond energies than methane. The C-H bond energy for methane is  $439 \text{ kJ mol}^{-1}$  compare to  $418 \text{ kJ mol}^{-1}$  for ethane/propane and the C-C bond energies for ethane and propane are only  $377$  and  $368 \text{ kJ mol}^{-1}$ , respectively [42]. Therefore, ethane and propane decompose via a lower energy pathway and the active carbon species are more likely to react with edges and defects forming multilayer graphene [44]. Lower decomposition pathway also makes the CVD process more difficult to control compare to methane. Liquid precursors such as methanol, ethanol, 1-propanol have also been used as the carbon source [45]. High quality graphene was produced at  $850^\circ\text{C}$  with quality comparable to that of methane with low defect intensity. Growth using solid carbon sources was successfully shown by Sun et al. [46] Poly(methyl methacrylate) (PMMA) was spin-coated ( $\sim 100 \text{ nm}$ ) on Cu film and temperatures of  $800\text{-}1000^\circ\text{C}$  was used under low pressure condition to form monolayer graphene with few defects. It was found that the graphene thickness changed from few layers to bi-layers and to monolayers when the hydrogen flowrate was increased. Solid carbon sources

such as fluorine and sucrose were also investigated in which solid powders were coated on the Cu film. Monolayer graphene was obtained with no defects. Ni film was used as a successful catalyst substrate to grow graphene using PMMA as the precursor [46]. Increasing number of studies have been carried out on the different types of carbon precursor for graphene synthesis and methane remains as one of the most commonly used precursors because of its high stability and low pyrolysis rate.

### **2.3.2.2 Temperature**

In order to activate the graphene growth, carbon precursor must be first decomposed into active carbon species. So far, temperature of around 900 °C to 1100 °C have been studied for growth on copper and nickel substrates [11, 12, 43, 47]. If the growth temperature is too low, defect density will significantly increase. This demonstrates the importance of temperature as a fundamental parameter for quality graphene synthesis. High temperature treatment can also remove volatile impurities and contaminants on the surface and increase grain size [6]. The high temperature used is close to the melting point of the metal, therefore the diffusion coefficient of the atoms becomes large, resulting in increased grain size [6]. To reduce energy demand, increasing efforts have been focused on synthesising graphene at lower temperature because of the cost associated with high temperature CVD.

A low energy alternative is the employment of plasma-enhanced chemical vapour deposition (PECVD). Here, decomposition of carbon precursors is done using energetic plasma electrons that trigger ionisation, excitation and dissociation instead of thermal heat [41, 48, 49]. Inductively coupled plasma-enhanced chemical vapour deposition (IC-PECVD) at temperature as low as 200 °C was carried out by Cheng et al. on polycrystalline nickel substrate, although quality is better enhanced compared to previously reported PECVD method, defects were still observed on the graphene synthesis [49]. CVD temperature between 100 °C to 300 °C was investigated by Jang et al. Graphene was synthesised under the oxygen free atmospheric pressure CVD using benzene at 300 °C for 5 mins, graphene of low defect intensity with 100 % surface coverage and >99 % monolayer graphene was produced. Temperature as

low as 100 °C was also investigated but exhibited low surface coverage because of the decrease in catalytic activity [50]. However, one safety concern with this method is that benzene is a known carcinogen that can damage reproductive organs.

### **2.3.2.3 Role of Hydrogen**

In addition to carbon precursor, hydrogen gas is also being fed into the reactor during graphene growth. So far, various composition and ratios of carbon precursor to H<sub>2</sub> have been investigated but the role of hydrogen remains a debatable subject in whether it assists or degrades the graphene growth process. Vlassiounk et al. suggested that hydrogen has two roles when participating in the growth, acting as an activator to form the active species and as an etching reagent that controls the size and shape of the graphene domains [51]. In the absence of hydrogen, carbon precursors have to chemisorb on the metal surface to form active carbon species which form the graphene. Such dehydrogenation reaction becomes the rate limiting step and as this reaction is not thermodynamically favourable, graphene growth is not desired. As a result, hydrogen acts as an additional catalyst to promote the formation of active carbon species and no graphene growth was observed in the absence of hydrogen [51]. However, other studies have shown that graphene quality deteriorates at high hydrogen concentration [52, 53]. Gao et al. found that increasing hydrogen concentration led to an increase number of wrinkles and inter-domain junctions contributing to the low quality graphene film obtained and the slow growth rate [52]. Where Losurdo et al. believed that the dissociative chemisorption of hydrogen competes with the decomposition of carbon precursors. Hydrogen therefore acts as an inhibitor for the decomposition reaction and suppresses the carbon atom deposition on copper substrate, thus producing poor quality graphene film [53]. In another study, Zhang et al. found that hydrogen plays a crucial role in terminating the graphene edges during CVD growth. At low hydrogen pressure, graphene edges tend to bond tightly to the catalyst surface, prohibiting the diffusion of active species beneath the top layer graphene resulting in the formation of monolayer graphene. Whereas at high hydrogen pressure, graphene edges are terminated by H and

are not bonded tightly to the catalyst surface, thus favouring the diffusion of active carbon species beneath the top layer graphene forming multilayer graphene. By controlling the hydrogen pressure, controlled layer synthesis can be realised [54]. Moreover, hydrogen gas is used as a diluent gas to reduce residual oxygen during the synthesis process [6].

## **2.4 Graphene and its potential applications**

Graphene's superior electrical, mechanical and thermal properties together with its ultra-thin 2D structure have generated significant research interests. Various applications have been explored, especially in the field of energy storage systems [13, 14], field effect transistors [55], microbial fuel cells [56], protective coatings [57-60] and in the field of membrane separations [61] [62] [63] [64].

### **2.4.1 Graphene protective coating**

Graphene exists as a two-dimensional hexagonal lattice with  $sp^2$  hybridisation. The presence of the  $\pi$  electron cloud formed by the p-orbitals overlap can repel any molecules passing by, making graphene impermeable to all gases and liquids and is chemically inert [4, 65]. With these extraordinary properties, graphene acting as protective coating have been widely explored.

The performance of graphene acting as a passivation layer against oxidation was first reported by Chen et al. [57] Oxidation resistance tests were carried out on CVD graphene coated Cu and Cu/Ni alloy by heating them in air at 200 °C for 4 h and immersing the samples into 30 w.w% hydrogen peroxide for 2 to 45 mins. After 4 hours of annealing in air, both graphene coated Cu and Cu/Ni foil showed no changes on their surfaces, whereas the uncoated sample became darker on appearance showing signs of oxidation, indicated in Figure 2.5. Furthermore, graphene grown copper penny immersed in hydrogen peroxide for 2 mins showed no substantial change in colour whereas the uncoated one became much darker in shade. Graphene has thus acted as a passivation layer for Cu

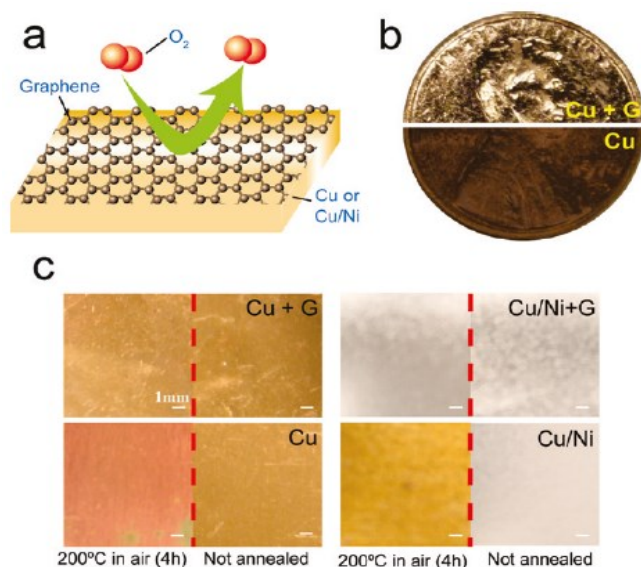


Figure 2.5. a) Schematic of graphene acting as protection barrier; b) Copper penny w and w/o graphene after 2 mins in  $H_2O_2$ ; c) Photographs of graphene protected or non-protected Cu and Ni/Cu alloy after annealing in air for 4h. Reproduced from Ref [57] with permission from American Chemical Society.

and Cu/Ni. Further testing was done to expose the samples for longer period. Results showed that after 2 days of annealing, monolayer graphene coated on Cu showed some signs of oxidation, whereas multilayer graphene coated on Cu/Ni still exhibit a shiny surface. Similar oxidation resistance test was carried out by Nayak et al. and Topsakal et al. where they discovered the surface was protected by graphene after annealing the graphene coated Ni in air for 3 hours [58, 59].

Corrosion inhibition of Cu and Ni were analysed using the electrochemical methods by Prasai et al. [60], Tafel analysis showed that graphene coated on Cu corroded 7 times slower than non-coated sample in aerated  $Na_2SO_4$  and Ni corroded 20 times slower than non-coated Ni. The slower corrosion rate in Ni is related to the multilayer graphene grown compared with monolayer grown on Cu, which is more susceptible to damage because of the reduced graphene thickness. Further corrosion test was conducted by Kirkland et al. using electrochemical test in aqueous media and the impermeable graphene layer was capable of enhancing the corrosion resistance for Cu and Ni [66]. Successful graphene growth and improved chemical resistance were also found on other metals such as Ag and Pt. Zhao et al. found out from the Tafel analysis that corrosion rate of the Ag thin film was reduced by about 66 times with the use of a graphene protective barrier [67]. Nilsson et al. found that the corrosion-inhibiting graphene coating protected platinum against  $O_2$  exposure [68].

Graphene's protection ability was also demonstrated in the application of proton exchange membrane (PEM) fuel cells. Lee et al. synthesised graphene on nickel foam for the use as flow distributor in PEM fuel cells with improved corrosion resistance, Tafel analysis indicated that graphene-coated nickel foam showed nine times lower corrosion current density than the uncoated ones [27]. Pu et al. have grown graphene on Ni and Ni/stainless steel for the use in PEM fuel cell bipolar plates. The graphene-coated stainless steel improved fivefold relative to the corrosion currents in non-coated samples [69]. In another scenario, Parra et al. found that graphene prevented microbial corrosion in metallic structures and reduced the release of  $\text{Ni}^{2+}$  ions when in contact with sweats [70].

Long term graphene protection is a debatable subject. In the study by Schriver et al., they have reported the protection of graphene on Cu from thermal oxidation at temperature of 185 °C and 250 °C for around 6 mins. However, at prolong exposure of 17 h for 250 °C, they discovered that graphene coated Cu showed similar optical images as that of oxidised non-coated Cu. They explained that graphene is only effective for short-term protection. Whereas at prolong exposure at ambient temperature for 18 months, graphene coated Cu was found to promote galvanic corrosion compared to the non-coated sample, where the samples became tarnished with small patches [71]. Graphite is cathodic to Cu and will promote galvanic corrosion of Cu [72, 73], therefore Schriver et al. proposed that the electronic conductivity property of graphene provides an electrical contact across the Cu surface and Cu protected region, and the charge transfer was maintained to the bulk of Cu thus enabling the complete electrochemical reaction to take place. Furthermore, stress will apply to the graphene-Cu from the oxide layer formed thereby inducing more defect areas for corrosion. Later study by Jo et al. revealed that the oxidative barrier properties of graphene can be improved using  $\text{H}_2$  plasma treatment on graphene-Cu [74]. From the study by Schriver et al., they showed that monolayer graphene on Cu is good for short-term protection. However, at long-term period, the metal underneath the graphene layer can be still be oxidised.

However, in the study by Stoot et al., they showed that multilayer graphene formed on nickel deposited stainless substrate (Ni-SS) can act as a protective coating under long period of Atlas testing [75]. The graphene-Ni-SS sample was immersed in high temperature NaCl solution for 504 h, where the non-coated Ni-SS showed signs of corrosion such as the formation of nickel oxides. The graphene coated sample showed no signs of deterioration, indicating the performance of the graphene as protective coating. Although these results contradict with the results found by Schriver et al., Stoot et al. proposed the contradiction between their results and Schriver et al. were that their graphene barrier film was demonstrated under wet environment, whereas Schriver et al. conducted in dry environment. Furthermore, Stoot et al. explained that multilayer was formed using nickel substrate compared to monolayer graphene formed on Cu by Schriver et al., thus greater protection was achieved. With increasing graphene layers, molecules such as water and oxygen will have a more complex, longer route penetrating through the multiple intercalative paths compared to if it is monolayer, thus demonstrating the enhanced protection, shown in Figure 2.6.

Overall, graphene's chemical inertness when used as a protective coating can improve the chemical resistance of metals. Although long-term protection of graphene on copper is a debatable subject, the formation of multilayer graphene on nickel has certainly enhanced the corrosion resistance. Therefore, multilayer graphene is an effective protective barrier on nickel.

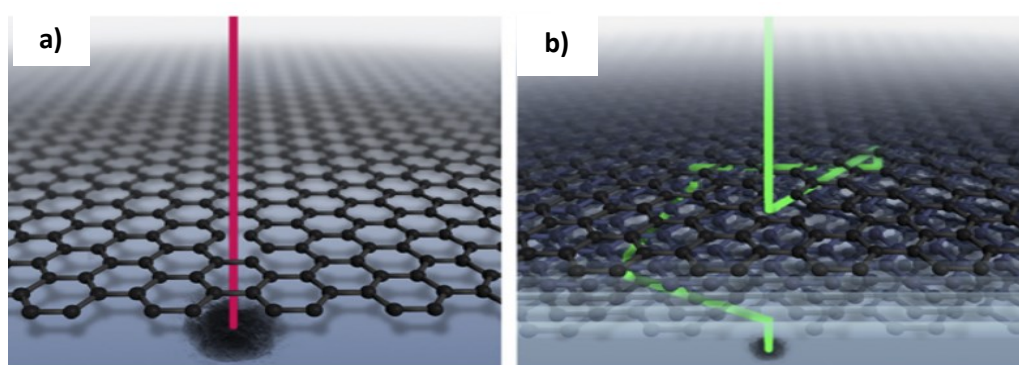


*Figure 2.6. Schematic demonstrating the diffusion paths of molecules through monolayer (a) and multilayer (b) graphene. Reproduced from Ref [75] with permission from Elsevier.*

### 2.4.2 Graphene and graphene-based membranes

Graphene's ultra-thin property together with the chemical inertness make graphene an attractive material for the use in membrane separation. Membrane is a selective barrier that allows certain molecules or ions to pass through as permeate while retaining certain molecules as the retentate, thus separating the desired molecules from the unwanted mixture. In membrane separation, permeation is inversely proportional to membrane thickness. As a result, graphene has the potential to achieve the ultimate permeation attributed to its ultra-thin thickness. Secondly, graphene can be used in extreme conditions, alkaline or acidic, high temperature or high pressure due to its superior chemical inertness. The properties that graphene exhibits thus opened up new possibilities for graphene membranes.

Pristine graphene is impermeable to all gases and liquids [4, 65] because of its high electron density created by the  $\pi$  electrons p-orbitals overlap which repels all molecules. Therefore, nanopores need to be created on the graphene surface for the desired separation. Selectivity can be achieved either by size exclusion or electrostatic repulsion between charged species, shown in Figure 2.7. This synthesis renders nanoporous graphene (NPG) which could be the next generation ideal membrane [76-78].

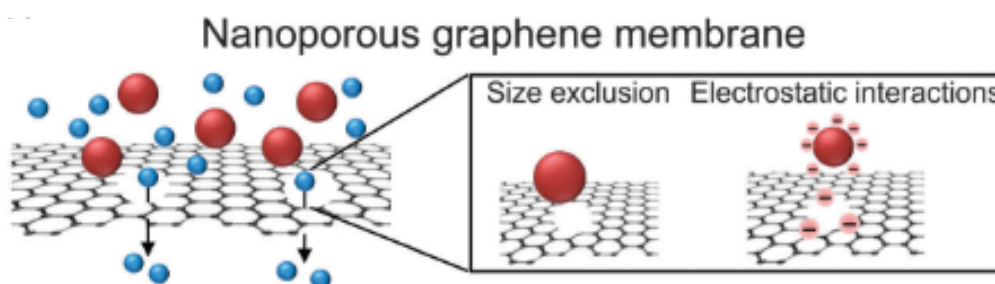


Figure 2.7. Nanoporous graphene membranes with nanopores. Reproduced from Ref [78] permission from Royal Society of Chemistry.

#### 2.4.2.1 Theoretical and simulation studies on nanoporous graphene membranes

In the earlier studies, Jiang et al. used the first principal density functional theory calculations to investigate the NPG's permeability and selectivity for gas separation. The graphene membrane with nitrogen-functionalised pores revealed selectivity in the order of  $10^8$  for  $H_2/CH_4$  mixture and a high hydrogen permeance, which is much more superior than the conventional membranes [79]. Hereafter, molecular dynamics (MD) simulations have been conducted to design series of NPG for  $H_2/N_2$  separation [80],  $CO_2/N_2$  separation [81], helium from noble gases and alkanes [82] and  $H_2$  from coal gas [83], all demonstrating promising separation performance. The permeability and selectivity can also be tuned by designing the size of the pores [83]. Sun et al. have shown that NPG membranes can be tuned to separate gases with different kinetic diameters. By changing the nanopore geometry, the membranes can be permeable to hydrogen and helium, but significantly less permeable to nitrogen (selectivity  $>10$ ), and virtually impermeable to methane (selectivity  $>100$ ) [84].

In addition to gas separation, the use of graphene membranes for seawater desalination have been intensely studied theoretically. In 2012, Cohen-Tanugi et al. used molecular dynamics to model nanometre sized pores ranging from 1.05 to 62 Å on monolayer graphene for salt water separation, where the pores were passivated with hydrogen atoms (hydrophobic) and hydroxyl groups (hydrophilic) [85]. They revealed that permeability is linearly related to pore area and water permeability can increase to as high as 5000 LMH ( $L\ m^{-2}\ h^{-1}$ )  $bar^{-1}$  with the hydroxylated pores, which is several orders higher than conventional membranes. Pore diameter was also found to be a critical parameter for salt segregation, where simulation result showed that salt can be rejected provided the pore diameter is smaller than 5.5 Å. Molecular dynamics also performed on multilayer NPG, studying the interaction between nanopores on different layers which affects the permeability and salt rejection, shown in Figure 2.8 [86]. Simulations showed that if the layer separation  $H$  is greater than 8 Å, they are considered as two separate barriers where the permeability can be calculated as resistance in series model. Whereas for  $H$  less than 8 Å, both layer separation  $H$  and pore offset are critical parameters that determine the permeability. For best performance separation, fully aligned pores

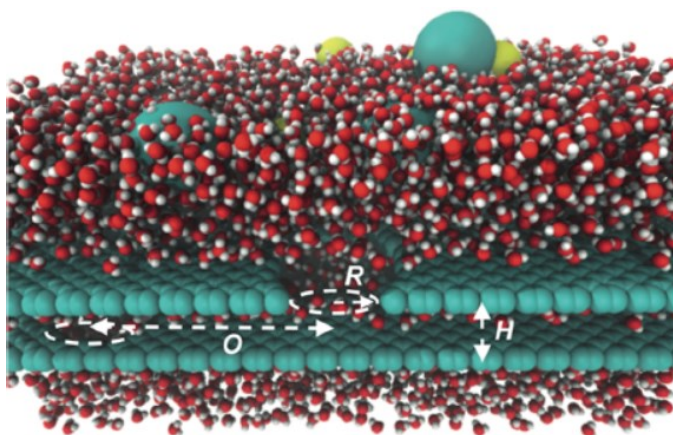


*Figure 2.8. Bilayer graphene membrane with nanopore radius  $R$ , separation layer  $H$  and pore offset  $O$ . (Red-white molecules representing water and large green molecules representing salt-NaCl). Reproduced from Ref [86] from American Chemical Society.*

with small separation layer is desired. However, if the pore offset cannot be controlled, very close separation layer can block the water flow, therefore sufficiently larger separation layer of 8 Å is preferred. Demonstrated by Sint et al., ion selectivity can be designed by choosing different functionalised nanopores in the graphene monolayers. Negatively charged pores terminated with nitrogen and fluorine favour cation passage, whereas hydrogen terminated pores favour the passage of anions [87].

The mechanical integrity of graphene as a membrane was explored by Cohen-Tanugi et al. [88] Through molecular dynamics simulations and continuum fracture mechanics, they revealed that NPG can stand up to 570 bar hydraulic pressure provided the underlying substrate has opening smaller than 1 µm. This is about ten times greater than the traditional pressure used for seawater reverse osmosis.

In summary, molecular dynamics simulation has demonstrated graphene membrane to be a promising material for membrane separation. In order to realise high selectivity and permeation, key parameters such as, pore size, termination sites and layers should be well controlled. These works also provide important guidance and comparison to experimental works performed.

#### 2.4.2.2 Preparation of nanoporous graphene membranes

Synthesis of graphene membranes have been widely carried out and most of the currently prepared membranes exist either in free-standing form or are supported on planar substrates [61] [62] [63] [64]. As demonstrated in the earlier sections, graphene can be synthesised in large scale using CVD on metal substrates, and thus this has been the most widely used approach for graphene membrane fabrication. Subsequently, after the CVD graphene growth, a polymer or polymer-free graphene transfer approach is adopted to achieve graphene supported on planar substrate for controlled pore generation to realise the high-performance membrane. In the polymer transfer approach, indicated in Figure 2.9a, PMMA is generally used and is spin-coated onto the metal-graphene. The metal layer is then etched using metal etchant leaving the PMMA-graphene layer which is then transferred onto the substrate and finally the PMMA layer is removed by dissolving in acetone and by thermal annealing [61, 89]. A variety of polymer-free approach have been adopted, such as the pressing or casting method. Boutilier et al. and O'hern et al. have demonstrated the transfer via a pressing method. Boutilier et al. first dissolved the copper in graphene-copper film by placing this in ammonium persulfate. After the copper was completely removed, graphene layer was left floating on the solution. The polished and cleaned substrate was then gently pressed into the graphene against surface tension, realising the graphene membrane (Figure 2.9b) [90]. Similar technique was also used by O'hern et al. [91]

Meanwhile, the casting method was demonstrated by Qin et al. and Kidambi et al. Polymer solution such as, poly(ether sulfone) (PES) in N-methyl- 2-pyrrolidone (NMP) was coated on the graphene-metal substrate. This was then immersed in water for phase inversion to happen, realising the support formation on graphene-metal. Finally the metal layer is etched using metal etchant forming the pristine graphene on planar substrate (Figure 2.9c) [63, 64].

A different graphene membrane synthesis approach was investigated by Huang et al., here, they have developed a nanoporous carbon film-assisted transfer method. A nanocarbon film was formed by first spin coating a solution of turanose and polystyrene-co-poly(4-vinyl pyridine) on the CVD graphene

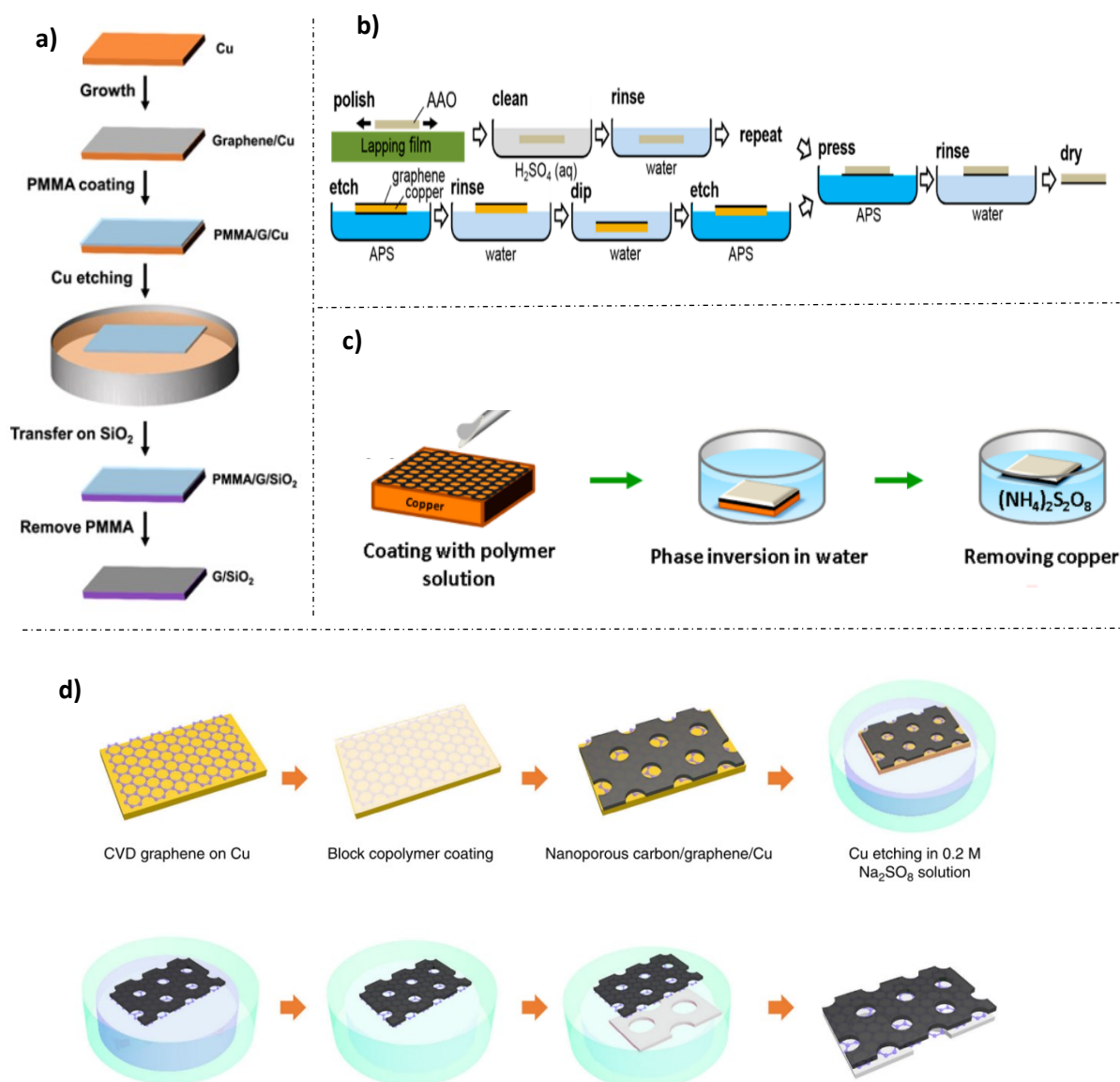


Figure 2.9. a) Schematic of the graphene transfer process onto a target substrate using PMMA. Reproduced from Ref [89] with permission from IOP Publishing; b) Schematic of the direct pressing method. Reproduced from Ref [90] with permission from American Chemical Society; c) Schematic of the graphene membrane formation using support created from the phase inversion process. Reproduced from Ref [63] with permission from American Chemical Society; d) Graphene transfer on target substrate using nanoporous carbon film. Reproduced from Ref [92], Open Source.

layer. Upon drying, phase separation happens where the block-copolymer film turns into hydrophobic and hydrophilic domains. The film was then pyrolysed in inert gases at 500 °C forming the nanoporous film on graphene. The metal layer was then etched leaving the nanoporous carbon film on graphene to be transferred onto a suitable substrate, shown in Figure 2.9d [92].

As demonstrated above, many transfer techniques have been explored, demonstrating the versatility of graphene transferring to a range of substrates.

Since pristine graphene membrane is impermeable to gases and liquids, pores have to be generated in order to achieve the desired generation. Various techniques have been deployed to induce nanometre sized pores onto the graphene, such as ultraviolet-induced oxidative etching [93], ion bombardment [62, 63] and oxygen plasma etching treatments [61, 90]. Examples are shown in Figure 2.10. In addition to controlled pore generation, selective molecular transport has also been demonstrated through intrinsic defects of 1-15 nm diameter pores, which were produced in monolayer graphene synthesised from low quality CVD process [62, 91]. In the next section, performance of the prepared nanoporous graphene membranes in the applications of liquid and gas separations are explored.

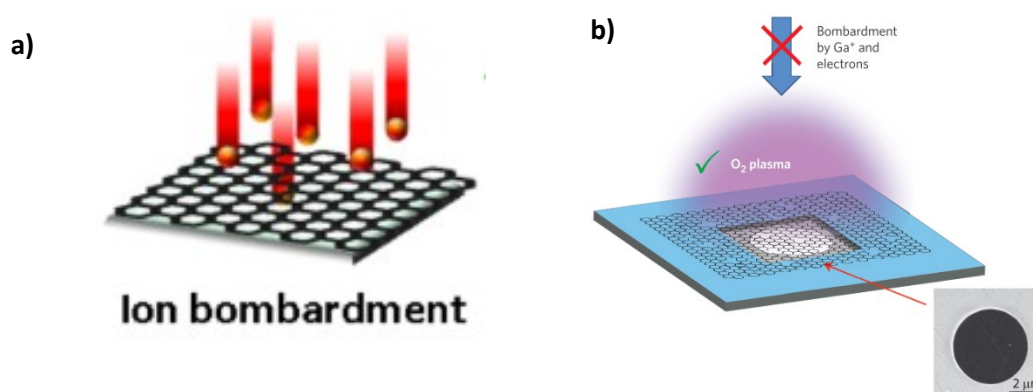


Figure 2.10. Pores generated by (a) ion bombardment. Reproduced from Ref [63] with permission from American Chemical Society or (b) by O<sub>2</sub> plasma treatment. Reproduced from Ref [61] with permission from Springer Nature.

### 2.4.2.3 Applications of nanoporous graphene membranes

#### 2.4.2.3.1 Liquid separation and performance

The use of graphene membranes in the application of desalination and water permeation have been studied intensely. Transport of water and ions through free-standing graphene membrane for desalination was demonstrated by Surwade et al. A 5-μm-diameter size suspended, single-layer graphene membrane consisting of nanometre-sized pores generated by oxygen plasma etching was developed (Figure 2.10). The permeation performance was strongly dependant on the exposure time to oxygen plasma. Extending the exposure time not only increased the number of defects but also enlarged the pores. Pore sizes ranging from 0.5-1 nm with density  $\sim 1 \times 10^{12} \text{ cm}^{-2}$  was achieved. The

membrane exhibited ~100% salt rejection and high-water selectivity over dissolved ions, such as  $K^+$ ,  $Na^+$ ,  $Li^+$ ,  $Cl^-$ . A remarkable water permeation flux of  $252 \text{ LMH bar}^{-1}$  was achieved using osmotic pressure as the driving force [61].

Centimetre-scale nanoporous monolayer graphene was created by O'hern et al., using multi-scale defect seal process [62]. They found that intrinsic defects in the size of 1-15 nm were formed during the chemical vapour deposition process and larger 100-200 nm defects from tears and cracks were generated during the graphene transfer process. Therefore, a two-step sealing process was implemented to enhance the integrity of the membrane. Intrinsic defects were sealed using atomic layer deposition of hafnia and Nylon-6,6 was synthesised to plug the large defects via interfacial polymerisation. Pores were then created using high-energy gallium ion bombardment followed by etching of the defects into sub-nanometre pores using acidic potassium permanganate. The water permeance was found to be 1.41 and  $0.43 \text{ LMH bar}^{-1}$  for the pores generated and non-pore generated membrane, respectively. Mean pore diameter was found to be 0.162 nm, with the larger pores exhibiting at 0.5 nm. The achieved membrane permeation is in the same order of magnitude as current reverse osmosis membranes for seawater desalination. The flux achieved without pore generation is likely from the residual defects and the polymer used to seal the defects. The prepared membrane showed ~70 % rejection of  $MgSO_4$ , ~90 % rejection of Allura Red and ~83 % rejection of dextran. It was hypothesised that the higher rejection of Allura Red is from the electrostatic repulsion between the anionic Allura Red molecule and the negatively charged pores [62].

Kidambi et al. synthesised  $>5 \text{ cm}^2$  nanoporous atomic thin graphene via a facile approach. By reducing the CVD temperature for graphene synthesis, in-situ nano-scale pores ( $\leq 2-3 \text{ nm}$ ) were created serving as the intrinsic defects for dialysis applications. The defects can be formed during different stages of the CVD process, such as during the growth state, within the grain boundaries of the individual graphene domains, or via the etching of the metal layer or during the cooling stage when methane no longer dissociates to form the carbon layer. Other factors such as hydrogen or other impurities can

also etch the grown graphene forming the defects [84, 94]. The prepared membrane showed effective desalting of molecules ( $\sim 0.2\text{--}1.355$  kDa) and proteins ( $\sim 14$  kDa), it also achieved permeance that is  $>2$  times greater than the conventional commercial polymeric membranes [64].

Large area of  $63\text{ cm}^2$  single-layered perforated graphene membranes have been developed by Qin et al. where the membrane can withstand pressure of up to 50 bar. Here, aqueous suspension of impermeable polystyrene nanoparticles were used to plug the defects created on the membrane following the graphene transfer. Hereafter, high energy gallium ions were used to nucleate pores and then etched using acidic potassium permanganate to open up the pores. Pore density of  $\sim 1.57 \times 10^{12}\text{ cm}^{-2}$  was achieved, realising water permeation flux of  $50\text{ LMH bar}^{-1}$ , which is at least 5 times better than conventional polymeric membranes. Rejection results show that the prepared membrane were able to reach 98 % rejection of Dextran 70K ( $\sim 7$  nm) and 90 % rejection for molecules with hydrated radius between 0.9 nm (328 Da) - 7nm [63].

Selective ion transport through nanopores was demonstrated by O'Hern et al. By using combination of ion bombardment followed by oxidative etching, pores of 0.4 nm with density exceeding  $10^{12}\text{ cm}^{-2}$  was achieved. Pores were cation-selective with negatively charged functional group terminating the pore edges at short oxidation times. At longer oxidation times ( $>15$  mins), the pores allowed permeation of salt molecules but rejected large organic molecules. By tuning the oxidation time, pore diameters can be tailored for organic separation or desalination purposes [95].

Larger pore sizes were created in the study by Celebi et al. and Wei et al. 50 nm pore size was created by Celebi et al. using gallium focused ion beam and a remarkably high water flux was obtained at  $10,000\text{ LMH bar}^{-1}$  [76]. Wei et al. have synthesised a four-layered graphene membrane with thickness of 2 nm. Here larger pore sizes were generated via the use of metal oxide nanoparticles to remove the carbon atom within the graphene lattice. Pore size of 50 nm was created with density of  $1.0 \times 10^7\text{ cm}^{-2}$ .<sup>1</sup> The average interlayer spacing of randomly stacked graphene layers is  $3.55\text{ \AA}$ , which is significantly smaller than the pores size. Therefore, Wei et al. explained that the molecular transport is through

the pores generated, which possess perpendicular pore channels, instead of through the narrow interlayer spacing. The flux obtained was tremendously high up to 4,600 LMH at 0.2 bar and 99 % rejection of 65 nm Au nanoparticles. The prepared 20 nm pores generated graphene membrane achieved 90 % rejection for 35 nm PS nanospheres after separating the mixture for 3 times [96].

As demonstrated above, experimental results show great advancement of graphene membranes in terms of liquid separation, in particular, desalination and nanofiltration. However, one of the major challenges currently is manufacturing graphene membranes in large scale and optimising pore generation. A summary of the above-mentioned notable of liquid separation results are listed in Table 2.1.

Table 2.1. Liquid separation performance of various prepared graphene membranes

| Graphene membranes                         | Size of membrane   | Pore size, defect density                             | Flux (LMH bar <sup>-1</sup> )                                    | Rejection                                                                                                                  |
|--------------------------------------------|--------------------|-------------------------------------------------------|------------------------------------------------------------------|----------------------------------------------------------------------------------------------------------------------------|
| Single layer porous graphene membrane[61]  | 5 µm               | 0.5 nm – 1nm,<br>~1×10 <sup>12</sup> cm <sup>-2</sup> | 252                                                              | 100 % Salt rejection                                                                                                       |
| Single layer porous graphene membrane [62] | Centimetre scale   | 0.162-0.5 nm                                          | 1.41                                                             | ~70 % MgSO <sub>4</sub><br>~90 % Allura Red<br>~83% dextran (4.4 kDa and ~3.7 nm)                                          |
| Nanoporous atomically thin membrane [64]   | >5 cm <sup>2</sup> | ≤2–3 nm                                               | ≥ 2 × permeance than conventional commercial polymeric membranes | Desalting molecules ~0.2–1.355 kDa and proteins (~14 kDa)                                                                  |
| Single layer porous graphene membrane [63] | 63 cm <sup>2</sup> | ~1.57× 10 <sup>12</sup> cm <sup>-1</sup>              | 50                                                               | 98 % rejection of Dextran 70K (~7 nm) and 90 % rejection for molecules with hydrated radius between 0.9 nm (328 Da) – 7 nm |
| Four-layered graphene membrane [96]        | -                  | 50 nm                                                 | 46,000 at 0.2 bar                                                | 99 % rejection of 65 nm Au nanoparticles                                                                                   |
| Perforated double-layer graphenem [76]     | -                  | 50 nm                                                 | 10,000                                                           | -                                                                                                                          |

#### 2.4.2.3.2 Gas separation and performance

In addition to liquid permeation, variety of studies have been carried out on gas separation. Koenig et al. have prepared micrometre-sized graphene membrane from mechanically exfoliated graphene [93]. Ultraviolet-induced oxidative etching was used to create the pores and the membrane was suspended on a 5  $\mu\text{m}$  diameter well etched on silicon oxide substrate. The microcavity formed under the graphene membrane were filled with the desired gas species. Gas molecules bigger than the etched pore will leak through and molecular transport of  $\text{H}_2$ ,  $\text{CO}_2$ , Ar,  $\text{N}_2$ ,  $\text{CH}_4$  and  $\text{SF}_6$  gases were tested. The  $\text{H}_2$  and  $\text{CO}_2$  leak rates for bilayer graphene was  $4.5 \times 10^{-23}$  and  $2.7 \times 10^{-23} \text{ mol s}^{-1} \text{ Pa}^{-1}$ , respectively. The  $\text{H}_2$  leak rate is similar to the rate computationally modelled by Blankenburg et al. [97]. The work presented in this study thus provides the fundamental limits of gas transport by effusion through angstrom-sized pores [93].

In 2014, Celebi et al. prepared free-standing double layer graphene membranes with pore densities of  $10^3$  to  $10^6 \text{ cm}^{-2}$  induced by gallium (10 nm -  $1\mu\text{m}$ ) and helium (< 10 nm pores) based focus ion beamed. As well as testing for water permeation mentioned earlier. The membrane was also tested for gas permeation. A 7.6 nm pore diameter membrane exhibited  $\text{H}_2$  permeance of  $10^{-2} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  and a selectivity of  $\text{H}_2/\text{CO}_2$  of around 8 [76].

One thing to highlight is Koenig et al. studied the performance in  $\sim$ one pore and Celebi et al. studied with pore density of  $\sim 10^6 \text{ cm}^{-2}$ . Boutilier et al. used ion bombardment followed by oxygen plasma etching to produce sub-nanometre pores with pore density of  $\sim 10^{11} \text{ cm}^{-2}$ . The  $\text{H}_2/\text{CH}_4$  and  $\text{H}_2/\text{CO}_2$  selectivity obtained were 4.22 and 6.61, respectively. Slightly lower  $\text{H}_2/\text{CH}_4$  selectivity was observed by Boutilier et al. compared to the study by Koenig et al., but a significantly higher permeability of  $1.2 \times 10^{-5} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  was achieved due to the centimetre-scale nanoporous graphene with higher pore density obtained by Boutilier et al. [90]

Kim et al. prepared varying number graphene layer supported on polymer substrate (Poly(1-methylsilyl-1-propyne) (PTMSP)). Defects were created after the graphene synthesis and transfer

process. By increasing the number of graphene layers, the performance was improved. Here, the  $O_2/N_2$  selectivity increased from 1.5 to 6, as the number of graphene layers increased from 0 to 5 layers. The  $O_2$  permeability decreased from 730 to 29 barrer, surpassing the  $O_2/N_2$  separation limitation of polymeric membranes [98].

Large area of  $1\text{ mm}^2$  single-layer graphene membrane was prepared by Huang et al., here, intrinsic defects were used as gas sieving pores formed by the presence of residual oxygen [92]. The membrane revealed  $H_2$  permeance ranging from  $5.2 \times 10^{-9}$  to  $7.2 \times 10^{-8}\text{ mol m}^{-2}\text{ s}^{-1}\text{ Pa}^{-1}$  with  $H_2/CH_4$ ,  $H_2/CO_2$ , and  $He/H_2$  ideal selectivity ranging between 4.8–13.0, 3.1–7.2, and 0.7–2.0, respectively. The  $H_2$  permeance experimental results were also consistent with that of Koenig et al. [93] By increasing the temperature, both permeance and selectivity were increased. At  $150\text{ }^\circ\text{C}$ , the  $H_2$  permeance increased to  $3.3 \times 10^{-8}$  -  $4.1 \times 10^{-7}\text{ mol m}^{-2}\text{ s}^{-1}\text{ Pa}^{-1}$  (100 - 1220 GPU), and the  $H_2/CH_4$ , and  $H_2/CO_2$  selectivities increased to 7.1–23.5 and 3.6–12.2, respectively. Gas selectivity were also improved by chemical functionalisation of the pore-edge. In the same study, Huang et al. used ozone-derived epoxy and carbonyl groups to oxidative functionalise molecular sized pores in graphene and to constrict the existing pores. At  $150\text{ }^\circ\text{C}$ , the  $H_2$  permeance decreased from  $2.3 \times 10^{-7}$  to  $1.2 \times 10^{-7}\text{ mol m}^{-2}\text{ s}^{-1}\text{ Pa}^{-1}$ , while the  $H_2/CH_4$  and the  $H_2/CO_2$  selectivities increased from 10.0 to 15.0 and 5.1 to 6.4, respectively. The size of the pores were shrunk restricting the diffusion of  $CH_4$  and thus the increase of selectivity [92].

As shown above, both experimental and simulation works have been carried out on nanoporous graphene membranes, demonstrating favourable performance in desalination, nanofiltration and gas separation. However, scalability is still a key challenge, where synthesising large area of graphene film in a geometry that favours scaling up is a key milestone to achieve.

#### 2.4.2.4 Graphene-based membrane performance

On the other hand, graphene oxide (GO), a chemical derivative of graphene has also been considered as a favourable material for membrane separation. The graphene structure consists of many oxygen-containing functional groups on the edges and basal planes [99], shown in Figure 2.11.

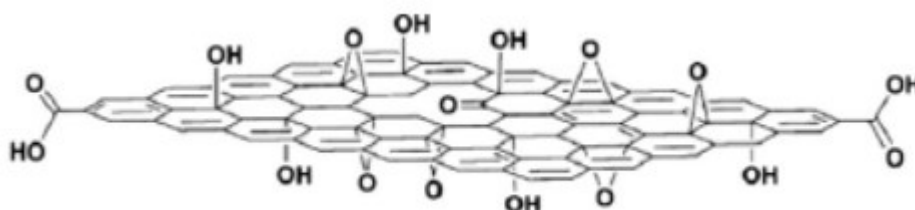


Figure 2.11. Graphene oxide structure. Reproduced from Ref [99] with permission from John Wiley Sons.

Graphene oxide is generally prepared using the modified Hummers method [100] and is usually dispersed in water or polar solvent. Free-standing GO membranes have been produced and various deposition methods have also been adopted to produce supported GO membranes, using methods such as vacuum filtration and pressure filtration to cast the GO suspension on planar or hollow fibre supports [101-104]. The GO flakes arrange themselves via a self-assembly process, where each flake is stacked on top of each other, forming a uniform laminar structure with hydrogen bonds between the flakes. The interlayer space can range from 6 to 13 Å and provides the flow passage for molecular transport. By tuning the interlayer space, the desired separation can be achieved [102, 104-106].

Nair et al. developed a sub-micrometre thick GO membrane that was completely impermeable to all liquids and gases including helium [102]. However, nanometre thick (<10 nm) GO membrane have shown to achieve gas permeation with considerable flux and high selectivity. A high CO<sub>2</sub>/N<sub>2</sub> selectivity of 20 was obtained with highly interlocked layer structures [98].

Water transport through GO membrane was studied by Joshi et al., here, micrometre thick laminates was prepared. At dry state, the GO membrane was vacuum-tight, but when immersed in water, the GO membrane retained all solutes >4.5 Å [107]. A high water permeation flux of 71 LMH bar<sup>-1</sup> was demonstrated by Huang et al. [108] Aba et al. prepared GO membrane supported on ceramic hollow

fibre and found that the membrane was also suitable for organic solvent nanofiltration because of its stability in organic solvents, such as acetone, methanol, toluene and *n*-hexane. The membrane exhibited flux of 3.97 and 6.35 LMH bar<sup>-1</sup> for methanol and acetone, respectively. While being able to reject molecules less than 327.3 Da, Aba et al. found that stability was an issue and shrinkage-induced stress occurred in air, where the membrane had to be stabilised by immersing in water [103]. Later on, Chong et al. discovered a route to stabilise GO membrane by introducing a porous PMMA sacrificial layer to create spacing between the GO and ceramic hollow fibres [109]. So far, relatively good results have been observed in GO membranes, however, highlighted by Chong et al., GO membranes pose another problem, which is the compaction problem [106]. Chong et al. discovered that GO membranes showed severe reduction in water permeability during filtration. The water flux dropped from tens of LMH bar<sup>-1</sup> to <0.1 LMH bar<sup>-1</sup> after testing for more than 10 hours. When pressure is continuously applied during water permeation, it is hypothesised that this causes compaction to the original loose and less ordered microstructure. The interlayer distance may not have been altered because of the strong hydrogen bond, but the spaces/cavities between the laminae may compress into an ordered microstructure [106]. The effective water transport is therefore significantly longer causing rapid decrease in water permeability. GO membranes may be a potential candidate in achieving relatively good separation performance, however, compaction problem occurs with GO membrane during pressure-filtration.

## **2.5 Potential micro-tubular substrates for graphene hollow fibre membranes synthesis**

Graphene has demonstrated great potential in the application of graphene membranes and as protective layer. One of the key challenges, however, is the challenge of industry scale-up. This is especially important for graphene membrane if it wishes to achieve commercialisation. Generally, membranes exist in different configurations, such as disc, plate, tubular and hollow fibre. The type of configuration selected will depend on the purpose desired such as the surface to volume ratio,

mechanical strength and its packing density. Disk and plate membranes have been widely used in research work. However, membranes of these geometries possess low separation-area-to-volume ratios, which makes them undesirable for commercialisation. Currently, hollow fibre is the most promising configuration for industry scale up because of its high membrane-area-to-volume ratio with packing density potentially up to 8000-10,000 m<sup>2</sup> m<sup>-3</sup> [110] and is favourable for module assembly.

Utilising the versatility of the CVD growth method on metal substrates. This promising graphene material can be grown on metallic micro-tubular supports, realising graphene hollow fibre membranes for the ease of commercialisation and large-scale operation. Herein, this thesis looks to explore the potential fabrication and applications of graphene hollow fibre membranes developed using metallic hollow fibre substrates/membranes. In the next sub-section, it will focus particularly on the preparation of metallic hollow fibre membranes, which will assist in the fabrication of graphene hollow fibre membranes.

### **2.5.1 Metallic hollow fibre membranes**

Metallic membrane is a subgroup of inorganic membranes which has attracted great attention because of its good thermal shock resistance, good electrical and thermal conductivities. The membrane is also more mechanically robust compared to ceramic membrane, making it ideal for brazing and welding [111, 112].

Metallic hollow fibre membranes can be classified as pristine metallic hollow fibre or metal deposited on hollow fibre. Pristine metallic hollow fibre membranes can be prepared using single material [111-113] or dual materials [28, 114, 115]. On the other hand, a metallic layer can be deposited on hollow fibre, forming metallic hollow fibres [116-119].

#### **2.5.1.1 Pristine metallic hollow fibre membranes**

One of the most widely used method for the preparation of pristine metallic hollow fibre membranes

is the combined phase inversion and sintering techniques [111, 113, 120]. Metallic dope suspension is first prepared comprising of metallic powders, solvent, polymer binder and dispersant. The suspension is then degassed and extruded out via the spinneret together with the internal coagulant into an external coagulant bath. Phase inversion takes place due to the presence of the non-solvent coagulants, solvent and the polymer binder in the dope suspension. When the dope suspension comes into contact with the coagulants, solvent diffuses out from the suspension while the coagulants diffuse into the suspension. This solvent and non-solvent exchange changes the thermodynamically stability of the suspension to metastable or unstable state, resulting in the precipitation process which forms the membrane precursors [110]. The membrane precursor is then straightened and sintered at high temperature dependent on the morphology wishes to obtain.

Porosity of the membrane can be tuned by the sintering temperature, demonstrated in the study by Meng et al. for nickel hollow fibre membrane. When the sintering temperature was increased from 600 °C to 900 °C, nickel particles were bonded into larger particulates, this coalescence resulted in higher relative density and smaller porosity, and a higher mechanical strength was obtained. When the temperature reached 950 °C, the membrane became gas-tight, which is ideal for hydrogen separation [120]. Mechanical robustness can also be strengthened at increasing temperature, Lee et al. show that the mechanical strength increased from 75 to 88 and 160 MPa for nickel hollow fibre sintered at 1100 °C, 1200 °C and 1300 °C, respectively [111]. Nickel hollow fibre membrane has demonstrated use in hydrogen separation [113], it is a relatively cheap replacement to palladium membrane for hydrogen separation. Gas-tight nickel hollow fibre with thickness of 256 µm was sintered at 1400 °C, 100 % H<sub>2</sub> permselectivity was shown with hydrogen permeation flux up to  $1.66 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$  at 1000 °C, the fibre was also found to be stable under CO<sub>2</sub>, CO and steam containing atmosphere. Nickel hollow fibre membrane has also been used as anaerobic electrochemical membrane bioreactor, with an average pore size of 1 µm, the membrane acted as both the cathode for hydrogen evolution reaction and membrane for filtration of the effluent [29, 121].

Other pristine metallic hollow fibre membranes such as stainless-steel has also been fabricated [112, 122, 123]. By changing the viscosity of the dope suspension with different particle loading and sintering temperature, different membrane morphologies were achieved. High mechanical strength of 750-1150 MPa was obtained by Luiten-Olieman et al. sintering the membranes at 1050 °C and 1100 °C [112]. Schmeda-Lopez et al. prepared stainless-steel hollow fibre membrane and studied the influence of metallic particle size and sintering temperature have on the membrane morphology [123]. At temperature of 950 °C, the stainless-steel particles did not coalesce and presented large pores of irregular shapes. When sintering temperature increased from 1000-1050 °C, greater particle coalescence was observed forming larger agglomerates. When large stainless-steel particles size was used at 45 µm, the membrane did not exhibit a neat hollow fibre structure, by decreasing the particles size to 6 µm, the structure became more compact and more homogenous. During the sintering step of metallic membrane, metal oxidation can occur on the surface and it is crucial any residual oxygen is removed from the sintering atmosphere. Rui et al. reported the sintering effect of stainless-steel membrane in atmosphere such as air, CO<sub>2</sub>, N<sub>2</sub>, He and H<sub>2</sub>. H<sub>2</sub> was found to be the most effective atmosphere, whereas air and N<sub>2</sub> caused metal oxidation, and He and N<sub>2</sub> atmosphere caused carbon formation. These results show that stainless steel is very susceptible to sintering atmosphere and can be easily oxidised [122]. In another instance, Chong et al. created a stainless-steel ceramic composite membrane, using ceramic nanoparticles to fill up the large pores around the stainless-steel particles, reducing its mean pore size down to 300 nm, which is much smaller than the usual pore size greater than 1 µm. The membrane also demonstrated a pure water flux as high as ~ 3000 LMH bar<sup>-1</sup> [115]. Recently, dual-layer Cu/Cu-Fe metallic micro-tubes were successfully fabricated using the phase-inversion facilitated co-extrusion/sintering approach. Graphene was synthesised on the outer copper layer and the inner Cu-Fe layer provides good mechanical support for the overall membrane. This high surface-area-to-volume ratio membrane has the potential to be used as membrane reactors or heat exchangers [28].

### **2.5.1.2 Deposition of metallic layer on hollow fibre supports**

Metallic hollow fibre membranes can also be prepared via depositing a metallic layer on hollow fibre support. Here, the hollow fibre support act as the scaffold providing the membrane with good mechanical integrity and structure. The support can be made of ceramic, metallic or glass supports.

This method is widely employed for palladium and palladium alloyed hollow fibre membranes and is studied extensively for hydrogen separation because of palladium's high permeability and selectivity towards hydrogen [116-119]. Gouveia Gil et al. have prepared a 1  $\mu\text{m}$  thick palladium membrane supported on alumina hollow fibre achieving hydrogen permeation flux of  $0.87 \text{ mol s}^{-1} \text{ m}^{-2}$  at  $450^\circ\text{C}$  and 165 KPa [119]. Metallic support may also be used, Mardilovich et al. developed palladium membrane supported on porous stainless-steel tubes via the eletroless plating method [114]. Palladium is an expensive metal which led to the findings of other metals for replacement, nickel was found to be a good and cheap alternative material. Although hydrogen permeability in nickel is lower compared to palladium, many researches have investigated the synthesis of nickel deposited hollow fibre membranes [124, 125]. Ernst et al. developed a nickel-plated alumina hollow fibre membrane for hydrogen separation. A thin nickel layer of 1-1.5  $\mu\text{m}$  was deposited via electroless plating, with the membrane achieving a permeation flux of  $2.5 \times 10^{-3} \text{ mol m}^{-2} \text{ s}^{-1}$  at  $600^\circ\text{C}$  [124].

#### **2.5.1.2.1 Electroless plating**

As mentioned above, most of the metallic layer deposited hollow fibre membranes prepared are via the electroless plating process. In this section electroless plating will be further discussed, mainly focusing on nickel and copper electroless plating.

Many metal deposition techniques are available, such as sputter coating, metal evaporation and electroplating. However, electroless plating emerged to be the most promising method because of the ease of preparation, low cost, scalability, uniform deposition and can be applied to a variety of complex substrates [126]. An electroless plating solution is first prepared, the substrate is then

immersed into the plating solution followed by the addition of reducing agent. Unlike electroplating which requires an external circuit to provide the flow of electrons [127]. Electroless plating is an autocatalytic process in which the reducing agent is oxidised, supplying the electrons for the metallic ions in the solution to be reduced, depositing the metallic layer on the activated support surface.

Electroless plating is a complex chemical reaction and the quality of the deposition can be influenced by the bath composition, temperature and pH. In general, the plating solution consists of the metallic source, complexing agent, stabiliser and the reducing agent. The metal source provides the fundamental metallic layer wish to be deposited. Alkaline condition is generally more thermodynamically favourable for electroless plating, but the solution can also precipitate at high pH, complexing agent is therefore added to prevent the metal precipitating by maintaining the level of free ions. Oxidation of reducing agent forms  $H^+$  and  $OH^-$ , altering the pH level in the solution, complexing agent also prevents the pH from decreasing during deposition and maintaining at high pH. Complexing agents such as sodium potassium tartrate and ethylenediamine-tetraacetic acid (EDTA) have been used [128]. The plating solution can be unstable and in the presence of active nuclei such as dust, it can lead to homogenous decomposition of the plating solution. Stabiliser is added to prevent this decomposition by adsorbing itself to the active nuclei and fencing them away from the reducing agent. However, excess use of stabilisers is not good because it can completely prevent the deposition of metallic layer on the support surface. 2-mercap tobenzothiazole and lactic acid have used as stabilisers. Reducing agent is added to release the flow of electrons, to be able to reduce the metal ions and form the metallic layer on the support [128].

Dependent on the support substrate used, prior to electroless plating, an activation and sensitisation steps maybe carried out to improve the catalytic activity of the substrate surface. These activation steps favour the metallic deposition process on substrate by encouraging the formation of nucleation catalytic sites. The process is generally carried out by first sensitising in tin chloride solution, to adsorb tin ions on the support, followed by rinsing to remove the chloride ions. The substrate is then

immersed in palladium solution, in which the palladium ions are reduced and seeded on the support substrate, replacing the tin ions. The active palladium seeds then act as the catalytic site which enhance the nucleation of metal on surface [125, 129].

For the case of nickel plating, hydrazine is used as the reducing agent if pristine nickel is required, here the only oxidation by-products are water and nitrogen. Other reducing agents such as sodium hypophosphite and sodium borohydride can be used, but they generally produce nickel alloy of nickel-phosphorous or nickel-boron [127, 130]. Temperature of the electroless nickel plating bath normally operates between 60-90 °C. Increasing the temperature favours the deposition because it is an endothermic reaction, however, temperature has to be carefully controlled to avoid self-decomposition and formation of metals in the solution [125, 130]. For pristine nickel obtained using hydrazine, the formed nickel particles tend to possess spiky feature, which are formed because of the  $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$  molecule, assisting the anisotropic growth [131]. Ogiwara et al. also mentioned that spiky nanoparticles are formed using hydrazine and not other reductant [132]. In the study by Haag et al., an optimised nickel-plating solution was investigated for a homogenous and pristine nickel deposition on alumina hollow fibre support. The optimised conditions were at temperature of 75 °C, pH at 9.6, nickel acetate and hydrazine concentration at 0.12 mol L<sup>-1</sup> and 0.4 mol L<sup>-1</sup>, respectively. Following heat treatment at 900 °C, the microstructure became compact and uniform, suitable for hydrogen separation [125]. Nickel electroless plating has also been used in the preparation of micro-tubular solid oxide fuel cells, in particular for the fabrication of Ni anode electrode by Kanawka et al. and Liu et al. [133, 134]. In these studies, yttrium stabilised-zirconia (YSZ) porous hollow fibre was used as the support and nickel was deposited via the electroless plating method. These studies demonstrate the feasibility of depositing continuous nickel layer on non-dense complex supports.

Electroless copper plating has also been studied. However, deposition of copper on hollow fibre support has not been investigated but research have been carried out on ceramic powders [135-137] and on art ceramics [138]. As we realise from earlier graphene literatures, CVD are commonly grown

on copper, therefore studies on electroless copper plating can be useful for further study relating to graphene hollow fibre membrane synthesis. Zhao et al. have successfully plated copper on a ceramic specimen [138], the plating solution composed of copper sulphate, sodium hydroxide and potassium sodium tartrate with the reducing agent being formaldehyde. Here, the effect of temperature and ratio of metal to reducing agent were studied. The highest plating rate achieved was of  $4.35 \mu\text{m min}^{-1}$  at 1:1 copper to formaldehyde concentration at temperature around  $40^\circ\text{C}$ , where the plating was finished in 5 mins. Formaldehyde is generally used as the reducing agent because of its high reactivity due to the  $\sigma$  and  $\pi$  orbitals formed in the carbon-oxygen double bond,  $\text{C}=\text{O}$ . In recent years, other reducing agents, such as glyoxylic acid and hydrazine have been used. This is because formaldehyde present health problems and can be carcinogenic [139]. In terms of complexing agent, sodium potassium tartrates have been used and they are preferred because they are more easily waste-treatable [140]. For deposition in the range of  $2\text{--}3 \mu\text{m}$ , temperature in the range of  $35$  to  $55^\circ\text{C}$  are selected. For the more heavily deposited layer around  $25 \mu\text{m}$ , under similar operating situation, temperature of  $55$  to  $80^\circ\text{C}$  is normally used [140]. Investigated by Hana et al., they concluded the optimum plating temperature to be  $40\text{--}45^\circ\text{C}$  for tartrate bath and  $45\text{--}60^\circ\text{C}$  for the EDTA bath. Furthermore, deposition rate increases with increasing pH of up to 12.5 for tartrate bath and 13.0 for EDTA bath [141]. Other external factors can also influence the copper deposition, Abba et al. explained that the use of ultrasound can enhance the plating process by thinning the diffusion layer at the substrate layer [142].

As discussed above, electroless plating is a promising method for the deposition of metallic layer on porous substrates. Nickel and copper electroless plating have been demonstrated, but further parameters tuning is required to achieve the desired properties for the desired application.

## 2.6 Summary, challenges & research motivations

Graphene has generated tremendous research interests since its successful isolation in 2004. Amongst the various graphene synthesis studied, chemical vapour deposition has emerged as the promising method in producing large area of high-quality graphene on metal substrates [5, 6]. There are currently two growth mechanisms proposed: surface adsorption and precipitation methods, where the difference in growth is governed by the solubility of carbon in the metal. Graphene has also demonstrated successful growth on dense and porous transition metal substrates. Nickel and copper have been the mostly studied transition metals and have revealed high-quality graphene growth [11, 12]. The metal provides catalytic activity to the CVD process by acting as a catalyst lowering the activation energy and acting as substrate for the graphene growth [6]. The potential applications of graphene discussed mainly focused on graphene membrane and graphene acting as protective coating. Both experimental works and molecular simulations indicate great potential of the nanoporous graphene membrane in achieving the ultimate permeation. Graphene acting as a protective coating is also successfully demonstrated. In particular, synthesising multilayer graphene provides greater protection because a more complex route is required for molecules to reach the underlying metal and damage it.

So far, only planar graphene membranes are synthesised and investigated. These are fabricated by CVD on flat sheet transition metal and then transferred onto the desired planar substrates. From an engineering perspective, the challenge of scale-up have to be tackled if graphene membranes wish to be deployed in large scale operations. On the other hand, metallic membrane's properties can be further enhanced if its chemical resistant can be improved by integrating graphene for future applications.

Since large area of high-quality graphene can be synthesised on metal substrate by CVD and many potential applications are realised from this graphene-metal material. This leads to the research motivation of fabricating graphene in hollow fibre geometry facilitated by the use of metallic hollow

fibre membranes and CVD. By developing hollow fibre membranes, the challenge of industry scale-up and commercialisation can be tackled. The research motivations of this PhD thesis are summarised below:

1. Graphene protected metallic hollow fibre membranes

Pristine graphene is inert and is impermeable to gases and liquids because of its  $sp^2$  hybridisation. Therefore, it has the ability to act as a protective coating, where molecules are repelled from the graphene surface. Metallic membranes on the other hand can be susceptible to corrosive conditions; therefore, the growth of graphene layers on metallic membrane can improve the lifespan of the metal and increase their range of potential applications. This is particularly important for porous material because they pose a higher corrosion rate than solid material due to its higher exposed surface area [143]. Here, graphene protected metallic hollow fibre membrane is synthesised, the characteristics of this improved chemical resistance membrane is explored and its applications in nanoparticles production is also investigated.

2. Pristine graphene hollow fibre membranes

Commercialisation and scalability of graphene membrane is a key challenge to be solved. At the moment, only freestanding and planar graphene membranes are prepared. These membranes have low surface-area-to-volume ratio and are difficult to scale up for large scale operation. Developing graphene membrane in a different geometry which will enable ease of module assembly is strongly desired. Generally, graphene used for membranes are prepared via CVD on metal substrates. This leads to the idea of synthesising graphene on dense metallic hollow fibre to realise formation of graphene in the micro-tubular form, subsequently using this as a scalable graphene hollow fibre membrane.

One of the key challenges with this method is finding the suitable metallic hollow fibre for graphene synthesis and turning this into graphene membrane. A dense metallic outer layer is required for the

synthesis of continuous graphene on hollow fibre. The hollow fibre support must be inert and porous for graphene to act as the selective layer. To fulfil these criteria, a dense metallic sacrificial layer is employed depositing on ceramic hollow fibre support using electroless plating. After the graphene formation, the metallic sacrificial layer is etched while the ceramic hollow fibre support remains intact to act as the support. CVD growth mechanism and interaction between metals and ceramic may be different dependent on the metals used. Therefore, two different transition metal substrates are studied. Copper and nickel sacrificial layers are investigated and the most effective sacrificial layer in obtaining a high performing graphene hollow fibre membrane is explored.

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## Chapter 3: Experimental

### 3.1 Phase-inversion

Phase inversion process was used for the synthesis of nickel and yttrium-stabilised zirconia (YSZ) hollow fibres. A dope suspension was first prepared consisting of the material powder, solvent, dispersant and was milled for 20 hours. The powders were uniformly dispersed in the suspension by deflocculating the agglomerates. Hereafter, polymer binder was dissolved in the suspension and was further milled for 24 hours to obtain the homogenous dope suspension.

Prior to the spinning process, the dope suspension was degassed under a vacuum chamber to remove any air bubbles trapped inside the suspension and to avoid pinholes forming during the spinning process. The degassed dope suspension was then transferred to the stainless-steel syringe, while the internal coagulant-deionised water was filled into a separate stainless-steel syringe. Both of the extrusion rates were controlled by the syringe pumps (Harvard Apparatus PHD 2000). A schematic of the spinning process is shown in Figure 3.1. The external coagulant-deionised water was stored in a large water bath, directly under the spinneret. As the suspension extrudes out from the spinneret into the external-coagulant bath, phase-inversion begins to take place. The membrane precursors formed

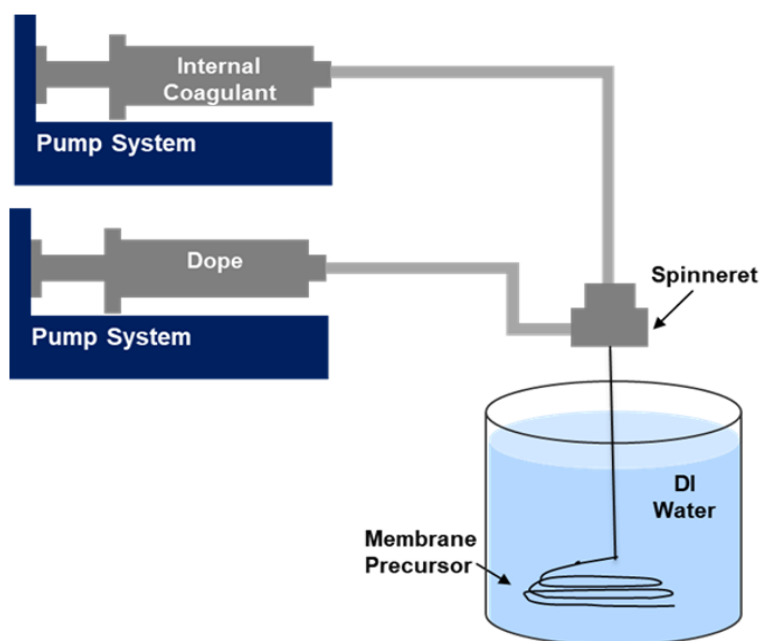


Figure 3.1. Schematic of the spinning process

were collected from the bath, dried, straightened, and then cut into the desired length for subsequent sintering.

For nickel hollow fibre membrane, commercially available nickel powders (APS 2.2-3.0 micron, 99.9% metals basis, VWR) were used as the fibre material. N-methyl-2-pyrrolidone (NMP, VWR-EMPLURA®) was selected as the solvent. Poly-methyl-methacrylate (PMMA, Acrypet VH, Mitsubishi Rayon, Japan) was used as the polymer binder. Arlacel P135 (Uniquema, Wilton, UK) was used as the dispersant to ensure homogeneous dispersion of the particles. The internal and external coagulants used were deionised water. The nickel dope composition and the spinning parameters are summarised in Table 3.1.

*Table 3.1. Dope suspension compositions*

| <b>Nickel hollow fibre</b> |                              | <b>wt.%</b> | <b>YSZ hollow fibre</b>           |                     | <b>wt.%</b> |
|----------------------------|------------------------------|-------------|-----------------------------------|---------------------|-------------|
| Nickel Powders             |                              | 63.4        | YSZ Powders                       |                     | 56.4        |
| NMP                        |                              | 28.0        | NMP                               |                     | 33.4        |
| PMMA                       |                              | 8.4         | PMMA                              |                     | 9.7         |
| Dispersant                 |                              | 0.2         | Dispersant                        |                     | 0.4         |
| <b>Hollow Fibre</b>        | <b>Dope extrusion rate</b>   |             | <b>Bore fluid extrusion</b>       | <b>Air gap (cm)</b> |             |
|                            | <b>(ml min<sup>-1</sup>)</b> |             | <b>rate (ml min<sup>-1</sup>)</b> |                     |             |
| Nickel                     | 10                           |             | 30                                | 5                   |             |
| YSZ                        | 10                           |             | 24                                | 2                   |             |

For yttrium-stabilised zirconia hollow fibres, Nano 3 mol% Y<sub>2</sub>O<sub>3</sub> stabilised ZrO<sub>2</sub> Ceramic Powder (YSZ, 30-60nm, Inframat Advanced Materials, USA) was used as the fibre material. NMP and PMMA were

used as the solvent and polymer binder, respectively. Arlacel P135 was used as the dispersant. The internal and external coagulants used were deionised water. The YSZ dope composition and the spinning parameters are summarised in Table 3.1.

## 3.2 Electroless plating

### 3.2.1 Sensitisation and activation of YSZ hollow fibres

Prior to the electroless plating process, the fibres were sensitised and activated as follow to enhance the catalytic activity on YSZ surface. The YSZ hollow fibres were sonicated in 25 wt% ethanol-water mixture for 30 minutes and left to dry in air. Both ends of the fibres were then sealed with Polytetrafluoroethylene (PTFE) tapes to prevent any solution reaching into the lumen. The sensitisation and activation solution were then prepared consisted of 1 g L<sup>-1</sup> tin (II) chloride (> 99.99 %, Sigma-Aldrich), 0.1 g L<sup>-1</sup> palladium (II) chloride (> 99.999 %, Sigma-Aldrich) and 0.01 M hydrochloric acid (37 %, VWR - AnalaR NORMAPUR). The fibres were first sensitised by immersing in SnCl<sub>2</sub> and H<sub>2</sub>O for 5 mins each, followed by immersing in PdCl<sub>2</sub> for 5 mins and finally surface washing in HCl and H<sub>2</sub>O for total of 5 mins. A schematic of the sensitisation and activation step is shown in Figure 3.2. Air bubbles were introduced into the solution to enhance the circulation of solution and mass transfer during the process. These sensitisation and activation steps were repeated 6 times using fresh batch of solution each time, in order to ensure complete coverage of palladium seeds on the YSZ hollow fibres. The activated fibres were then dried for the electroless plating to take place.

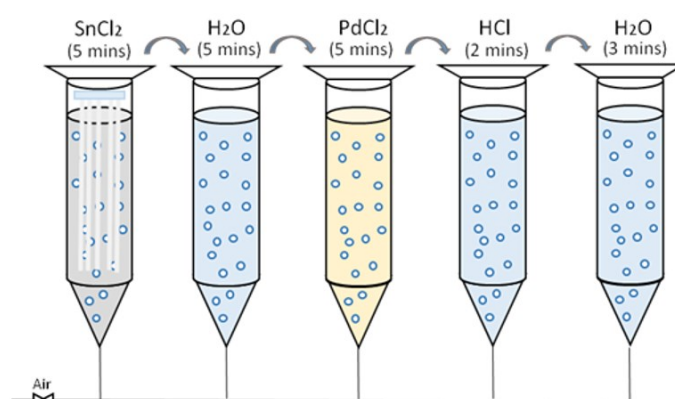


Figure 3.2. Schematic of the sensitisation and activation step on YSZ hollow fibres

### 3.2.2 Electroless plating

Electroless plating was employed to deposit the metal sacrificial layer on the YSZ hollow fibres. A metal deposition solution was first prepared. The activated YSZ hollow fibre was sealed with PTFE tape at both ends to prevent plating taking place inside the lumen. The fibre was immersed into the plating condition followed by the addition of reducing agent. The plating solution was maintained at the desired temperature using a heating plate. Dependent on the requirement, air bubbles were introduced into the solution to enhance the circulation of solution and mass transfer during the process. A schematic of the electroless plating process is shown in Figure 3.3.

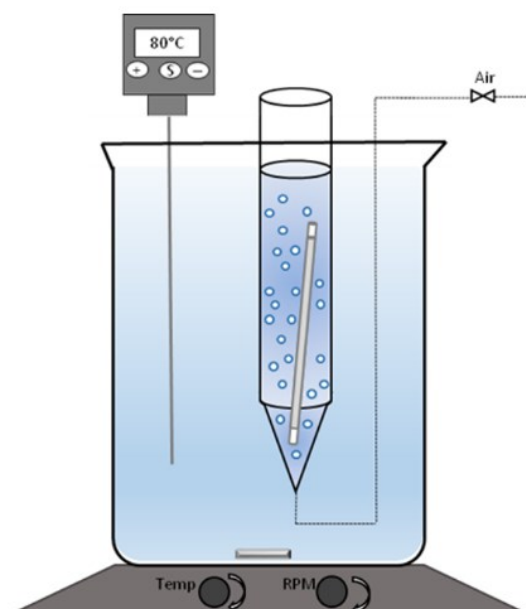


Figure 3.3. Schematic of the electroless plating process

## 3.3 Sintering and annealing of hollow fibre membranes

### 3.3.1 Sintering of YSZ hollow fibres

The YSZ hollow fibre precursors were sintered in a controlled atmosphere in air to realise the final structure with improved mechanical property. The precursors were first placed on a series of ceramic racks and then placed into the Carbolite RHF 1600 chamber furnace. The temperature profile used for the sintering is as follows:

1. Ramp to 500 °C with a 2 °C min<sup>-1</sup> heating rate

2. Anneal at 500 °C for 3 hours
3. Heat to 1145 °C with a 3 °C min<sup>-1</sup> heating rate
4. Anneal at 1145 °C for 5 hours
5. Cool down to room temperature

### 3.3.2 Annealing of metallic hollow fibre membranes

Pristine metallic hollow fibre membranes were annealed to gain the mechanical integrity and the following reactor set-up was used for the annealing. The metallic hollow fibre membrane was suspended at the two ends with small quartz tubes, which was then inserted into a 1 cm diameter quartz tube, shown in Figure 3.4. The whole quartz tube set-up was then placed into Carbolite® wire wound single zone tube furnace and annealed. Due to the nature of the metallic hollow fibre, the annealing process must be carried out in an inert environment, hydrogen and helium atmospheres (CP grade helium was purchased from BOC and hydrogen was produced from Peak Scientific hydrogen generator) were used to anneal the metallic hollow fibre membrane. Atmospheric pressure was used for the annealing process.

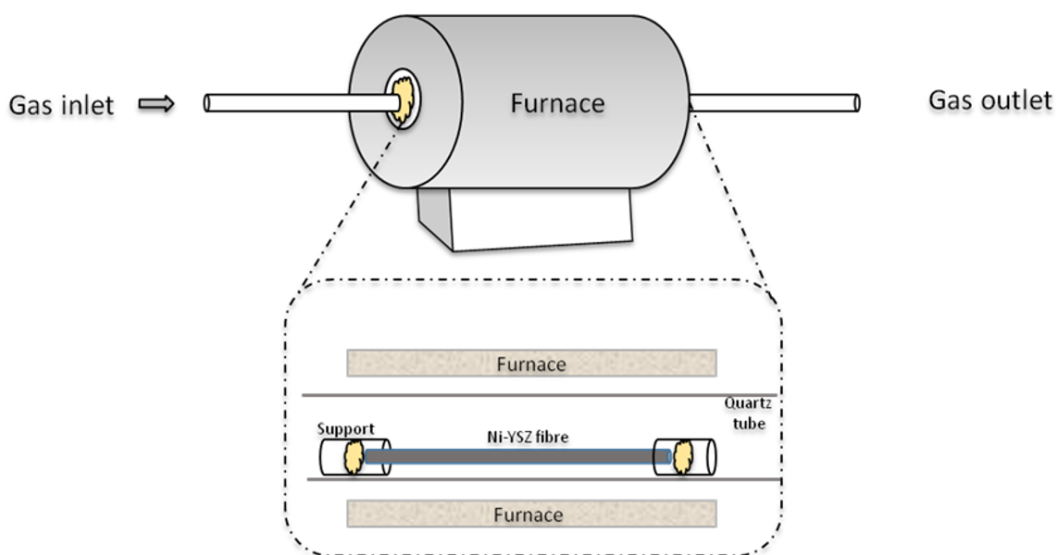


Figure 3.4. Schematic of the annealing & CVD set-up

For the nickel and copper electroless plated fibres. The same set-up and similar atmosphere were used. The aim of the annealing was to improve the metal surface smoothness and to obtain larger metal

grain boundaries suitable for graphene synthesis. The individual sintering condition used for the metallic hollow fibre can be found in the respective chapters.

### **3.4 Graphene synthesis via CVD growth**

After the formation of the metallic hollow fibres, graphene growth was then carried out to realise the superior graphene layer on the metallic hollow fibre surface. The same reaction set-up was used as Figure 3.4, however, the reactor conditions were now changed. Since the same set-up is used, an in-situ chemical vapour deposition (CVD) process can be carried out. During the CVD reaction, methane (Research grade, BOC) was fed into the reactor at a certain ratio with hydrogen. The methane: hydrogen ratio and growth time used for the individual fibres can be found in the respective chapters. After the CVD process, the fibre was drawn out immediately from the furnace. Drawing out the quartz tube allows for rapid cooling to take place enabling the final formation of graphene layer.

### **3.5 Etching of the metal sacrificial layer**

Dependent on the different sacrificial layer used, different etching methods were investigated. Ferric chloride (Sigma Aldrich) and ammonium persulfate (Sigma Aldrich) were used for the copper etchant. While artificial defects and nitric acid (68 %, VWR - AnalaR NORMAPUR) were needed for the removal of nickel layer. Details of the different etching methods used can be found in the individual chapters.

### **3.6 Post-etching defect-patching treatment**

Post etching, defects maybe formed on the graphene layer supported on YSZ hollow fibre and affect the integrity of the membrane. Therefore, post-etching defect-patching treatment was carried out to seal the defects using graphene flakes. Graphene flakes dispersed in N-Methyl-2-pyrrolidone (NMP, VWR-EMPLURA®) was prepared using the method liquid exfoliation of graphite. Graphite (powder, <150 µm, 99.99 % trace metals basis, Sigma-Aldrich) was selected and 10 mg ml<sup>-1</sup> of graphite in NMP

was prepared and sonicated for 1 hour. The dispersion was then left to stand for 1 hour before pipetting the top half of the dispersion into centrifuge tube. The dispersion was then centrifuge for 30 mins at 2000 RPM. After centrifugation, top half of the dispersion was collected. The prepared graphene flakes in NMP (G-NMP) was then diluted 50× and was used to seal the defects.

A dead-end filtration system was implemented. The hollow fibre was sealed into a stainless-steel holder using epoxy resin with the other end of the fibre also sealed with epoxy resin. The G-NMP dispersion was filled into a stainless-steel vessel and the hollow fibre was mounted onto the vessel. Defects presented on the hollow fibre were then sealed using graphene flakes by permeating the G-NMP dispersion at 10 bar through the hollow fibre. By observing the amount of NMP permeated through, the amount of defects presented on the hollow fibre can be indicated. At scenario where there is unmeasurable amount of NMP collected, defects present are scarce, and the flakes only patched on area where there are defects and would not add additional thickness to the graphene layer. A schematic of the dead-end filtration set-up is shown in Figure 3.5.

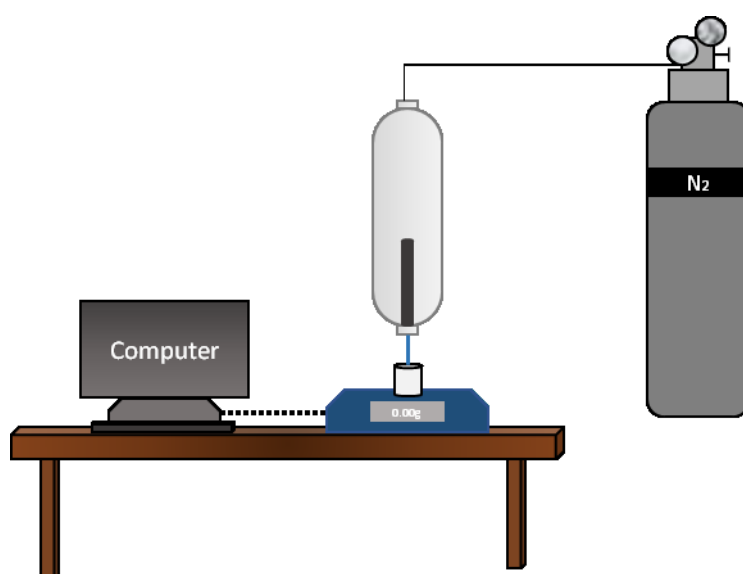


Figure 3.5. Schematic of the dead-end filtration set-up

## 3.7 Characterisation

### 3.7.1 Scanning Electron Microscopy

The morphology and microstructure of the samples were characterised using scanning electron microscope (SEM, LEO Gemini 1525 FEGSEM). The samples were first broken into small pieces suitable to be placed on the stud for SEM. Carbon tape was attached onto the stud followed by placing the samples to be characterised. For clearer imaging, non-conductive samples were coated with 10 nm gold or chromium under vacuum using sputter coating. Silver paint was also used to paint areas which require additional conductivity or are not covered by chromium.

### 3.7.2 Raman spectroscopy

Raman spectroscopy was used to characterise the quality of the graphene layer using the WITec system with 532 nm excitation energy. Raman spectra has two distinguished peaks for identifying graphene, the G band at  $\sim 1580\text{ cm}^{-1}$  and the 2D band at  $2670\text{ cm}^{-1}$  [1]. The G band corresponds to the in-plane  $\text{sp}^2$  vibrations, and the 2D band is the second harmonic of the D band, it is the result of a two phonon lattice vibrational process representing an ordered crystalline structure is formed. There is also the D band, which is known as the defect or disorder band and it represents a ring breathing mode from  $\text{sp}^2$  carbon rings, the ring is adjacent to a graphene edge or a defect [1-3]. Monolayer graphene is formed if the peaks are symmetrical at both  $1580\text{ cm}^{-1}$  and  $2670\text{ cm}^{-1}$  with the intensity of 2D to G ratio,  $I_{2D/G}$  being  $\sim 2$ . Whereas multilayer graphene is formed if the 2D band is broader and the intensity of G band is significantly higher resulting in the  $I_{2D/G}$  being  $\sim 0.5$ . Generally, as the graphene layer increases, the G band also increases leading to a lower  $I_{2D/G}$ , which is an indication of multilayer graphene, wavenumber of the G band also decreases if multilayer graphene is obtained [3]. In addition, the 2D band in multilayer graphene becomes broader compared to monolayer graphene because successive graphene layers cause the 2D band to split into overlapping modes [3].

### 3.7.3 Mechanical strength

The mechanical property of the hollow fibres was determined using the three-point bending method with the Instron tensile tester- 10 kN load cell (Instron, UK). The bending stress  $\sigma_F$  of the hollow fibres was calculated using the equation below.

$$\sigma_F = \frac{8FLD_0}{\pi(D_o^4 - D_i^4)} \quad (3.1)$$

where  $F$  represents the fracture force (N);  $L$ ,  $D_o$  and  $D_i$  represent the sample holder distance (m), the outer and inner diameters of the hollow fibre samples (m), respectively.

### 3.7.4 Pore size and pore size distribution

The pore size and the pore size distribution of the hollow fibres were determined using gas-liquid displacement measurements (PoroLux 1000 Porometer). The hollow fibres were sealed onto a stainless-steel holder using epoxy resin with the other end of the fibre also sealed with epoxy resin. The samples were then wetted with Porefil wetting liquid (perfluoroether) and placed into the system. Nitrogen gas was used between pressures of 0 to 10 bar and was introduced into the hollow fibre, finally the data was collected and logged by the system.

### 3.7.5 Porosity

The porosity of the hollow fibre was determined using the following equation:

$$Porosity = \frac{V_{envelope} - V_{skeleton}}{V_{envelope}} \quad (3.2)$$

Where

$$V_{envelope} = \frac{(D_o - D_i)^2}{4} \times \pi \times L \quad (3.3)$$

and

$$V_{skeleton} = m \times \rho_{pyc} \quad (3.4)$$

The average density of the hollow fibre  $\rho_{pyc}$  was determined using pycnometer (Micromeritics Accupyc II 1340),  $m$ ,  $L$ ,  $D_o$  and  $D_i$  denote the mass, length, outer and inner diameters of the sample (cm), respectively.

## 3.8 Performance

### 3.8.1 Liquid Permeation

Liquid permeation was evaluated also using the dead-end filtration setup in Figure 3.5, the system was pressurised to 8 bar and the permeate through the membrane was collected in a vial, the weight was captured and logged into the computer. The permeation flux  $J$  ( $\text{L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ ) was calculated using the equation:

$$J = \frac{V}{A \times t \times \Delta P} \quad (3.5)$$

Where  $V$  is the permeate volume (L),  $A$  is the effective membrane area ( $\text{m}^2$ ),  $t$  is the time of permeate collection (h), and  $\Delta p$  is the transmembrane pressure gradient (bar).

### 3.8.2 Rejection tests

Rejection tests were carried out also using the dead-end filtration set-up. Polyethylene glycol (PEG, 400-35000 MW, Sigma-Aldrich), polystyrene (PS, 1300 MW, Agilent Technologies) and rose bengal (1018MW, dye content 95%, Sigma-Aldrich) were used. 1 g  $\text{L}^{-1}$  PES and PS in methanol (VWR-AnalaR NORMAPUR) solutions and 25 ppm of rose bengal in methanol solution were prepared and filled into the test vessel of the dead-end filtration set-up. The rejection tests were carried out at 8 bar and the permeate was collected and analysed after the initial 3 hours to avoid possible adsorption on the hollow fibre. The PEG and PS concentration of the feed and permeate were measured using Agilent HPLC (1100 series) system, while the dye concentrations were determined by a UV-spectrometer (UV-2101PC, Shimadzu). The rejection is calculated using the equation:

$$R_{Dye} = \left(1 - \frac{C_p}{C_f}\right) \times 100 \% \quad (3.6)$$

Where  $R_{Dye}$  is the rejection of the G-YSZ-HF to PEG, PS and dye,  $C_p$  and  $C_f$  are the concentrations of the permeate and the feed, respectively.

### 3.8.3 Gas-tightness test

The gas-tightness test was conducted using the pressure-drop setup made of Swagelok VCR® fittings. The set-up consisted of a high-precision pressure transducer (Mensor CPT6180) with reading uncertainty of 0.01. Prior to testing, all the fitting connections were tested to be leak-free. The hollow fibre was then sealed into the stainless-steel holder using epoxy resin and mounted into the setup. The set-up chamber was first cleaned by sweeping through with test gas for few minutes to remove any impurity gases, the chamber was then filled and pressurized with the gas to the target pressure. The inlet and outlet of the chamber were closed, leaving hollow fibre to be the only path for gas to leak or permeate. The pressure inside the gas chamber was monitored by the pressure transducer and logged by the computer. A schematic set-up is shown in Figure 3.6.

The permeance of the gas through the membrane can be calculated using the equation:

$$P = \frac{V}{\Delta p \times R \times T \times A} \times \frac{dp}{dt} \quad (3.7)$$

Where  $P$  denotes the permeance ( $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$ ),  $V$  is the volume of the gas chamber ( $\text{m}^3$ );  $\Delta p$  is the pressure difference across the membrane (Pa),  $R$  is the gas constant ( $8.314 \text{ J mol}^{-1} \text{K}^{-1}$ );  $T$  is the measured temperature (K);  $A$  is the membrane surface area ( $\text{m}^2$ ); and  $\frac{dp}{dt}$  is the pressure drop rate.

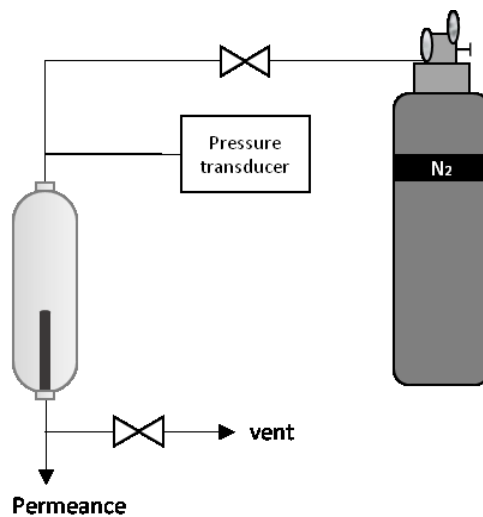


*Figure 3.6. Schematic of the gas-tightness set-up*

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## **Chapter 4: Graphene-protected nickel hollow fibre membrane and its application in the production of nanoparticles for high-performance catalysts**

### **Abstract**

Amongst the various potential applications studied, graphene as a protective coating has raised many interests. This ultra-thin material is chemically inert, and it is impermeable to gases and liquids, therefore it has the ability to act as a protective coating to enhance the lifespan and chemical resistance of metals. In this study, graphene-protected nickel hollow fibre (G-Ni-HF) membrane was fabricated using the phase-inversion and facile single-stage in-situ sintering-chemical vapour deposition (CVD) process. The non-protected nickel hollow fibre membrane dissolved in nitric acid within a few hours, whereas the G-Ni-HF membrane remained intact. These results confirm the improved chemical resistance on the porous nickel hollow fibre membrane and the formation of the graphene protective coating. The as-prepared G-Ni-HF membrane featuring well-controlled pore structure, good chemical stability and mechanical robustness can be used in a variety of applications that involve harsh conditions. Herein, we demonstrated its use in membrane emulsification to prepare  $\text{TiO}_2$  microspheres, where a highly acidic condition is essential. The microspheres prepared using G-Ni-HF membrane possess a hierarchical asymmetric egg-white structure that is distinct from the symmetric microspheres obtained by normal emulsification method. The asymmetric  $\text{TiO}_2$  microspheres also exhibit substantially improved catalytic activity to CO oxidation after impregnating with a palladium catalyst.

### **4.1 Introduction**

Attributed to the high electron density created from the  $\pi$  electron p-orbitals overlap, graphene is impermeable to all gases and liquids [1, 2]. Therefore, amongst the potential applications studied,

graphene as a protective coating has attracted many interests [3-10]. CVD graphene acting as a protective coating on Cu and Ni have been demonstrated by several oxidation resistance tests, such as long-term 18 months exposure in air at atmospheric conditions and annealing in air at 200 °C and 500 °C, as well as immersing in hydrogen peroxide [7, 11, 12]. Corrosion test in aerated sodium sulphate solution showed that graphene coated copper corroded 7 times slower than pure copper and the Tafel analysis showed mechanically transferred graphene on nickel corroded 20 times slower than pure nickel [8]. Lee et al. and Pu et al. demonstrated the use of graphene-coated nickel foam and graphene-coated stainless steel in the application of proton exchange membrane (PEM) fuel cells [9, 10]. Tafel analysis of these study indicate that graphene-coated nickel foam showed 9 times lower corrosion current density than the uncoated ones [9], and the graphene-coated stainless steel improved fivefold relative to the corrosion currents in non-coated samples [10]. However, long term protection of graphene still remains to be a debatable subject, where Schriver et al. found that graphene promoted galvanic corrosion in copper [13] but Stoot et al. found that CVD graphene coated on nickel/stainless steel protected the metal surface after 504 hours in boiling 3.5 wt% NaCl solution [14]. Stoot et al. explained the contradiction was caused by the difference in testing environments, the former being dry environment and the latter being wet condition. Furthermore, in the latter case, multilayer graphene grown on nickel provides greater protection compared to monolayer graphene on copper, this is because molecules have to go through a more complex route until they reach to the metal surface [14]. Therefore, growth of multilayer graphene can certainly enhance the life span of metal substrates.

The unique properties that graphene exhibit therefore have opened a new avenue for metallic membranes by improving its chemical resistance. Metallic hollow fibre membranes possess good thermal shock resistance and good thermal conductivities, they are also more ductile, less susceptible to impacts compared to ceramic membranes and are capable of welding or brazing for large scale operation [15, 16]. However, metallic membranes can be susceptible to corrosive conditions; therefore, the growth of graphene layers in improving the lifespan of the metal can certainly increase

their range of potential applications. This is especially important for porous metals because porous material generally have higher corrosion rate than a corresponding solid material of the same chemistry due to its higher exposed surface area [17]. Therefore, more efforts need to be focused on developing enhanced corrosion resistance metal membrane materials [18].

In this study, we prepared graphene protected porous nickel hollow fibre (G- Ni-HF) membrane using the phase-inversion and CVD method. The G-Ni-HF showed substantially improved resistance to the attack from strong acid alongside excellent mechanical property. Amongst various potential applications in harsh conditions, we used the G-Ni-HF membrane in a highly acidic emulsification scenario to obtain hierarchical asymmetric egg-white structured  $\text{TiO}_2$  microspheres, which are non-achievable using traditional emulsification methods. We also demonstrated that the microspheres obtained using the G-Ni-HF improved the catalytic activity to CO oxidation significantly after loading with palladium catalyst compared to their counterpart prepared by the traditional emulsification method.

## **4.2. Experimental**

### **4.2.1 Fabrication of graphene-protected nickel hollow fibre membranes**

The Ni hollow fibre membrane precursors were fabricated using the phase-inversion process described in Chapter 3.1. The precursors were then collected, straightened and dried; these were then placed inside the Carbolite® wire wound single zone tube furnace for the sintering-CVD process to take place. Details of the annealing and CVD system used can found in Chapter 3.3 and 3.4. The fibres were first annealed at 900 °C under 5 °C min<sup>-1</sup> heating rate, at a concentration of 4:1 He:H<sub>2</sub> ratio for 2 hours. Following the annealing, methane was fed into the system for the in-situ CVD process to take place. Graphene synthesis was conducted at 900 °C under atmospheric pressure with methane as the carbon precursor under 1:1 H<sub>2</sub>:CH<sub>4</sub> concentration for 20 mins. After the CVD process, the fibre was

drawn out immediately from the furnace for rapid cooling, this allows precipitation process to take place for the formation of graphene using nickel as the metal catalyst.

#### **4.2.2 Preparation of TiO<sub>2</sub> microspheres using G-Ni-HF membranes**

G-Ni-HF membranes were used in the application of membrane emulsification for the preparation of water-in-oil (W/O) emulsion to produce TiO<sub>2</sub> microspheres. As a comparison study, TiO<sub>2</sub> prepared from conventional emulsification technique and membrane emulsification using G-Ni-HF membranes were studied. The composition of W/O micro-emulsion used was modified using the recipes by Wu et al. and Yan et al. [19, 20] The aqueous phase containing titanium precursors consisted of titanium(IV) butoxide (Reagent grade, 97 %, Sigma-Aldrich), 10 M HCl (37 %, VWR - AnalaR NORMAPUR) and ammonium sulphate (≥99.0 %, Sigma-Aldrich). For every 3.4 ml titanium(IV) butoxide used, 4 ml of 10 M HCL and 9.2 g L<sup>-1</sup> ammonium sulphate were used. The oil phase contained 31 vol% Triton X-100 (Sigma-Aldrich), 19 vol% 1-hexanol (VWR) and 50 vol% cyclohexane (anhydrous, 99.5 %, Sigma-Aldrich).

During the membrane emulsification method, the G-Ni-HF membrane was connected to a syringe and immersed into the oil phase stirred at 360 RPM, shown in Figure 4.1a. The syringe was then filled with the aqueous phase and permeated through the porous G-Ni-HF at a rate of 1 ml min<sup>-1</sup> controlled by a syringe pump (Chemyx N6000). The injection continued until the aqueous to oil volume ratio reached 1:11.7 and a total volume of 123.5 ml micro-emulsion was prepared.

In the case of the emulsion prepared with the conventional emulsification method (Figure 4.1b), the same volume fraction of the aqueous phase was added dropwise into the oil phase stirred at 360 RPM, and then the mixture was kept stirring for 30 mins.

Hereafter, both of the prepared micro-emulsions were transferred separately into two Teflon inner-liner stainless-steel autoclaves and were kept at 120 °C overnight. The TiO<sub>2</sub> microspheres were then collected, washed repeatedly in water and ethanol and dried. Finally, the microspheres were loaded

with palladium catalyst and the performance in CO oxidation were tested. Detailed experimental procedures can be found in Additional Information A.

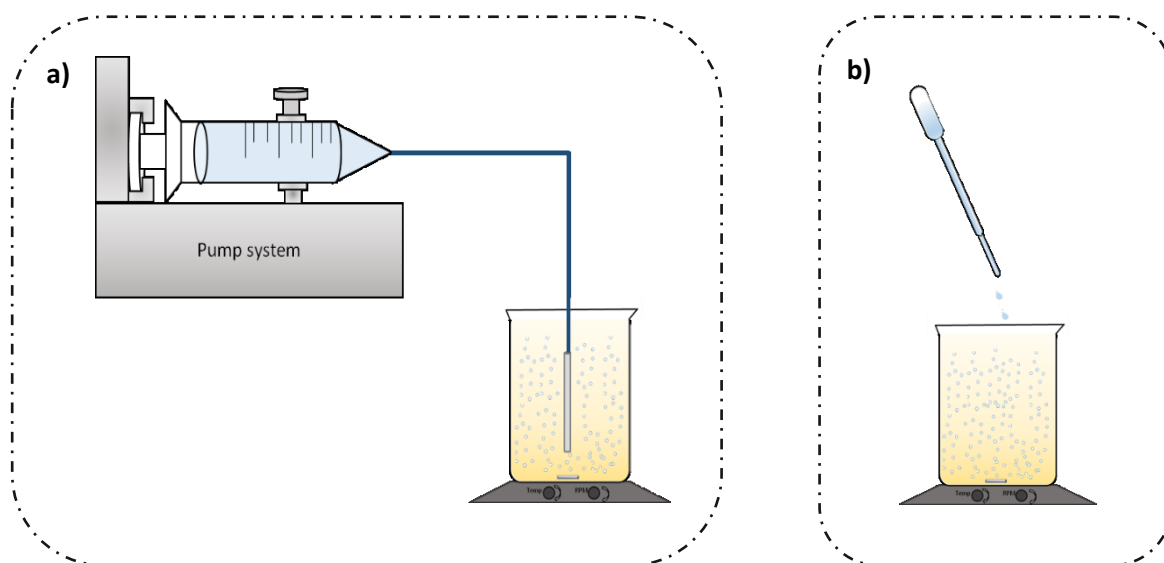


Figure 4.1. a) Membrane emulsification using G-Ni-HF membrane; b) Conventional emulsification method

### 4.2.3 Characterisations

The G-Ni-HF membranes were characterised using SEM, Raman spectroscopy. The pore size and the pore size distribution of the G-Ni-HF were determined using gas-liquid displacement measurements. Porosity of the hollow fibre was determined using helium pycnometry. Mechanical strength of the hollow fibres was determined using the three-point bending method. Corrosion tests of the graphene protected, and pristine nickel hollow fibre membranes were conducted by immersing the membranes in 0.5 M, 1 M and 2 M of nitric acid. Characterisation of the microsphere products were characterised using SEM, TEM and XRD, detailed characterisation procedures and catalysis performance for TiO<sub>2</sub> microspheres can be found in Additional Information A.

## 4.3 Results and discussion

### 4.3.1 Graphene protected nickel hollow fibre membranes

Nickel hollow fibre membrane precursors were successfully fabricated via the phase-inversion method.

Hereafter, the precursors were annealed using the single-stage in-situ sintering-CVD process to realise the final graphene protected nickel hollow fibre (G-Ni-HF) membranes. As a comparison, pristine nickel hollow fibre (Ni-HF) and G-Ni-HF membranes were prepared and are shown in Figure 4.2, the non-protected Ni fibre exhibits a lighter shade compared with its graphene coated counterpart because of the graphene formation.

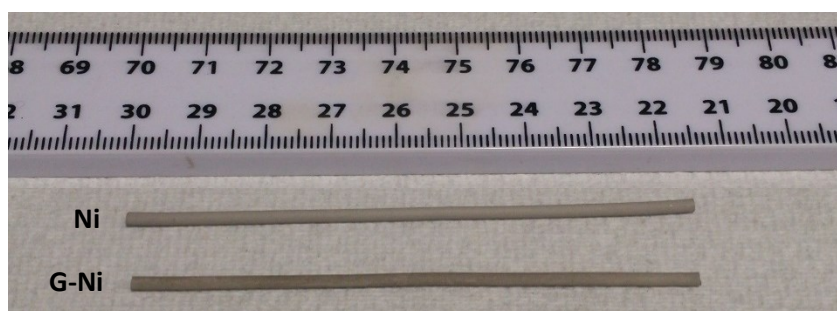


*Figure 4.2. Photographs of pristine nickel (top) and graphene protected nickel (bottom) hollow fibres membranes (bottom).*

The morphology and microstructure of the hollow fibres obtained are shown in Figure 4.3a-e. The hollow fibre fabricated exhibits a good and concentric structure with a homogenous thickness (Figure 4.3a). As revealed in Figure 4.3b&c for pristine Ni-HF (without CVD growth), the surface is smooth and clean, suggesting the absence of oxidation and contamination. A porous microstructure is obtained at 900 °C sintering temperature, where the nickel particles coalesced together forming larger agglomerates. For the case of G-Ni-HF, successful growth of graphene layer on the porous nickel hollow fibre is shown in Figure 4.3d&e. Formation of graphene grain boundaries can be easily observed in Figure 4.3e, compared to the smooth pristine nickel surface and grain boundaries shown in Figure 4.3c. Wrinkles also appeared on the graphene surface (Figure 4.3e), these were formed due to the difference in thermal expansion coefficient between nickel and graphene [21]. It is also an indication of the synthesis of continuous and uniform graphene layer. The impurity-free graphene surface displayed also highlights the lack of oxidation during the CVD process.

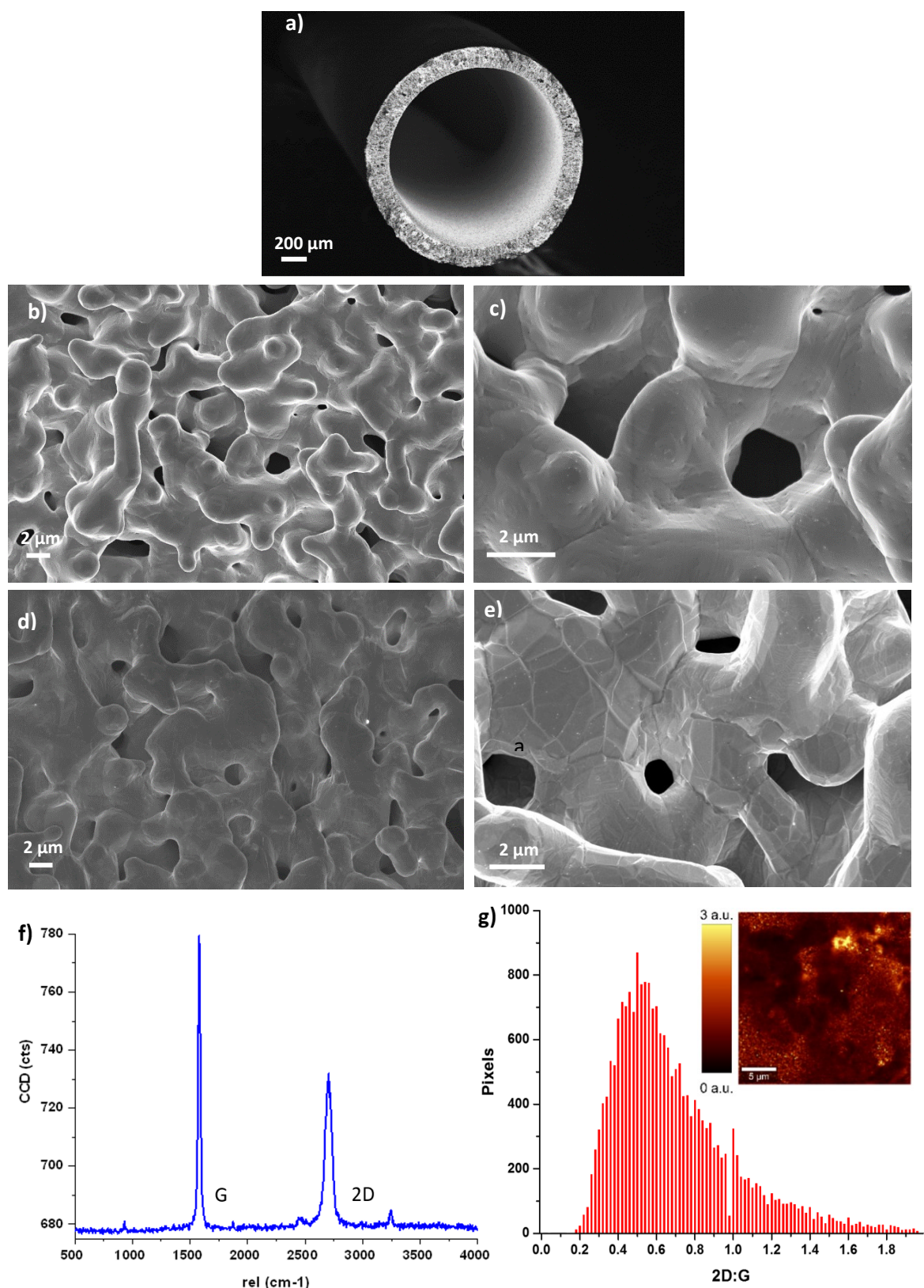


Figure 4.3. SEM images of a) cross-sectional surface of the hollow fibre; b&c) pristine Ni-HF membrane surface; d&e) G-Ni-HF membrane surface; f) Raman spectra of G-Ni-HF membrane; g) 2D:G ratio distribution in a 25  $\mu\text{m}$  × 25  $\mu\text{m}$  scanned area (inset-Raman mapping of 2D:G ratio)

two distinguished peaks for identifying graphene, the G band at  $\sim 1580\text{ cm}^{-1}$  and the 2D band  $2670\text{ cm}^{-1}$

<sup>1</sup> [22]. Monolayer graphene is formed if the peaks are symmetrical at both  $1580\text{ cm}^{-1}$  and  $2670\text{ cm}^{-1}$  with the intensity of 2D to G ratio,  $I_{2D/G}$  being  $\sim 2$ . Whereas multilayer graphene is formed if the 2D band is broader and the intensity of G band is significantly higher resulting in the  $I_{2D/G}$  being  $\sim 0.5$ . In the current study, multilayer graphene was formed indicated by Figure 4.3f where the intensity of the G peak is about 2 times higher than the 2D peak. The graphene is also of high-quality because of the lack of D peak at  $1350\text{ cm}^{-1}$ , which normally represents the presence of defects on the surface [22, 23].

Figure 4.3g indicates the distribution of the  $I_{2D/G}$  ratio on a  $25\text{ }\mu\text{m} \times 25\text{ }\mu\text{m}$  scanned area where most of the ratios concentrate near  $\sim 0.5$ , indicating that majority of the graphene layers formed are multilayer graphene. The Raman mapping in the inset of Figure 4.3g indicates homogeneous formation of multilayer graphene, where large area of the scanned surface exhibit similar colour shading. These results are in line with the previous studies [11, 14, 24], further confirming the graphene growth mechanism in nickel is by the precipitation method. There are areas in the scanned area which have low 2D and G intensities, these are caused by the membrane roughness and the curved nature of the hollow fibre geometry where the laser beam was not able to focus. Therefore, the 2D and G bands were not detected accurately, and the distribution of the histogram became slightly broad and there are certain areas on the Raman mapping which have dark and yellow spotting.

#### 4.3.2 Properties of G-Ni-HF membranes

The porous G-Ni-HF membrane features a narrow pore size distribution with a mean flow pore size of  $3.8\text{ }\mu\text{m}$  (Figure 4.4a) and a porosity of 52.5 %. The membranes fabricated were very ductile compared to the ceramic yttrium-stabilised zirconia (YSZ-open channel structure) hollow fibre membrane. Three different G-Ni-HFs were tested for mechanical test and exhibit consistent results shown in Figure 4.4b. The G-Ni-HF membranes yield after  $\sim 9\text{ N}$ , exhibiting a breaking load at 12.7 N and a bending stress in the region of 140 MPa, these are much higher compared with the brittle ceramic fibre (open-channel structure) with 7.4 N breaking load and a bending stress of 100 MPa. The higher mechanical strength is favourable for large scale applications because the fibres are less susceptible to impacts and allow

for welding and brazing. The breaking load and bending stress of the hollow fibres are tabulated in Table 4.1.

Table 4.1. Breaking load and bending stress of hollow fibre membranes

| Sample           | Breaking<br>load (N) | Bending stress<br>(MPa) |
|------------------|----------------------|-------------------------|
| G-Ni-HF Sample 1 | 12.7                 | 140.0                   |
| G-Ni-HF Sample 2 | 12.7                 | 139.8                   |
| G-Ni-HF Sample 3 | 12.7                 | 140.3                   |
| Ceramic-YSZ      | 7.4                  | 100.0                   |

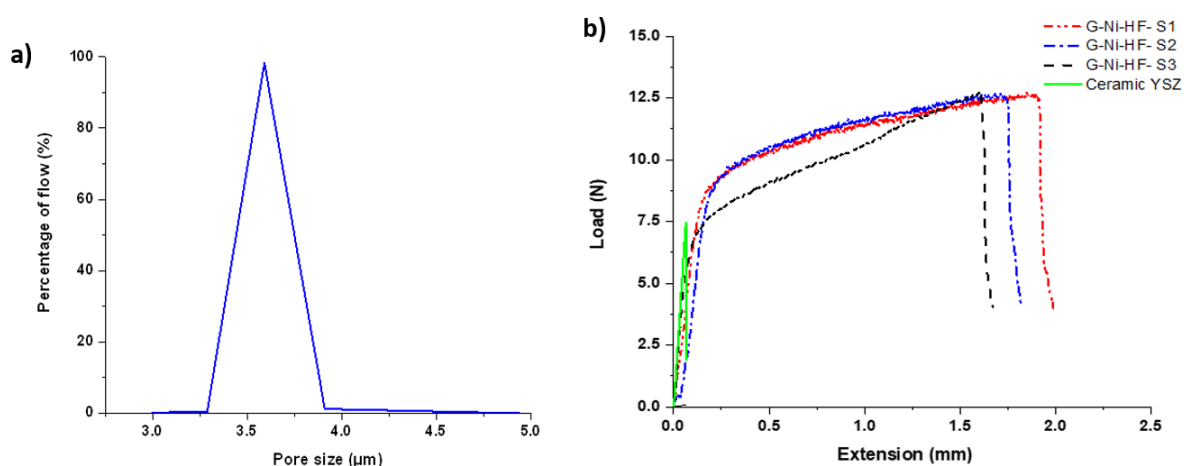


Figure 4.4. a) Pore size distribution of G-Ni-HF membrane; b) Load Vs Extension for G-Ni-HF and YSZ hollow fibres

### 4.3.3 Corrosion Tests

Chemical resistance tests on G-Ni-HF were tested by immersing in 0.5 M, 1 M and 2 M of nitric acid. After immersing both types of fibre in 0.5 M nitric acid for 3 hours, the G-Ni-HF remained in its hollow fibre geometry with a uniform thickness across the entire cross-section and a shiny metal surface, shown in Figure 4.5a-d. Whereas the pristine Ni-HF completely dissolved in 3 hours. SEM images show that the G-Ni-HF still exhibits a porous structure (Figure 4.5e&f), further confirming the growth of graphene and its ability to act as a protective layer for the nickel hollow fibres. Similar results were

obtained for 1 M and 2 M nitric acid, where the pristine Ni-HF dissolved completely within a few hours and the G-Ni-HF remained in its hollow fibre geometry.

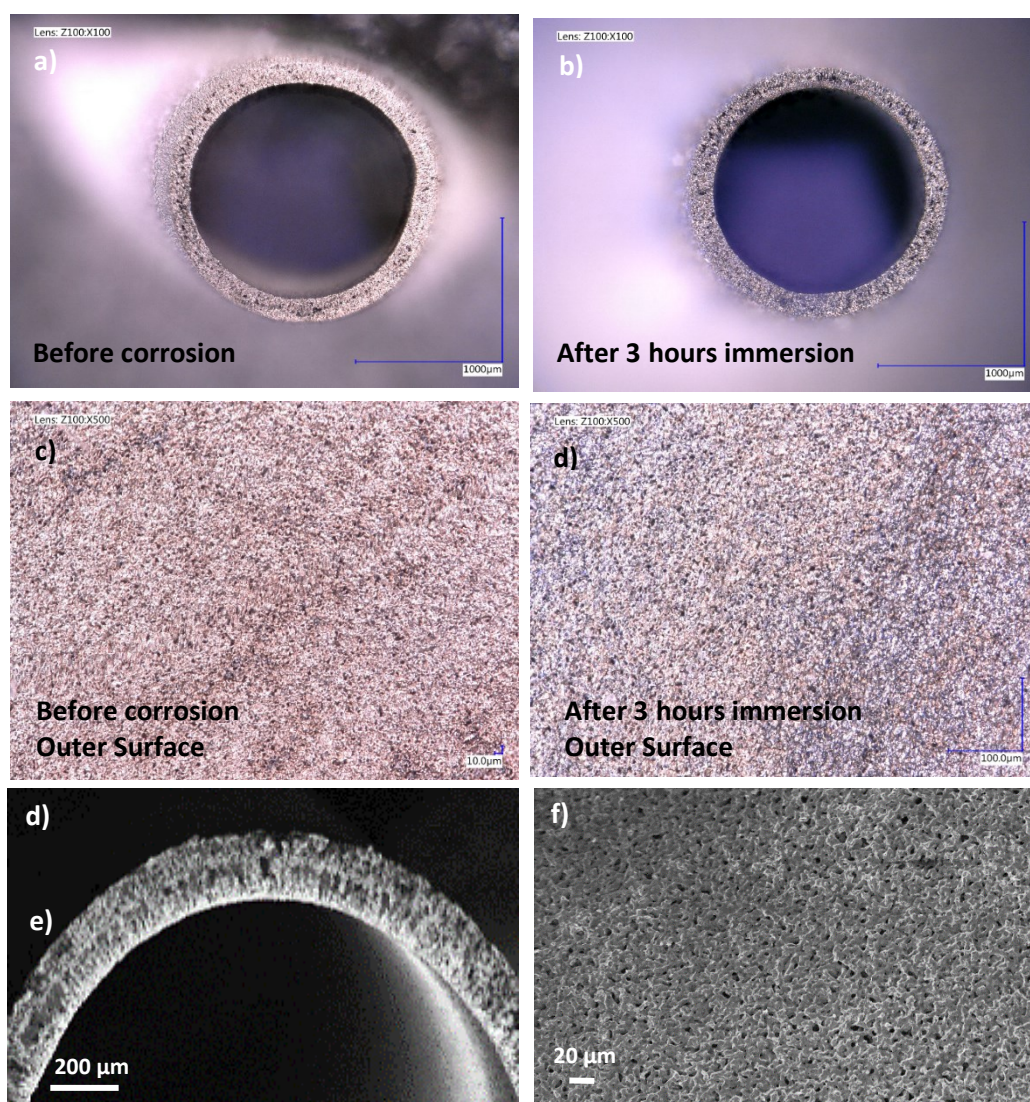


*Figure 4.5. Images of the G-Ni-HF before (a&c); and after (b&d) immersing in 0.5M nitric acid for 3 hours; e&f) SEM images of the G-Ni-HF after 3 hours immersion in 0.5 M nitric acid*

Long-term corrosion test was also carried out on the hollow fibres after immersing the fibre in 0.5 M for 5 days. The general structure of the G-Ni-HF remained; however, the fibre became soft and the nitric acid solution turned into light green solution due to the formation of nickel nitrate. Grain boundaries and surface defects are areas which are more susceptible to corrosion, therefore after prolonged immersion, the solution managed to contact the underlying nickel and dissolved it. Nevertheless, corrosion rate did decrease significantly compared with the pristine nickel sample. Raman Spectroscopy was used to characterise the G-Ni-HF surface after the long-term corrosion test.

2D and G bands are still observed after 5 days immersion, indicating the existence of the graphene layer. As a result, multilayer graphene formed in the current study did protect the nickel hollow fibre membrane, where the corrosion rate decreased significantly, and the graphene layer still remained intact after long term immersion in nitric acid.

#### **4.3.4 Synthesis of TiO<sub>2</sub> microspheres using G-Ni-HF membrane**

As demonstrated above, the prepared G-Ni-HF membrane features uniform pore structure, excellent chemical stability and mechanical robustness, making it a favourable membrane candidate when harsh conditions are needed. Furthermore, the graphene protective layer also makes the membrane hydrophobic [25] [26], making it an ideal dispenser to produce water-in-oil (W/O) emulsions [27]. Generally, emulsion droplet is formed when the dispersed phase is permeated out from the pores of the porous membrane into the continuous phase. The droplet grows at the pore's tip and detach when the growth is complete. It is important a well-defined droplet size distribution is achieved, and thus the contact angle between the membrane surface and dispersed phase need to be maximised, i.e. the membrane surface cannot be wetted by the dispersed phase, or else, a spherical shape droplet is not obtained after detachment [27]. Therefore, the formation of water-in-oil (W/O) emulsion is more favourable using hydrophobic membrane than hydrophilic membrane and vice versa. As studied by Leenaerts et al., graphene has a hydrophobic feature. It was found that the binding energies of the water molecules in a water cluster is more than a magnitude higher than the adsorption energies between graphene and the water cluster, making graphene a hydrophobic material [25]. Lee et al. also confirmed the hydrophobicity behaviour of graphene coated nickel, demonstrating a contact angle of 123° [26]. Herein, the prepared G-Ni-HF membrane was deployed in a highly acidic water-in-oil membrane emulsification for the preparation of TiO<sub>2</sub> microspheres, a material widely employed in the production of pigments, sunscreen, paints and catalysts [28, 29]. To complete the comparison study, TiO<sub>2</sub> microspheres formed using conventional emulsification technique was also studied and compare to TiO<sub>2</sub> formed using G-Ni-HF membrane emulsification.

Morphology and size distribution of the  $\text{TiO}_2$  microspheres obtained by G-Ni-HF membrane emulsification method are shown in Figure 4.6a-c. The size distribution of the microspheres ranges from 1.4 to 3.3  $\mu\text{m}$  (Figure 4.6a). As revealed by Figure 4.6b, the microspheres exhibit an asymmetric egg-white like structure with a thick, dense shell, while the core of the microsphere consists of loosely packed agglomerates. The microsphere surface also shows a unique wavy pattern highlighted in Figure 4.6c. In the case of the conventional emulsification method (Figure 4.6d-f), a relatively broad size

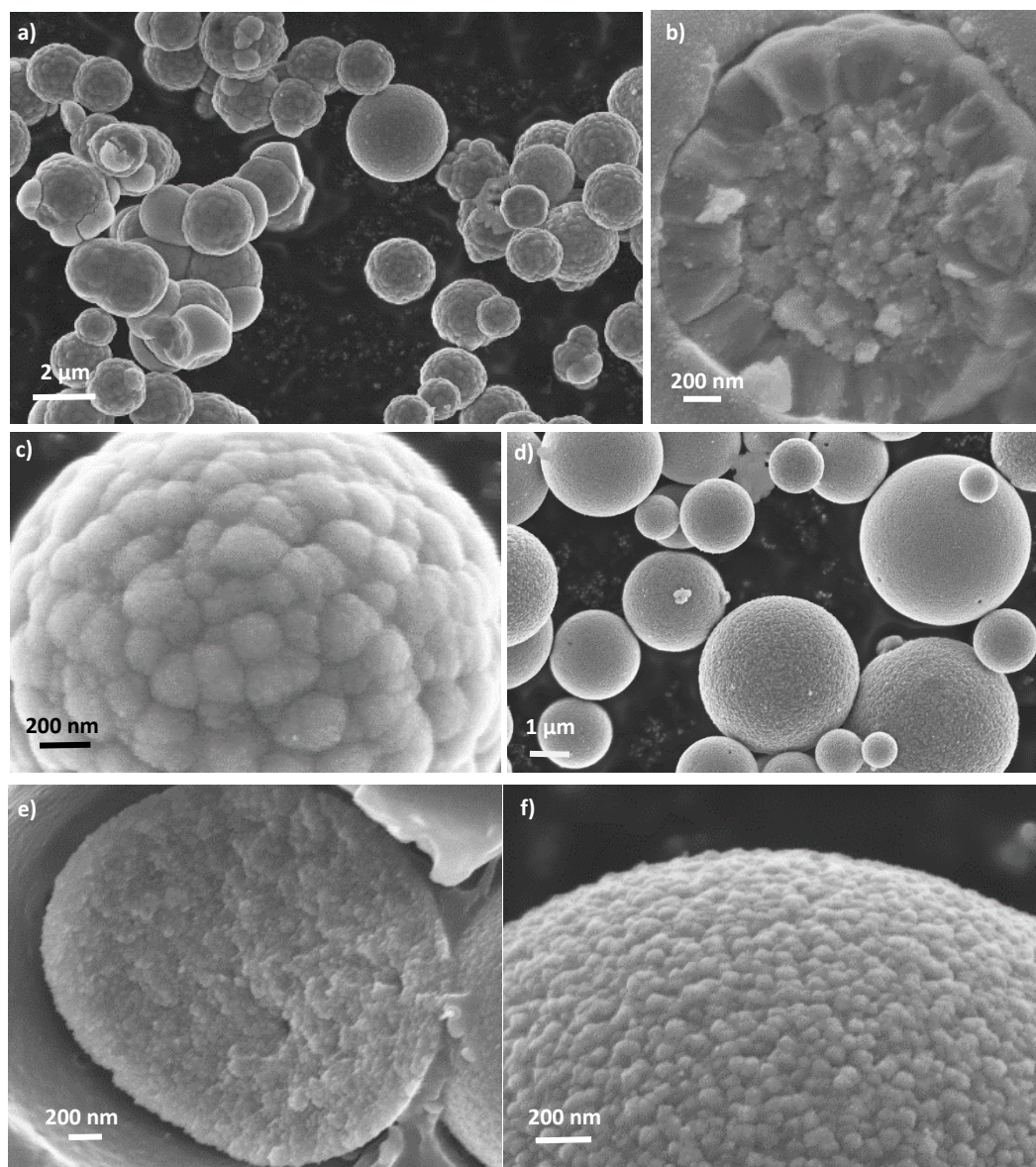


Figure 4.6. Morphology of  $\text{TiO}_2$  microspheres; a-c) Asymmetric egg-white  $\text{TiO}_2$  microspheres prepared using G-Ni-HF membrane; d-f) Symmetric homogeneous  $\text{TiO}_2$  microspheres prepared using the traditional emulsification method.

distribution (up to 400% diameter variation) was observed, ranging from 0.9 to 4.4  $\mu\text{m}$  (Figure 4.6d).

The microspheres exhibit a homogeneous structure that consists of agglomerates of nanoparticles,

with the agglomerate size to be approximately 30-40 nanometres. Figure 4.6e&f show the agglomerates were uniformly distributed over the surface and the bulk. Particularly, all the microspheres show an undisturbed shape that is close to a perfect sphere (Figure 4.6d). It is speculated that the change in the structure of the microspheres was due to the difference between the traditional turbulence-induced and membrane-induced emulsification methods. It can be attributed to the stability of the water-oil interface during emulsion formation, which leads to the different distributions of nuclei in the aqueous phase droplets when the two methods were used. Detailed hypothesis on the  $\text{TiO}_2$  formation mechanism and the microspheres characteristics can be found in Additional Information A.

#### **4.3.4.1 High-performance catalysts based on the microspheres prepared by the G-Ni-HF**

The asymmetric structure  $\text{TiO}_2$  microspheres prepared by the G-Ni-HF membrane can potentially be used to gain controlled distribution of active sites in catalysts and thus improve catalytic performance [30, 31]. This was demonstrated using the catalytic oxidation of CO on palladium catalysts, where  $\text{TiO}_2$  microspheres prepared by both the traditional and the membrane emulsification methods were used as the catalyst carrier. To assure that the two catalysts have the same catalytic kinetics to CO oxidation, the catalysts were tested at low weight hourly space velocity (WHSV) in a differential-reactor condition. The Arrhenius study obtained shows that both catalysts exhibit almost identical activities with an activation energy of 113.1 and 115.7  $\text{kJ mol}^{-1}$  for symmetric homogenous and asymmetric egg-white structure, respectively (see Additional Information A). We then further investigated the catalytic performance of both catalysts at higher WHSVs. As shown in Figure 4.7, the conversion of Pd- $\text{TiO}_2$  with homogeneous structure rapidly dropped from 100 % to 47.7 % as the WHSV increased from 30000 to 90000  $\text{ml h}^{-1} \text{g}_{\text{cat}}^{-1}$  while the Pd- $\text{TiO}_2$  with egg-white structure could still maintain 100 % CO conversion, indicating a 300 % enhancement in the capable range of maintaining full conversion. From the  $\text{TiO}_2$  characterisation studies (Detailed study can be found in Additional Information A), both microspherical supports show similar BET surface area, pore size, porosity and the catalysts have same

kinetics, therefore the change in catalytic performance at high WHSVs can be solely attributed to the accessibility to active sites. The result suggests a rapid and drastic loss of accessibility to active sites for homogeneous  $\text{TiO}_2$  as the increase in WHSV decreases the contact time, whereas such decrease in contact time shows negligible influence on egg-white  $\text{TiO}_2$  microspheres whose active sites were more concentrated near the outer shell of sphere. In addition, the overall performance degradation of homogeneous  $\text{TiO}_2$  as the WHSV increased from 30000 to 330000  $\text{mL h}^{-1} \text{g}_{\text{cat}}^{-1}$  is up to 160 % (82.3 % vs 51.4 %) of the egg-white  $\text{TiO}_2$ , shown in Figure 4.7. This demonstrates the effectively improved tolerance towards WHSV variation from the unique egg-white configuration introduced during the simple, membrane emulsification-assisted synthesis. It can be well proved that catalyst support prepared by the G-Ni-HF membrane provides markedly improved efficiencies in the utilization of precious metal catalysts, which is extremely critical for next-generation industrial catalysis.

#### 4.4. Conclusion

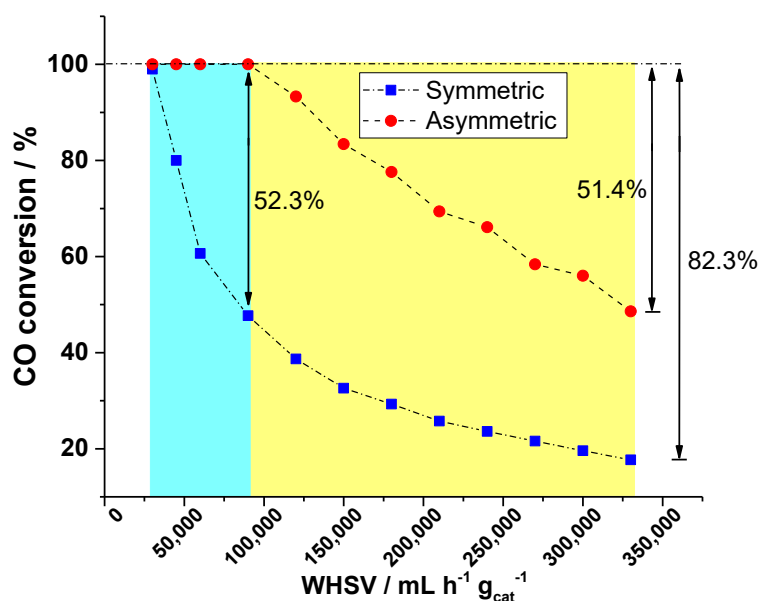


Figure 4.7. Catalytic activity of asymmetric & symmetric  $\text{TiO}_2$ -Pd catalysts for CO oxidation as a function of weight hourly space velocity (WHSV)

In this study, graphene protected nickel hollow fibre membranes were successfully fabricated using the phase-inversion and facile single-stage-sintering-CVD process. Both SEM images and Raman Spectroscopy confirm the formation of high-quality multilayer graphene. The metallic G-Ni-HFs were

ductile and possess a bending stress in the region of 140 MPa. They also exhibit a narrow pore size distribution with a mean flow pore size of 3.8  $\mu\text{m}$  and a porosity of 52.5 %. Graphene acting as a protective coating was successfully demonstrated by immersing the G-Ni-HF in 0.5 M, 1 M and 2 M nitric acid and compared with non-protected Ni-HF. Results showed that the non-protected Ni-HF dissolved within a few hours, whereas the graphene protected hollow fibres still remained in its hollow fibre geometry with a uniform thickness. Long term (5 days) immersion of G-Ni-HF showed that the fibre still remained in its general structure and Raman spectroscopy confirmed the existence of the graphene layer on the G-Ni-HF. However, the hollow fibre did become soft after prolonged immersion, possibly because of the defects and grain boundaries. Nevertheless, these results indicate the protection ability of graphene where the corrosion rate of the Ni hollow fibres were significantly reduced. As a result, this graphene protective coating can increase the range of potential applications for Ni hollow fibres. The prepared G-Ni-HF membrane was deployed in the application of water-in-oil membrane emulsification for the synthesis of  $\text{TiO}_2$  microspheres in acidic condition. Hierarchical egg-white structure microspheres were obtained using the G-Ni-HF membrane emulsification technique, compared to homogeneous structure microspheres obtained by the conventional method. The  $\text{TiO}_2$  microspheres were adopted as catalyst support and using catalytic oxidation of CO as the benchmark study to assess the catalytic activity. The unique asymmetric structure encouraged an egg-white distribution of catalysts (Pd), whereby majority of the active sites concentrate at the outer shell with shortened diffusion paths, and a significant enhancement on catalytic performance was observed at region which is mass transfer-limiting, in comparison to the homogenous structure obtained by the conventional emulsification method.

### **Note:**

This Chapter has been published in the Journal of Membrane Science

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## Additional Information A

### 1. Characterisation of TiO<sub>2</sub> microspheres

X-ray diffraction (XRD) were obtained using X'pert Pro PAN-analytical instrument using Cu K $\alpha$  as the X-ray source. 40 kV and 20 mA were used as the voltage and current, respectively.

The % content of the anatase phase to rutile phase was determined by finding the intensity ratio of the anatase (101) peak at 25° and rutile (110) peak at 27°, using the following equations [20]:

$$f_a = \frac{1}{1 + \frac{1}{K} \frac{I_R}{I_A}} \quad (\text{A.1})$$

Where  $f_a$  is the fraction of anatase phase, and  $I_R$  and  $I_A$  are the intensities of the rutile (110) and anatase (101) diffraction peaks, respectively.  $K$  is 0.79 when  $f_a \geq 0.2$  and  $K$  is 0.68 when  $f_a \leq 0.2$ .

Porosity of the microspheres were obtained as follows. Firstly, small amount of water was added into both types of TiO<sub>2</sub>, this turns the microsphere powders into a wet paste. This was then stirred overnight and was then placed in the refrigerator, to ensure all water molecules enters the pores of the microspheres. Hereafter, the wet paste was transferred into a Simultaneous Thermal Analyser (STA 449 F5 Jupiter) and maintained at 298 K under N<sub>2</sub> atmosphere. The evaporation rate of the water was recorded with time and the system stopped when all the water was evaporated off, i.e. when the weight of the TiO<sub>2</sub> maintained constant for 1 hour under the measurement. An example of this measurement is shown in Figure A.1. Looking at Figure A.1, the steady water evaporation rate before 142 min accounts for the evaporation of water that exist in the surrounding area of the microspheres. After 142 min, water evaporation rate then drops till 210 min, this accounts for the evaporation of water trapped inside the pores within the microspheres. Hereafter, all the water was evaporated off and the evaporation becomes constant at 0 ml min<sup>-1</sup>. By converting the mass of water evaporated

between 142-210 min and the mass of  $\text{TiO}_2$  remained into volume basis, the porosity of the microspheres can then be obtained using the following equation:

$$\text{Porosity} = \frac{\text{Volume of water}}{\text{Volume of water} + \text{Volume of dry TiO}_2} \quad (\text{A.2})$$

The same method was used to obtain porosity data for both types of microspheres.

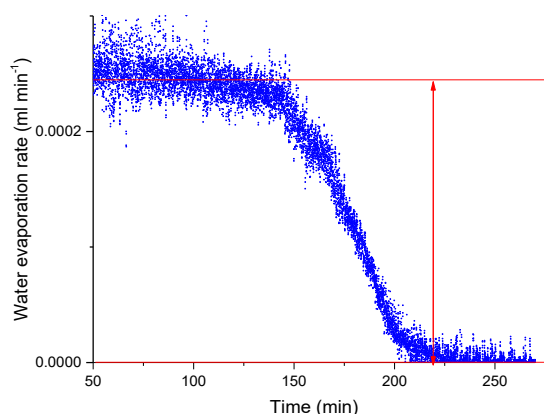


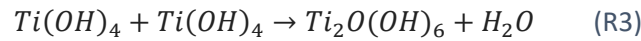
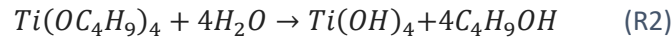
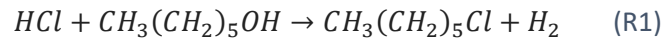
Figure A.1. An example of water evaporation rate of the  $\text{TiO}_2$  microspheres under STA for porosity measurement

Primary particle size of both types of  $\text{TiO}_2$  microspheres was obtained using Transmission Electron Microscopy (TEM, JEOL EM-2100F TEM Instrument). Scanning electron microscopy (SEM LEO Gemini 1525 FEGSEM) was used to characterise the morphology of the microspheres. Brunauer-Emmett-Teller (BET) surface areas were determined by the  $\text{N}_2$  adsorption-desorption method at 77 K (Micromeritics 3Flex Instrument). All the samples were degassed at 393 K before BET measurements.

## 2. $\text{TiO}_2$ microspheres formation mechanism and characteristics

The difference in structural formation is thought to be caused by the way aqueous phase dispersed into the continuous phase. This affects the mass transfer during the precipitation reaction and emulsion formation, finally influencing the product morphology. In this W/O emulsion, HCl was used as a hydrolysis inhibitor in the aqueous phase. However, at the interface, the presence of hexanol in

the oil phase, which was added as the co-surfactant, would react with HCl and forms water, shown in Reaction 1.



This led to the increase of local pH at the interface, thus initiating the hydrolysis reaction, as displayed in Reaction 2, followed by condensation reactions (Reaction 3 & 4) [28] resulting in the nucleation of solid titanium species. If the water-oil interface is stable, the nuclei will stay at the interface; meanwhile, in the remaining liquid phases, a concentration gradient will be formed between the bulk solution and the interface, driving reactants ( $Ti(OC_4H_9)_4$ , HCl and hexanol) to diffuse towards the

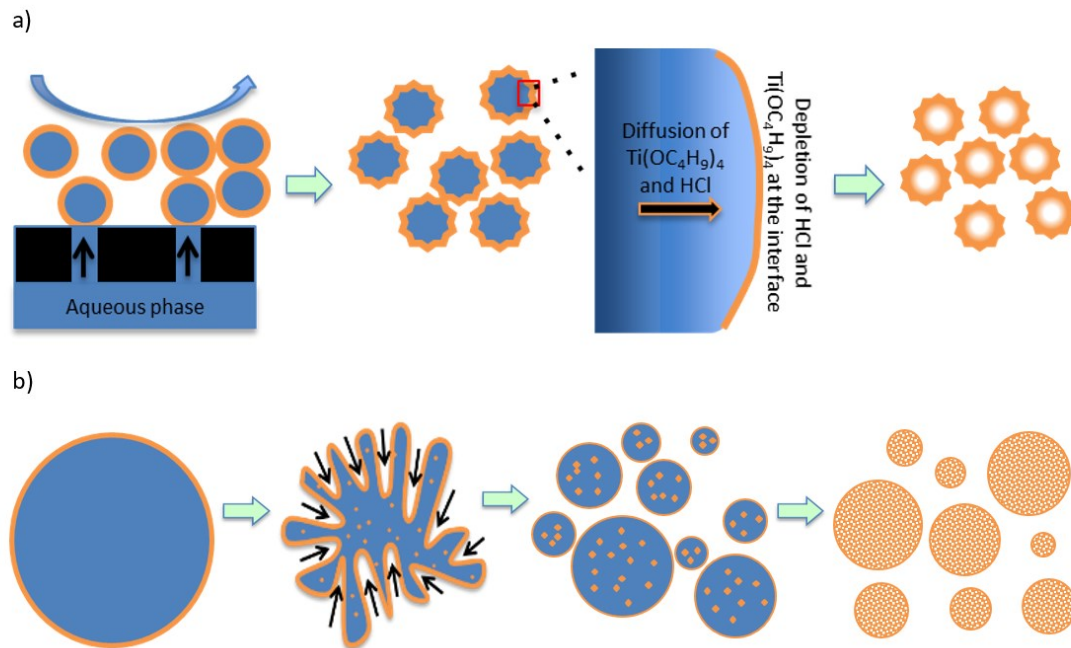


Figure A.2. Schematics of the formation mechanism of  $TiO_2$  microspheres. a) Formation of egg-white structure microspheres using membrane emulsification; b) Formation of homogenous microspheres using the conventional emulsification technique

interface and the interfacial reaction continues. Such a diffusion-reaction process at the interface leads to the enrichment of titanium at the interface, but scarce at the centre of the aqueous phase,

and a hierarchical egg-white structure can be expected. If the interface is unstable, say, the interface is broken and the big droplets split to several smaller droplets, the formed nuclei can be dispersed from the interface to the bulk due to the re-distribution of materials accompanying droplet splitting. The dispersed nuclei serve as the growth centre for subsequent hydrothermal reactions. In this case, a homogeneous structure can be expected. The different formation mechanisms of the microspheres are illustrated in Figure A.2

The stability of a liquid droplet under disturbance has been intensively studied. In a stirred vessel, it is understood that the turbulent stress, or the turbulent kinetic energy, will be balanced by the interfacial and viscous energies at the critical droplet diameter [32]. The droplets larger than the critical diameter will breakup, and the droplets smaller than this diameter will be stable. In the case of the conventional method, the initial large droplets keep splitting until all droplets fall below the critical diameter, which corresponds to the maximum microsphere size in Figure 4.6d in the thesis. For the membrane emulsion case, all initial droplets formed through membrane pores were smaller than the critical diameter, which is reflected by the smaller microsphere sizes in Figure 4.6a compared to the maximum size in Figure 4.6d. Hence the droplets were stable throughout the membrane emulsification process, and the water-oil interface was also maintained in a stable state. As the interfacial reaction occurs, concentration of solid content increases at the interface, which may lead to a dramatic increase of the local viscosity. These increase result in the liquids transitioning to solid state at the interface. During such process, traces of disturbance on the droplet surface are captured during stirring, forming a wavy surface morphology on the final microspheres as demonstrated in Figure 4.6c. But this will not happen for the conventional method since all solid contents will be re-distributed, and the transitioning stage from liquid to solid will only happen during the later static hydrothermal process, during which the disturbance has long gone, and then a perfectly spherical shape is obtained.

Microspheres formed from both methods have almost the same phase compositions, with the majority being the anatase phase, which is identified by the strong diffraction peaks at 25 ° and 48 ° (Figure A.3) [20, 33].

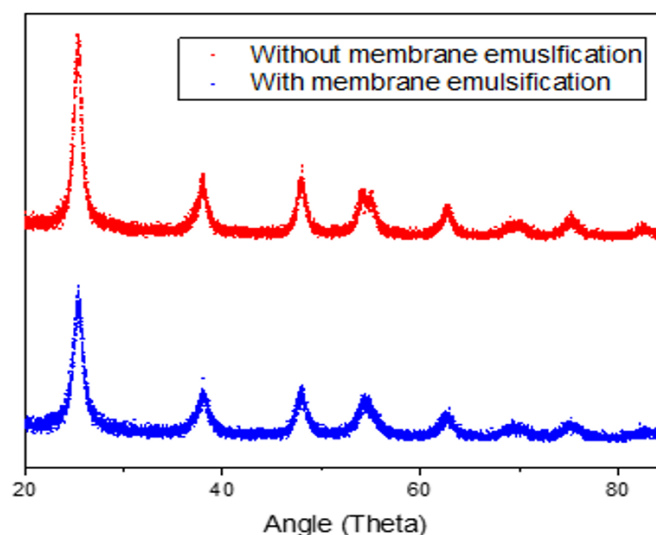


Figure A.3. XRD analysis of the  $\text{TiO}_2$  microspheres

It is understandable since both of the oil and aqueous phase compositions are the same for both preparation methods, and such results imply that the change in mass transfer during microsphere formation doesn't affect the chemistry involved. The fraction of anatase  $\text{TiO}_2$  estimated were 83 % and 80 % for the products prepared with the conventional method and with membrane emulsification, respectively. The ratio of anatase to rutile phases was not tuned in the current study, however, as shown by Yan et al., by changing the concentration of ammonium sulphate in the aqueous phase, the amount of anatase phase to rutile phase can be varied [20]. BET surface area obtained for egg-white and homogeneous  $\text{TiO}_2$  microspheres were  $210 \text{ m}^2 \text{ g}^{-1}$  and  $219 \text{ m}^2 \text{ g}^{-1}$ , respectively, both with an average pore diameter of 5 nm. The porosities of egg-white and homogeneous microspheres were 62 % and 68 %, respectively. The change in mass transfer during microsphere formation has no strong influence on the primary particle size of  $\text{TiO}_2$  and the overall porosity of the microspheres, but instead only on the distribution of  $\text{TiO}_2$  within the sphere. Primary particle size of  $\text{TiO}_2$  are shown in Figure A.4 with both structures exhibiting a size of around 10 nm.

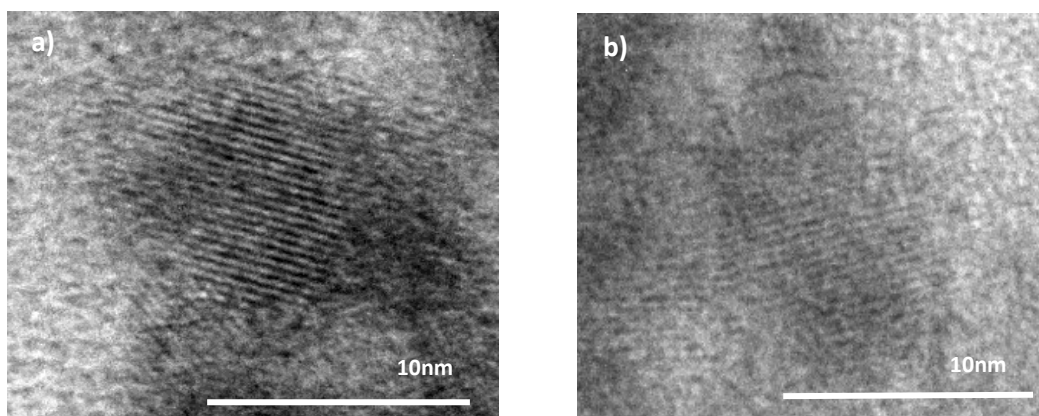


Figure A.4. TEM images of  $\text{TiO}_2$  particle, a) egg-white structure; b) homogeneous structure

### 3. Catalytic performance of $\text{TiO}_2$ microspheres using CO oxidation

$\text{Pd-TiO}_2$  catalyst with 0.6 % Pd loading was prepared by incipient wetness impregnation using  $\text{PdCl}_2$  aqueous solution. After the impregnation, the Pd precursor was pre-treated at 500 °C in air (BOC) for 1 hour to decompose the  $\text{PdCl}_2$ , followed by a reduction step using diluted  $\text{H}_2$  (25%  $\text{H}_2$  in argon, BOC) at 500 °C. The catalytic activity of the two types  $\text{Pd-TiO}_2$  catalyst under varied weight hourly space velocity (WHSVs) was evaluated for CO oxidation at atmospheric pressure.

For the Arrhenius plot kinetic study, 45 mg mixture of 1 wt%  $\text{Pd-TiO}_2$  catalyst in 99 wt% silicon carbide (Sigma-Aldrich) was loaded into a micro-fixed-bed reactor (I.D. 4 mm stainless-steel tube). A schematic of the set-up is shown in Figure A.5. The catalyst was diluted in silicon carbide to achieve less than 10 % CO conversion, in order to keep a working condition close to a differential reactor, which is favoured for kinetic study of catalysts. Hereafter, 20 ml  $\text{min}^{-1}$  of diluted CO (10 % CO balanced with argon, BOC) and 20 ml  $\text{min}^{-1}$  of air were preheated through a heating coil before being fed into the reactor. A range of reaction temperature from 573 to 513 K were studied to obtain the activation energies. Both catalysts exhibit almost identical activities with an activation energy at 113.1 and 115.7  $\text{kJ mol}^{-1}$  for symmetric homogenous and asymmetric egg-white structure, respectively (Figure A.6).

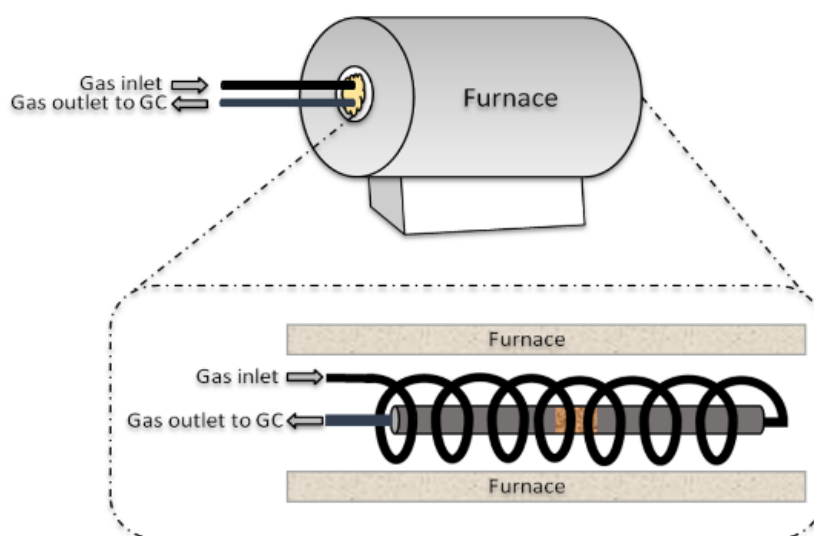


Figure A.5. Schematic of the CO oxidation set-up

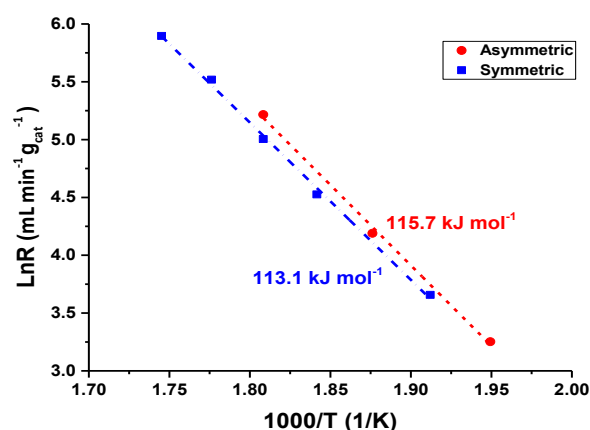


Figure A.6. Arrhenius plot for CO oxidation

For the activity study on different WHSVs, the same set-up was used, 40 mg of Pd-TiO<sub>2</sub> catalyst was loaded into a micro-fixed-bed reactor (I.D. 4 mm stainless-steel tube). 10 ml min<sup>-1</sup> of diluted CO (10% CO balanced with argon) and 10 ml min<sup>-1</sup> of air were preheated before being fed into the reactor, with additional argon (0-200 ml min<sup>-1</sup>) as the dilution gas to adjust the WHSV (30000-330000 ml h<sup>-1</sup> g<sub>cat</sub><sup>-1</sup>). 443 K was selected as the reaction temperature to eliminate the influence from intrinsic kinetics so the influence of TiO<sub>2</sub> spherical structure on the mass transport could be investigated. The composition of effluent gases was analysed using an online gas chromatography (Varian 3900) with a thermal conductivity detector (TCD). The CO conversion was subsequently calculated using the equation below:

$$\% \text{ conversion of CO} = \frac{C_{CO \text{ Inlet}} - C_{CO \text{ Outlet}}}{C_{CO \text{ Inlet}}} \times 100 \quad (\text{A.3})$$

Where  $C_{CO \text{ Inlet}}$  and  $C_{CO \text{ Outlet}}$  are the concentration of CO at the inlet and outlet, respectively.

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## **Chapter 5: Pristine graphene membranes supported on ceramic hollow fibre prepared via a copper sacrificial layer assisted CVD approach**

### **Abstract**

Graphene when being used as membranes, potentially promises high permeation flux and can be operated in extreme conditions attributed to its chemical inertness. Currently, continuous, atomic thin graphene membranes can only be made on flat sheet which limits mass production because of the low surface-area-to-volume ratio. To tackle this challenge, we have successfully devised an unprecedented method to fabricate graphene membranes supported on ceramic hollow fibre via a sacrificial layer approach. Copper was first selected as the sacrificial layer material because it has demonstrated to be a good catalyst for CVD, producing high quality monolayer to few layers graphene. Firstly, a continuous copper sacrificial layer was deposited on the yttrium-stabilised zirconia (YSZ) hollow fibre via the electroless plating method. Copper dewetting was observed during high temperature synthesis; therefore, a short-duration high-temperature CVD approach was implemented to enable the graphene growth while preventing the dewetting behaviour. After this, ferric chloride was used to successfully remove the copper layer and defect-patching treatment was carried out to eliminate any major defects formed during the leaching and CVD process. Herein, a continuous ultra-thin graphene layer sitting on YSZ hollow fibre was obtained and confirmed by Raman spectroscopy. Although reasonable flux was demonstrated, the prepared membrane using copper as the sacrificial layer revealed compaction problem.

### **5.1 Introduction**

The ultra-thin property that graphene exhibits has triggered significant interests in membrane technology. Permeability is inversely related to membrane thickness, this means graphene's 2D ultra-

thin thickness can potentially achieve the ultimate permeation, making it an ideal material for membrane separation [1-3]. Graphene is also chemically inert, enabling its use in extreme conditions and applications. The properties that graphene possess thus opened up many new possibilities for researchers in the field of membrane and membrane reactors [1, 4-9].

Efforts to synthesise graphene membranes have been widely carried out. Surwade et al. have developed a 5- $\mu\text{m}$ -diameter size suspended, single-layer graphene membrane consisting of nanometre-sized pores generated by oxygen plasma etching, the membrane exhibited  $\sim 100\%$  salt rejection and a high water permeation flux of  $252\text{ LMH bar}^{-1}$  using osmotic pressure as the driving force [4]. O'hern et al. have created centimetre-scale nanoporous monolayer graphene and used multi-scale processes to seal the defects, achieving  $\sim 90\%$  rejection of Allura Red [6]. While Kidambi et al. have created  $>5\text{ cm}^2$  nanoporous atomic thin membranes and demonstrated its use in dialysis applications [10]. Large area of  $63\text{ cm}^2$  single-layered perforated graphene membranes have been demonstrated by Qin et al., achieving a water permeation flux of  $50\text{ LMH bar}^{-1}$  and  $98\%$  of Dextran (7 nm) rejection [8]. As demonstrated above, graphene membranes are currently prepared either in free-standing form or are supported on planar substrates. Generally, chemical vapour deposition (CVD) is first carried out on a flat transition metal substrate for graphene synthesis. Subsequently a polymer or polymer-free graphene transfer approach is adopted to achieve graphene supported on planar substrate. In the former method, PMMA is generally used and is coated onto the metal-graphene followed by etching of the metal layer. The PMMA-graphene layer is then transferred onto a substrate and finally the PMMA layer is removed by dissolving in acetone and by thermal annealing [4]. A polymer-free method can be the pressing or casting method. The pressing method involves etching the metal layer, followed by placing the supporting substrate on top of the graphene and then pressed against the membrane, adhering the support to the graphene [11, 12]. Whereas the casting method involves a phase inversion-process, a polymer solution is first coated on to the graphene, followed by immersion in water bath, finally forming a porous support membrane directly on the graphene [8, 10].

Studies so far have presented the feasibility of nanoporous graphene membrane in separation, nevertheless, challenges remain before it can become the next generation ideal membrane. The challenge of industry scale-up must be tackled before it can reach commercialisation. However, flat sheet geometry limits mass production because it has low membrane-area-to-volume ratio. A new synthesis route of graphene membrane in a different geometry is therefore needed. Hollow fibre membrane on the other hand offers high packing density potentially up to 8000-10,000 m<sup>2</sup> m<sup>-3</sup> and is favourable for module assembly [13]. From the engineering perspective, it would be a breakthrough if graphene can be synthesized on the hollow fibre geometry. Hollow fibre possesses a tubular shape, therefore the traditional graphene membrane synthesis-transfer method cannot be adopted here, as the graphene sheet cannot be pressed or wrapped around the hollow fibre with both ends sealed. Alternative approach to synthesise and transfer large area of graphene membrane in tubular form is therefore imperative.

In this study, we have devised an unprecedented preparation of graphene membranes supported on hollow fibre geometry via a sacrificial layer assisted CVD approach. Since graphene can be synthesised on transition metal via CVD, and the shape and area of graphene synthesised are governed by the shape and area of the metal substrates. This led to the idea of growing graphene directly on metallic hollow fibre. Herein, a dense metal sacrificial layer is deposited on a porous ceramic hollow fibre support. Hereafter, the metal layer is removed while the ceramic hollow fibre remains intact to act as the scaffold for structure and mechanical integrity. Amongst the various transition metals studied for CVD growth, copper was chosen because it has shown to produce high quality graphene for the use in membrane applications [4, 6, 10]. A schematic of the synthesis procedure is shown in Figure 5.1. Copper sacrificial layer is first deposited on YSZ hollow fibre via electroless plating. A short-duration high-temperature CVD approach was then adopted to achieve graphene growth on the copper plated hollow fibre, this was then followed by etching in ferric chloride to remove the sacrificial layer. Finally, defects introduced are sealed with graphene flakes, realising the final ultra-thin pristine graphene hollow fibre membrane.

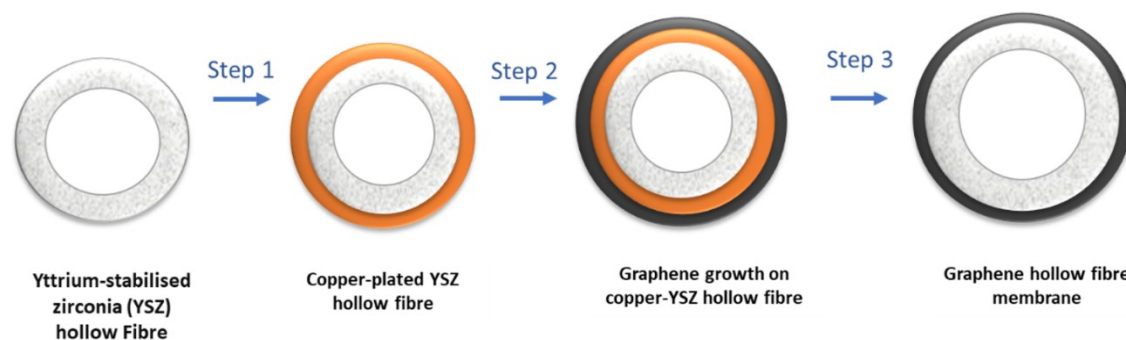


Figure 5.1. Illustration of preparation procedure for obtaining graphene hollow fibre membranes

## 5.2 Experimental

### 5.2.1 Preparation of copper plated YSZ hollow fibre

The YSZ hollow fibres were activated and copper sacrificial layer was deposited using the electroless plating method, described in Chapter 3.2. The plating solution used consisted of copper sulphate (>99 %, Sigma Aldrich), potassium sodium tartrate tetrahydrate (99 %, Sigma Aldrich) and sodium hydroxide (>98 %, Sigma-Aldrich). The reducing agent used was glyoxylic acid (Sigma Aldrich) or formaldehyde (Sigma Aldrich). Summary of the plating composition studied is found in Table 5.1 and detailed study in achieving a dense copper sacrificial layer can be found in Additional Information B.

Table 5.1. Composition of electroless copper plating studied

| Compound                               | Concentration mol dm <sup>-3</sup> |
|----------------------------------------|------------------------------------|
| Copper sulphate                        | 0.030-0.080                        |
| Potassium sodium tartrate tetrahydrate | 0.117-0.150                        |
| Sodium hydroxide                       | 0.250 -0.320                       |
| Glyoxylic acid or formaldehyde         | 0.030-0.240                        |

### 5.2.2 Annealing and graphene growth via CVD

After the electroless copper plating has taken place, the plated copper-YSZ (Cu-YSZ) was annealed using Carbolite® wire wound single zone tube furnace at a range of 530 °C to 900 °C under 5 °C min<sup>-1</sup>

heating rate in vacuum, at a concentration of 4:1 He:H<sub>2</sub> ratio for 2 hours. After the annealing process, the Cu-YSZ-HF was drawn out of the furnace, allowing the temperature of the heating zone to ramp up to the required 1000 °C CVD temperature for graphene synthesis. After the furnace reached 1000 °C, the plated fibre was inserted back into the furnace and methane was fed into the reactor at 1:1 H<sub>2</sub>:CH<sub>4</sub> concentration for 210 seconds. This short-duration high-temperature CVD process was adopted to prevent copper dewetting happening at high temperature synthesis, which will be further explained in the next Section. After the CVD process, the fibre was drawn out immediately from the furnace and graphene-copper YSZ hollow fibre was obtained.

### **5.2.3 Etching of copper sacrificial layer and post-etching defect-patching treatment**

The intermediate copper sacrificial layer must then be etched to realise the final graphene layer as the selective barrier on YSZ hollow fibre. The graphene-copper-YSZ-hollow fibre (G-Cu-YSZ-HF) was snapped in half and immersed in copper etchant to leach away the sacrificial layer. In order to ensure complete removal of the copper layer, the hollow fibre is normally immersed for more than 2 hours. Post etching, defects may be formed on the graphene layer supported on YSZ hollow fibre and affect the integrity of the membrane. Therefore, post-defects treatment was carried out to seal any defects using graphene flakes. Graphene flakes dispersed in NMP (G-NMP) was prepared using the method liquid exfoliation of graphite and was forced through the G-YSZ-HF at 10 bar using the dead-end filtration set-up. Defects presented on the G-YSZ-HF were then sealed by the graphene flakes.

### **5.2.4 Characterisation and performance tests**

The morphology and microstructure of the hollow fibres were characterised using SEM and Raman spectrometry. Solvent permeation tests were carried out using the dead-end filtration set-up described in Chapter 3.7.

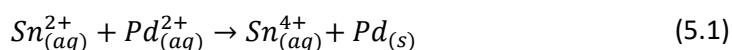
## 5.3 Results and discussions

### 5.3.1 Formation of copper sacrificial layer on YSZ hollow fibre

For the preparation of copper sacrificial layer on YSZ hollow fibre, various copper deposition techniques have been explored, including metal evaporation, sputter coating, electrocoating and electroless coating. Copper plating on ceramic substrates have been attempted, in particularly on ceramic powders [14-16] and on art ceramics [17]. The amount of literatures available for electroless metal plating on ceramic hollow fibres, however, are not vast, they mainly focused on the use in solid oxide fuel cells or hydrogen separation membranes [18-20]. The employment of electroless plating on ceramic hollow fibre to produce graphene membrane has not yet been explored. The current study thus explores the effective deposition of a copper sacrificial layer on YSZ hollow fibre for CVD graphene growth and the eventual synthesis of graphene hollow fibre membrane.

Yttrium-stabilised Zirconia (YSZ) hollow fibre was selected as the ceramic support because of its good mechanical strength, smooth surface property and high chemical resistance. YSZ hollow fibres were prepared via the phase inversion and sintering method. The fibres consist of a smooth outer layer, sponge-like and micro-channel structures, as shown in Figure 5.2a&b. It has an average flow pore size of 71 nm and mechanical strength of 228 MPa. The structure and surface smoothness obtained are ideal for the synthesis and application of graphene membranes, possessing a high surface-area-to-volume ratio, which will provide the necessary support for electroless copper plating and the eventual graphene growth. Figure 5.2c shows the microstructure of the YSZ outer surface.

The next step was to obtain a dense copper sacrificial layer on the YSZ hollow fibre for CVD graphene growth. YSZ fibre itself has inherently poor catalytic activity and needs to be pre-treated prior to successful electroless copper plating. The fibres were first sensitised by adsorbing  $\text{Sn}^{2+}$  ions on the ceramic surface, followed by exchange with  $\text{Pd}^{2+}$  palladium ions. The tin-palladium exchange occurs when the  $\text{Sn}^{2+}$  ions are oxidised and replaced by Pd seeds, shown in the equation below.



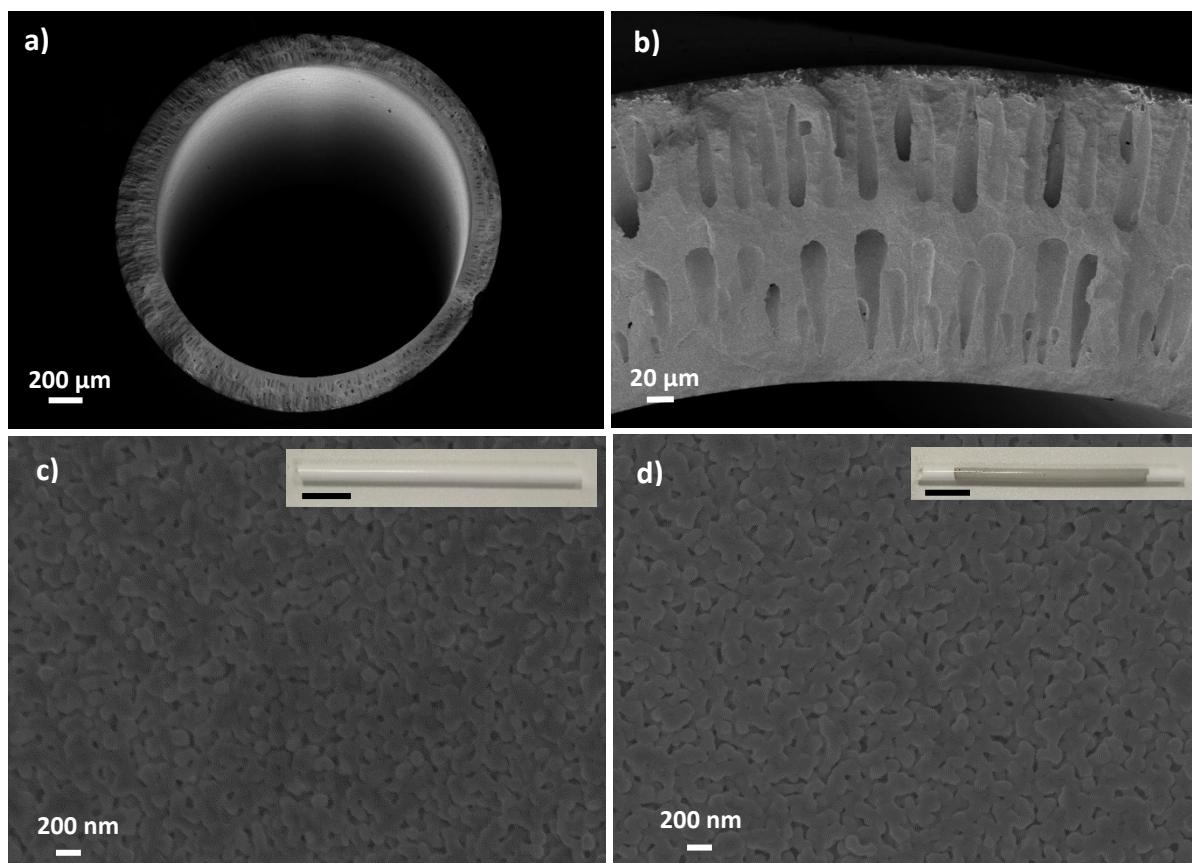


Figure 5.2. SEM images of a& b) cross-sectional image of YSZ hollow fibre; c) plain YSZ outer surface, (inset- photograph of plain YSZ hollow fibre, 1cm scale); d) Pd seeded YSZ outer surface, (inset- photograph of Pd seeded YSZ, 1cm scale)

Due to the deposition of palladium seeds on the YSZ hollow fibre, the white outer surface has transformed into a greyish colour. However, SEM image in Figure 5.2d shows that the surface of the activated seeds does not affect the porous structure of the YSZ support.

Hereafter, the activated Pd-YSZ hollow fibre was immersed into the plating solution for the deposition of copper sacrificial layer via electroless plating. Electroless plating is a non-galvanic plating method that involves a redox reaction which can be described by two half reactions; anodic oxidation of the reducing agent and the cathodic reduction of the metal ions [21]. In the presence of hydroxyl ions, reducing agent is oxidised releasing electrons which are then used in the cathodic area, where copper ion is reduced into copper and deposit on the substrate surface. At increased pH, the electrode potential for the oxidation half-reaction becomes more negative, therefore copper deposition is thermodynamically more favourable when placed in alkaline condition. However, at elevated pH, copper precipitation happens, complexing agent is therefore added to control the metal ions in

solution. This is to prevent precipitation within the solution and to allow the solution to be operated at higher pH values. Careful control of the concentration is also needed because if the metal is too complexed, there will be insufficient free metal ions for plating to happen.

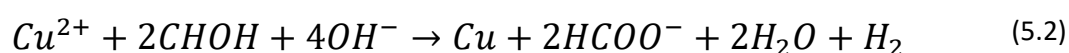
In this study, the copper plating solution consisted of copper sulphate as the copper source, sodium hydroxide as the alkaline source and potassium sodium tartrate as the complexing agent. Both formaldehyde and glyoxylic acid were tested as the reducing agent. Detailed study on tuning the various parameters, such as copper sulphate concentration, reducing agent and the temperature of the plating bath can be found in Additional Information B.

After investigating the various parameters, a continuous copper sacrificial layer depositing on YSZ hollow fibre (Cu-YSZ-HF) was obtained using the electroless copper plating condition summarised in Table 5.2, operating at 45 °C with the use of formaldehyde as the reducing agent, followed by annealing at 530 °C.

*Table 5.2. Electroless copper plating composition*

| <b>Compound</b>                               | <b>Concentration mol dm<sup>-3</sup></b> |
|-----------------------------------------------|------------------------------------------|
| <b>Copper sulphate</b>                        | 0.060                                    |
| <b>Potassium sodium tartrate tetrahydrate</b> | 0.150                                    |
| <b>Sodium hydroxide</b>                       | 0.320                                    |
| <b>Formaldehyde</b>                           | 0.060                                    |

The reaction takes place as indicated in the equation below. In the presence of alkaline condition with OH<sup>-</sup> ions, copper ions are reduced and deposit on the activated YSZ surface, whilst formaldehyde is oxidised with the release of hydrogen and water.



The plated copper fibre exhibits an amorphous structure shown in Figure 5.3a. Annealing was then carried out under vacuum in He/H<sub>2</sub> atmosphere to remove impurities and oxides from the plated surface, and to obtain a smoother copper layer suitable for graphene synthesis. When the copper plated YSZ hollow fibre was exposed to temperature above 550 °C, a behaviour of copper dewetting was discovered. This resulted in the formation of copper islands and copper globules as shown in Figure 5.3b&c. The lighter areas are the YSZ surface and the darker areas are the copper deposits. It was found that copper dewetting happens because of the wettability issue between the ceramic and metal, i.e. the wettability of Cu on YSZ surface is low. Copper has a melting point at 1085 °C, when the annealing temperature is sufficiently high and exposed under vacuum condition, a phenomenon called partial wetting appears, where the cohesive attraction between copper atoms is greater than the

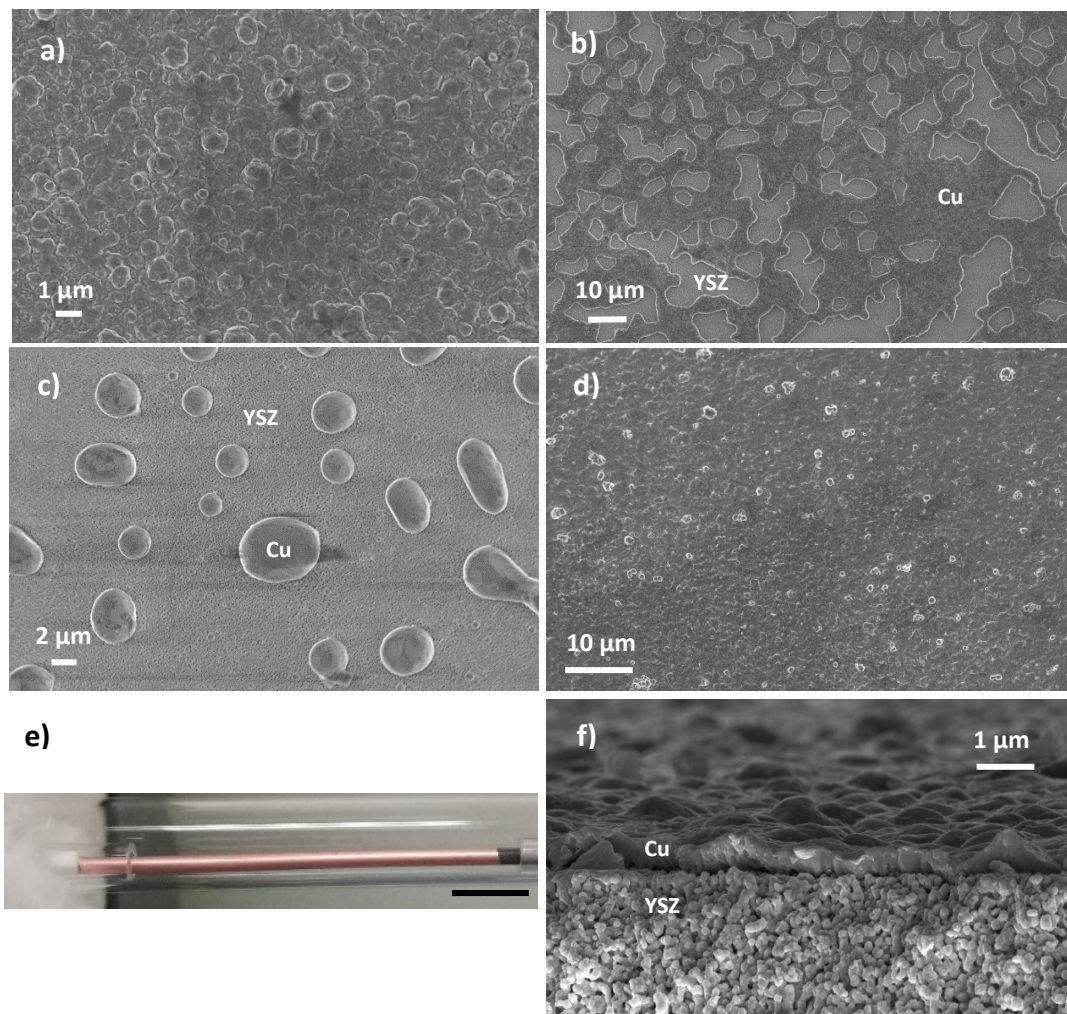


Figure 5.3. a) SEM image of plated Cu-YSZ-HF; b&c) copper dewetting on YSZ surface; d) SEM image of Cu-YSZ-HF after annealing; e) Photograph of Cu-YSZ-HF after annealing (1cm scale); d) cross-sectional image of Cu-YSZ-HF

adhesive interaction between copper and YSZ surface, resulting in the formation of copper globules or islands. Similar behaviour was observed by Ismach et al., where they found copper dewets and evaporates into finger like structure and dots on dielectric material during high temperature synthesis [22]. By lowering the annealing temperature, the copper ceramic partial wetting was reduced, therefore, 530 °C was selected as the annealing temperature. Finally, a continuous copper sacrificial layer was deposited on the YSZ hollow fibre with the absence of copper islands or globules (Figure 5.3d). The annealed fibre shows a dense and shiny feature, indicating the densification and continuity of the Cu-YSZ-HF (Figure 5.3e). The thickness of the copper layer obtained is shown in Figure 5.3f, with the copper sacrificial layer exhibiting a thickness of around 400 nm.

### **5.3.2 Graphene growth via CVD on Cu-YSZ-HF**

After the successful deposition of a continuous copper sacrificial layer on YSZ hollow fibre, chemical vapour deposition was carried out for the synthesis of graphene layer. Methane has been the most commonly used CVD catalyst and has demonstrated to produce high quality monolayer to few layer graphene. Amongst the other hydrocarbons, methane has the highest hydrogen to carbon atom ratio [23], therefore graphene synthesis using methane is normally carried out above 900 °C because of the strong C-H bond. Possessing a higher decomposition temperature also means decomposition rate is easier to control compare to other hydrocarbon such as C<sub>2</sub>H<sub>4</sub> [24]. Using the annealing temperature of 530 °C for CVD therefore would not be possible to break down methane into radicals for graphene synthesis. Other lower decomposition temperature carbon precursor, such as C<sub>2</sub>H<sub>4</sub> was attempted. However, 530 °C was still too low to achieve good quality graphene growth on copper.

The challenge of synthesising graphene on copper-YSZ while mitigating the dewetting behaviour had to be tackled. Previous literatures show that graphene can be synthesised in around 5 minutes instead of longer synthesis time of 30 mins to hours [25-27]. Using similar concept, a shorter duration growth was proposed, the synthesis time was tuned where quality graphene film was formed before copper

dewetting begins to take place. Herein, a short-duration high-temperature CVD process was implemented. A range of 60 seconds to 30 mins growth time was investigated at 1000 °C, under 1:2 CH<sub>4</sub>:He ratio in vacuum, with methane used as the carbon precursor. In order to achieve an in-situ annealing-CVD process, the Cu-YSZ-HF was pulled out from the heating zone after annealing at 530 °C, and the CVD temperature was ramped up to 1000 °C, once the CVD temperature is reached, the fibre was inserted back to the heating zone for a certain period of time for CVD to take place before being withdrawn. Drawing out the fibre during the ramping process prevents copper dewetting, so that the Cu-YSZ-HF is only exposed to high temperature for minimal time. Finally, successful graphene growth and coverage was obtained at 210 seconds CVD time. As shown in the inset of Figure 5.4a, the graphene coated copper-YSZ hollow fibre (G-Cu-YS-HF) exhibits a continuous, shiny colour, indicating the continuity of the graphene-copper layer supported on the YSZ hollow fibre. Cross-sectional view of the G-Cu-YSZ-HF was obtained using TEM, shown in Figure 5.4a. It is evident that a crystalline copper layer exists sitting on the YSZ porous support for graphene synthesis, the copper did not penetrate into the porous support. A layer of platinum was sputtered on the graphene-copper for the sample preparation in focused ion beam for the characterisation in TEM. Formation of the graphene layer can be observed on the copper grains shown in Figure 5.4b, the presence of wrinkles (shown in red circle) indicate the presence of a continuous graphene layer, wrinkles were formed by the graphene layer during the cooling stage due to the difference in thermal expansion coefficient between the copper and graphene. Copper is generally susceptible to moisture and oxidation when exposed at high temperature, therefore by performing the CVD process under vacuum instead of atmospheric, the obtained surface is less susceptible to oxidation and a clean surface can be obtained as shown in Figure 5.4b&c. The SEM image in Figure 5.4c shows that within the 210 seconds CVD synthesis time, severe copper dewetting did not take place and a large area of continuous graphene-copper layer exists on the YSZ surface. However, in some areas, copper dewetting did happen as shown in Figure 5.4d. It is realised that copper dewetting would be difficult to eliminate fully. However, provided that the high temperature exposure time is short, graphene can be synthesised before the copper dewets, and a

continuous graphene layer can still be obtained. As indicated in Figure 5.4d, although copper dewetting happened and the underlying porous YSZ surface is exposed, there is a continuous film covering the exposed YSZ surface, featured by the semi-transparent nature of the porous area. This evidence proves that graphene can be formed provided the copper dewetting happens after the graphene synthesis. Similar results was obtained by Ismach et al., they discovered that graphene can be formed directly on dielectric surface without post-etching treatment, this was achieved when the copper dewets and evaporates after graphene was grown [22]. Quality of the graphene layer was attempted to be explored using Raman spectroscopy, however, because of the presence of the copper layer underneath, Raman spectra was not able to be deduced. This was caused by the luminescence of the copper which has much larger Raman scattering intensity and has high spectral background [28, 29]. However, quality of the graphene was characterised after successful removal of the copper layer, which will be discussed in the next Section.

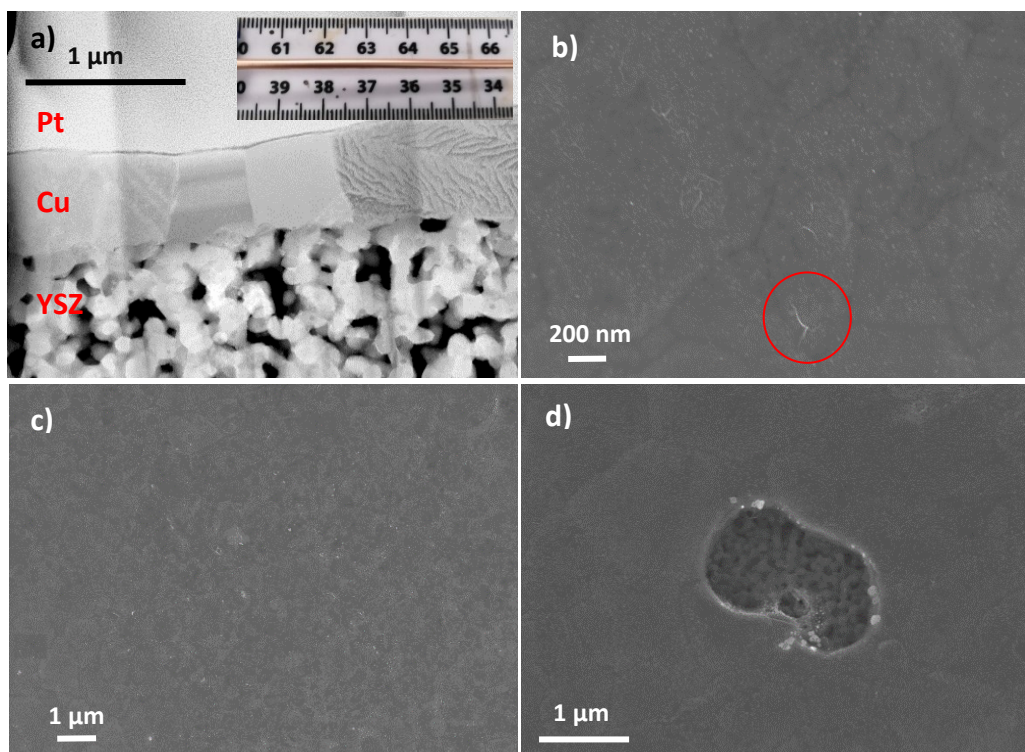


Figure 5.4. a) Cross sectional view of G-Cu-YSZ-HF under TEM (Inset- photograph of G-Cu-YSZ-HF); b&c) SEM images of G-Cu-YSZ-HF surface; d) copper dewetting on G-Cu-YSZ-HF

### 5.3.3 Etching of copper sacrificial layer

Copper sacrificial layer was etched to achieve the pristine graphene layer supported on YSZ hollow fibre. Ferric chloride was selected as the etchant because it is a widely used copper etchant that can slowly and effectively etches the copper without formation of any gaseous product which can disrupt and crack the graphene layer [30]. The G-Cu-YSZ-HF was snapped in half and was immersed into a 0.1 M ferric chloride solution. Copper was leached away by allowing the etchant solution to enter the snapped edges of the fibre. The solution may also enter through the porous YSZ substrate into the copper since graphene may not have formed in between the YSZ and copper surface under the short duration growth time.

After the successful removal of copper sacrificial layer, pristine graphene layer supported on YSZ hollow fibre (G-YSZ-HF) was obtained. Figure 5.5a shows the photograph of G-YSZ-HF with the copper sacrificial layer removed. The dark grey colour on the YSZ hollow fibre is thought to be attributed by the palladium seeds deposited during the activation step. In Figure 5.5b the morphology of the YSZ hollow fibre support is clearly seen, indicating the electronic-transparent property of the obtained graphene layer. Raman spectra in Figure 5.5c indicates the existence of graphene crystal lattice with the presence of 2D and G peaks. Multilayer graphene was observed from the 2D to G ratios, which concentrate around 0.7 (Figure 5.5d). Monolayer is generally formed on CVD copper due to the low carbon solubility in copper which limits the growth to monolayer. However, it was later demonstrated that multilayer graphene can also be synthesised on copper under certain CVD conditions and parameters such as, surface roughness, density of defects and impurities on the copper surface can play a role in the formation of multilayer graphene [26].

In particular, several studies have revealed that impurity such as silicon oxide nanoparticles can act as catalyst for graphene growth, where they can decompose carbon precursors and become nucleation sites for the growth of successive graphene layer [26]. In our experimental set-up, quartz wool was used as support to hang the fibre during CVD (Schematic illustration can be found in Chapter 3.3.2);

looking at Figure 5.4d, there are some white spots observed on the graphene-copper surface, which is the appearance of the  $\text{SiO}_2$  particles. Therefore, the presence of the  $\text{SiO}_2$  acted as catalyst and promoted the formation of multilayer graphene on the hollow fibre. Nevertheless, the graphene layer obtained is homogenous and continuous indicated by the Raman mapping in the inset of Figure 5.5d, where a uniform colour shading is observed.

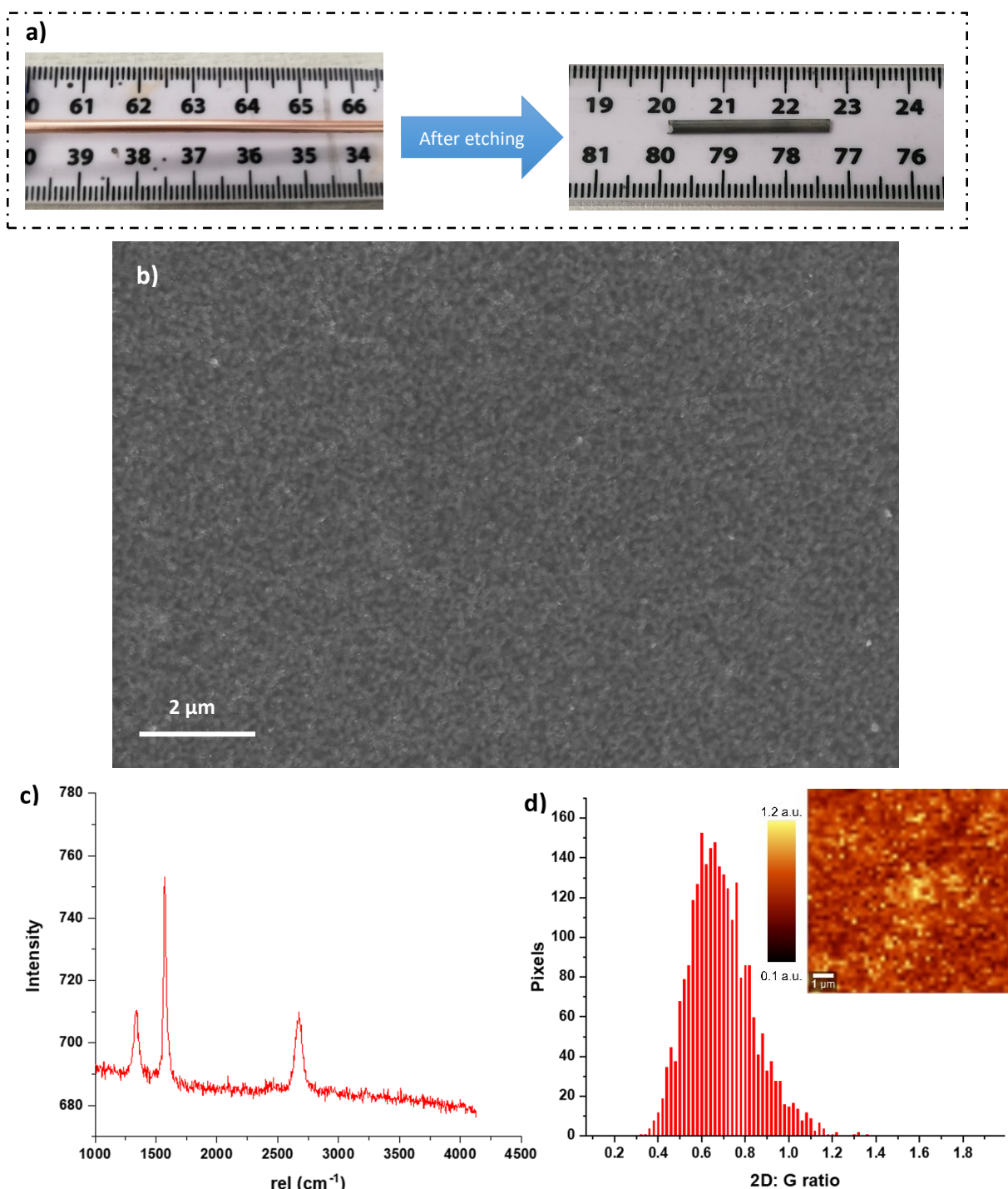


Figure 5.5. a) Photograph of the copper sacrificial layer removed using ferric chloride; b) SEM image of G-YSZ-HF; c) Raman spectra of G-YSZ-HF; d) Distribution of 2D:G ratio (inset-Raman mapping of 2D:G ratio)

### 5.3.4 Post-etching defect-patching treatment

So far, pristine graphene supported on YSZ hollow fibre geometry have been prepared. From the Raman spectra indicated in Figure 5.5c, a D peak is found indicating the presence of defects on the graphene layer. These defects might be formed due to the leaching process or by the short-duration high-temperature CVD process. The presence of these defects provides uncontrolled flow passage through the membrane, therefore these defects were sealed using graphene flakes, to minimise the non-selective effects. This was done by patching the defects formed with graphene flakes.

Pristine graphene flakes dispersed in NMP was permeated through the G-YSZ-HF at 10 bar. By measuring the amount of NMP permeated through the G-YSZ-HF, the level of defect formation imposed on the G-YSZ-HF can also be deduced. For higher quality G-YSZ-HF sample with minimal defect formation, unmeasurable quantity of NMP had permeated through. This is because minimal amount of graphene flakes was required to patch the defects. Whereas, if measurable amount of NMP was permeated through the G-YSZ-HF, this means that large amount of graphene flakes was required

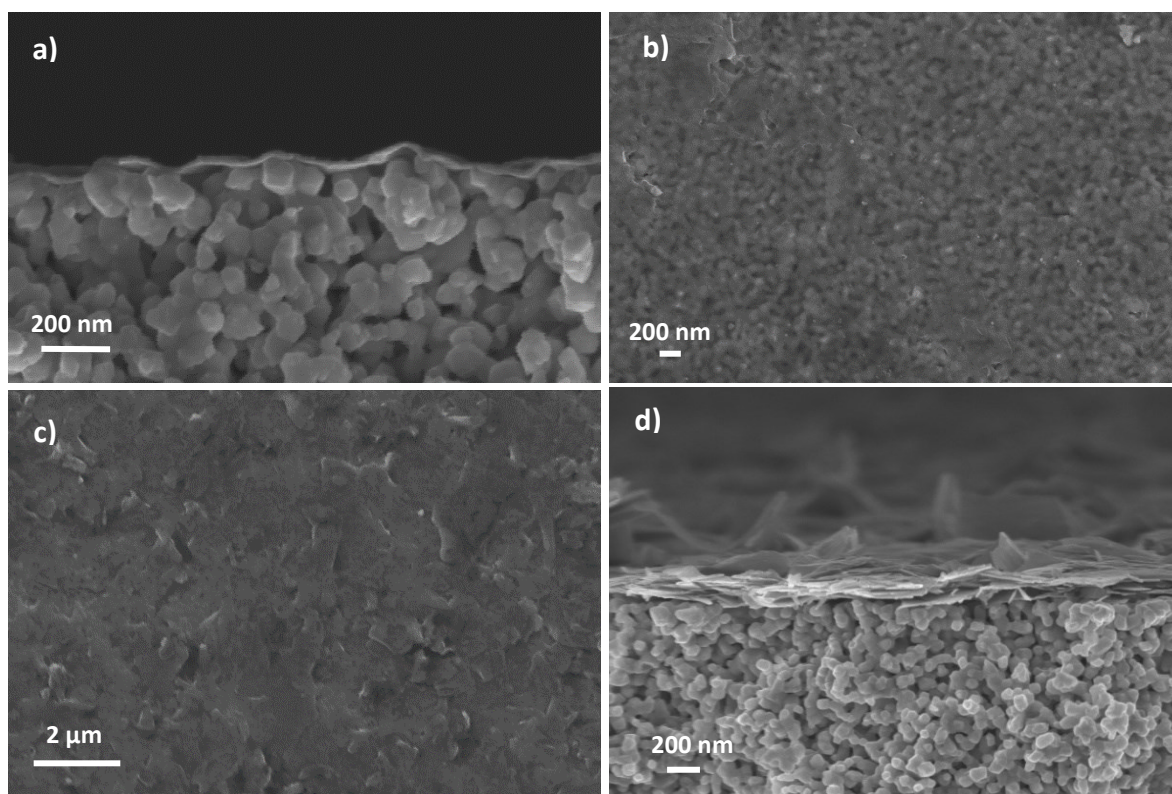


Figure 5.6. a) Cross-sectional & b) Outer surface of G-YSZ-HF post defect-patching treatment; c) Cross-sectional & d) Outer surface of direct deposition of graphene flakes on plain YSZ hollow fibre

to patch on the defects, thus greater quantity of NMP was collected. The thickness of the graphene layer was not altered because the flakes selectively patched only on area where defects were presented. As revealed in Figure 5.6a, the graphene layer supported on YSZ hollow fibre exhibits an ultra-thin thickness after defects were covered by graphene flakes. The underlying YSZ morphology can still be clearly observed due to the transparency of the graphene layer (Figure 5.6b). If graphene flakes were filtered onto plain YSZ fibre directly without the presence of the initial graphene layer, a thick, chaotic graphene layer was observed from the top surface and cross-section (Figure 5.6c&d). The underlying YSZ structure could no longer be observed, and the graphene selective layer is of few hundred nano-meters thick (Figure 5.6d), hindering the permeation flux and can result in compaction problem. Thus, this direct deposition method is not favourable for the preparation of pristine graphene hollow fibre membrane.

### **5.3.5 Performance of graphene membrane supported on YSZ hollow fibre**

From the earlier literatures, defect-free graphene is found to be impermeable to gases and liquids [31], pores have to be generated in order to achieve the desired separation [4, 6]. In the current study, since defects were covered by graphene flakes, the narrow space between the flakes and the graphene layer can serve as intrinsic pores without the need of post pore-generation, allowing molecules to permeate through the membrane. Both the CVD graphene and the graphene flakes tend to have corrugated surfaces caused by wrinkles, ripples and crumples [32]; when they are in contact, flow passages of nanometre size would be formed around the corrugations which would allow molecules of certain size to pass. Methanol and ethanol permeation were carried out on the pristine graphene hollow fibre membrane, exhibiting an average steady permeation flux of 10.6 and 2.49 LMH bar<sup>-1</sup>, respectively. However, for some of the graphene hollow fibre membrane samples prepared, compaction was observed, where flux declined after 30 mins of testing. This result could be caused by the large number of defects presented during the CVD or leaching process and thus large amount of graphene flakes were needed to cover the defects. The large quantity of graphene flakes needed

resulted in similar behaviour to that of graphene oxide membrane where compaction was observed [33]. During the solvent permeation, pressure applied could compact the loosely packed and less ordered graphene flakes structure, this compaction compresses the spaces between the flakes leading to a more densely and orderly packed microstructure, thus decreasing the solvent permeation. For cases which needed large amount of graphene flakes to seal the defects, more of the loosely packed graphene flakes structures exist, therefore compaction is evident. Whereas if minimal amount of graphene flakes were used to seal major defects, which were the case for some of the samples, compaction was not observed. This is because there were minimal loosely packed graphene flakes structure present on the hollow fibre, and the hollow fibre was covered vastly by the continuous graphene layer formed from CVD, this graphene layer has high rigidity and therefore will not be influenced by compaction in pressure-driven applications. This behaviour was further confirmed by testing a graphene hollow fibre membrane obtained by direct deposition of graphene flakes on YSZ plain hollow fibre, under ethanol permeation, flux declined by 60 % in 1 hour.

From the study so far, the use of copper sacrificial layer did assist to produce graphene hollow fibre membrane, however at times, large number of defects were needed to be sealed with graphene flakes, resulting in non-selective layers to dye molecules and the compaction problem of the membrane. It is hypothesised that these problems arise because of several reasons. Firstly, by using copper as the sacrificial layer on YSZ hollow fibre for CVD, wettability issue occurred, and a shorter graphene growth time was needed to reduce copper dewetting. This affected the quality of graphene synthesised, and post-etching, the quality of graphene layer remained will not be the highest quality, thus large quantity of graphene flakes was needed to seal the defects produced. As a result, alternative catalyst sacrificial layer should be considered to grow higher quality graphene and potentially eliminate the wettability issue, whereby after leaching, it will require less graphene flakes to seal the defects.

## 5.4 Conclusion

In this study, graphene hollow fibre membrane was prepared via a copper sacrificial layer assisted CVD approach. A continuous copper sacrificial layer was successfully deposited on YSZ hollow fibre via the electroless plating method. Copper dewetting was observed during high temperature exposure, therefore optimal annealing temperature was studied and at 530 °C, a continuous and shiny annealed copper layer was obtained for graphene synthesis. Next, a short-duration high-temperature CVD approach was implemented at 1000 °C for 210 seconds to enable the graphene growth while preventing the behaviour of copper dewetting. The copper sacrificial layer was then etched in 0.1 M ferric chloride, leaving the pristine graphene layer supported on YSZ hollow fibre. Post-treatment was carried out using graphene flakes dispersed in NMP to cover any large defects presented. Hereafter, the unprecedented ultra-thin pristine graphene membrane supported on YSZ hollow fibre was prepared, demonstrating a methanol and ethanol flux of 10.6 and 2.49 LMH bar<sup>-1</sup>, respectively. However, compaction problem was observed from some samples prepared, where flux declined after 1-hour testing, and the membranes could not provide useful selectivity. Therefore, alternative catalyst sacrificial layer needs to be proposed to see if this compaction problem can be resolved and a better graphene hollow fibre membrane can be achieved.

## Additional Information B

### 1. Study of electroless copper plating condition

Electroless plating was employed to deposit the copper sacrificial layer on the YSZ hollow fibre. In the study by Zhao et al., copper was successfully plated on ceramic specimen [17], their recipe was modified and employed as the starting point for the current study. The plating solution by Zhao et al. composed of copper sulphate, sodium hydroxide and potassium sodium tartrate with the reducing agent being formaldehyde. Formaldehyde is a commonly used reducing agent for copper plating, however, formaldehyde is carcinogenic, and the toxicity can damage the tracheas of the human body.

Therefore, a safer alternative, glyoxylic acid was also studied in addition to formaldehyde [34]. The composition of the plating solution used is shown in Table B.1 and various parameters, such as copper sulphate concentration, reducing agent concentration, temperature of the plating bath were investigated to achieve the optimum plating condition.

*Table B.1. Composition studied for electroless copper plating*

| <b>Compound</b>                               | <b>Concentration mol dm<sup>-3</sup></b> |
|-----------------------------------------------|------------------------------------------|
| <b>Copper sulphate</b>                        | 0.030-0.080                              |
| <b>Potassium sodium tartrate tetrahydrate</b> | 0.117-0.150                              |
| <b>Sodium hydroxide</b>                       | 0.25 -0.320                              |
| <b>Glyoxylic acid or formaldehyde</b>         | 0.030-0.240                              |

Glyoxylic acid was first employed, and the effect of plating temperature on the deposition quality was observed. Temperature ranged from 25 °C to 70 °C was studied with the rest of the parameters shown in Table B.2.

*Table B.2. Composition of electroless plating starting with glyoxylic acid*

| <b>Compound</b>                               | <b>Concentration mol dm<sup>-3</sup></b> |
|-----------------------------------------------|------------------------------------------|
| <b>Copper sulphate</b>                        | 0.047                                    |
| <b>Potassium sodium tartrate tetrahydrate</b> | 0.117                                    |
| <b>Sodium hydroxide</b>                       | 0.250                                    |
| <b>Glyoxylic acid</b>                         | 0.047                                    |

Starting at 25 °C the plating process was extremely slow taking a few days to a week to observe visible deposition on the YSZ hollow fibre. The temperature was then increased to 45 °C and the plating procedure was improved, taking around 5 hours for complete visible deposition. Higher temperature

was attempted at 70 °C, where complete deposition was achieved in 2 hours. However, the kinetics at 70 °C was very fast and copper particles were observed to be floating in solution, indicating the possibility of the copper nuclei formed faster in solution than on the catalytic hollow fibre surface. This could also cause poor adhesion to the fibre surface, affecting the quality of the sacrificial layer. Thus 45 °C was selected as the plating temperature. The result obtained also correlates well with the study by Hanna et al. [35], where they found the optimal plating temperature to be 40-45 °C. Above 50 °C, stability of the plating solution decreased resulting in rapid decrease of copper deposition rate.

After plating, the copper-YSZ hollow fibre (Cu-YSZ-HF) was annealed under vacuum in H<sub>2</sub>/He atmosphere at 900 °C to remove unwanted impurities and oxides, and to achieve smoother copper surfaces suitable for CVD graphene growth. Temperature of 900 °C was chosen because it's close to the condition required for CVD and an in-situ CVD process can be carried out. However, after annealing, a continuous copper layer was not observed, instead copper dewetting was seen on the hollow fibre surface. As shown in Figure B.1, majority of the surfaces were covered with copper islands instead of one continuous layer, and in extreme scenarios, copper globules were observed. The lighter areas in Figure B.1 are the YSZ hollow fibre surface and the darker areas are the copper deposits. It was initially hypothesised that copper dewetting was caused by insufficient plating thickness, therefore further parameters were tuned to rectify this.

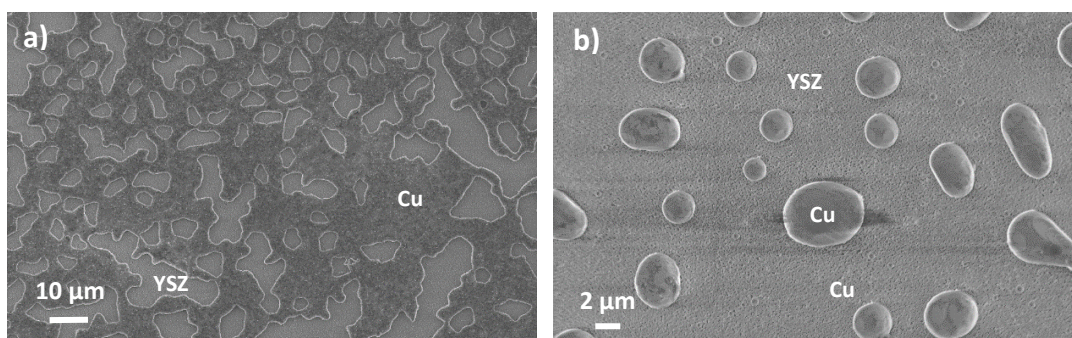


*Figure B.1. SEM images of copper dewetting on YSZ surface*

Next the reducing agent ratio was tuned with the rest of parameters kept the same as Table B.2. The reducing agent to copper ion concentration ratio was increased and tested at 2:1, 3:1 and 4:1 ratio. Increasing the concentration of reducing agent was thought to improve the plating quality because

more metal ions could be reduced with increased reducing species, and any rate limiting effects can also be removed. However, results showed otherwise where plating was observed to be less effective and the plating rate was much slower than that was at 1:1. Similar findings was obtained by Honmaa et al., where they found increasing reductant concentration had no effect on the deposition rate [34]. This result could be caused by the increased of pH when glyoxylic acid concentration was increased, since electroless plating is generally more favourable in alkaline condition. Abbas et al. explained the behaviour was due to glyoxylic acid reacting with sodium hydroxide, affecting the pH stability in the copper solution and leads to a low plating rate [36].

Hereafter, copper ion concentration was tuned to further improve the copper thickness and to prevent copper dewetting taking place. Initial concentration started at 0.047 M where visible plating was observed prior to annealing, higher concentration of 0.06 M and 0.08 M were then investigated. After annealing, more dense copper area was realised at 0.06 M and 0.08 M than at 0.047 M, and shinier copper layer was observed. Therefore, copper concentration at 0.06 M and 0.08 M have improved the copper plating deposition but no major difference was observed between the use of 0.06 M or 0.08 M. In the study by Honmaa et al., they also discovered that copper deposition rate increased when copper ion concentration increased from 0.045 to 0.06 M, as the concentration approaches to 0.06 M, the curve started to plateau, indicating that increasing copper ion concentration beyond 0.06 M did not significantly increase the deposition rate, which is similar findings to our current study [34]. 0.06 M was therefore selected as the chosen concentration. Since the copper concentration was increased by a factor of 1.28 and to maintain the same pH and complexing agent ratio as of the study by Zhao et al., both sodium hydroxide and tartrate concentrations were also increased by a factor of 1.28.

So far, copper dewetting problem has still not been resolved, therefore a series of other reaction conditions were altered to improve this. This involved testing the rate in which glyoxylic acid was added to the plating bath, increasing further the complexant concentration and introducing the effect

of bubbling or ultrasound to the solution. However, none of these parameters improved the situation. Finally, the reducing agent was changed to formaldehyde and all the tuned parameters for glyoxylic acid were applied on formaldehyde, as indicated in Table B.3. Here, plating rate was significantly enhanced, complete deposition was achieved in 6 minutes instead of few hours in glyoxylic acid. Bubbling was also observed from the solution which is attributed to the formation of hydrogen. The copper plated hollow fibre also possesses a shinier surface than glyoxylic acid, shown in Figure B.2. Therefore, formaldehyde deemed to be a better reducing agent than glyoxylic acid, in terms of reduction of time and quality of the deposition layer. The higher activity in formaldehyde is due to the presence of the carbonyl group  $\text{-COH}$ , where the carbon-oxygen double bond,  $\text{C=O}$ , is formed by both  $\sigma$  and  $\pi$  orbitals, which can be readily oxidized to form carboxyl  $\text{COOH}$  group [37]. Whereas glyoxylic acid appears to react with sodium hydroxide, altering the pH stability in the plating solution [36]. Next, the fibre was annealed to see if this coverage was enough to achieve a continuous layer. Unfortunately, situation did not improve, copper islands and globules were again observed after annealing at  $900^\circ\text{C}$ .



Figure B.2. Photograph of copper plated YSZ hollow fibre using a) Glyoxylic acid, b) Formaldehyde (1 cm scale)

Based on the investigation so far, complete deposition was achieved after plating prior to annealing. However, there appears to be a consistent problem upon annealing, where the copper deposits dewet and became islands or globules. It was then hypothesised that the annealing condition might be the factor to improve this. The plated fibres obtained using parameters listed in Table B.3 with formaldehyde were annealed at a series of lower temperatures. Finally, at temperature of  $530^\circ\text{C}$ , a continuous copper sacrificial layer was deposited on the YSZ hollow fibre with the absence of copper islands or globules.

Table B.3. Electroless plating condition used

| Compound                               | Concentration mol dm <sup>-3</sup> |
|----------------------------------------|------------------------------------|
| Copper sulphate                        | 0.060                              |
| Potassium sodium tartrate tetrahydrate | 0.150                              |
| Sodium hydroxide                       | 0.320                              |
| Formaldehyde                           | 0.060                              |

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## **Chapter 6: Pristine graphene membranes supported on ceramic hollow fibre prepared via a nickel sacrificial layer assisted CVD approach**

### **Abstract**

Copper dewetting and compaction problems were observed from the graphene hollow fibre membrane prepared via the copper sacrificial layer approach in Chapter 5. Herein, a new sacrificial layer material is proposed using nickel. A dense and continuous nickel sacrificial layer is deposited on the porous YSZ hollow fibre via electroless plating. In comparison to copper, nickel dewetting did not happen during high temperature synthesis, and a high integrity multilayer graphene was obtained from 900 °C chemical vapour deposition. Following the graphene growth, thermal oxygen etching followed by nitric acid etching were performed to successfully remove the nickel layer and post-etching defect-patching treatment was carried out to eliminate any major defects formed during the leaching process. Herein, a continuous ultra-thin graphene layer sitting on YSZ hollow fibre was obtained and confirmed by Raman spectroscopy. The achieved graphene hollow fibre membrane exhibits a methanol flux of 2.4 LMH bar<sup>-1</sup> and a remarkable 98.8 % rose bengal rejection. Compaction problem was not observed like the case with copper, indicating the minimal amount of graphene flakes needed to seal major defects that were present from the leaching process. This study thus demonstrates a big step towards successful engineering of pristine graphene membrane on micro-tubular supports with reasonable performance.

### **6.1 Introduction**

Chapter 5 successfully demonstrated the preparation of graphene hollow fibre membrane via the copper sacrificial layer approach. However, performance results showed low integrity of the prepared membrane, revealing the problem of compaction during pressure-driven applications. High

temperature synthesis is normally required for CVD graphene growth; however, copper dewets on ceramic material when subjected to temperature close to their melting point. To rectify these problems, this Chapter proposes an alternative sacrificial layer material to address the issues raised from the use of copper sacrificial layer.

In this study, nickel was proposed as the sacrificial layer exhibiting a melting point at 1455 °C, which is higher than the melting point of copper at 1085 °C. In this way, higher CVD temperature and longer synthesis time can be implemented on the nickel deposited YSZ hollow fibre without metal dewetting. Like copper, nickel has demonstrated to be a good catalyst for the synthesis of graphene under CVD. Unlike copper, graphene growth on nickel is by a different mechanism. Solubility of carbon is much higher in nickel (~0.9 at. % at 900 °C) [1] than in copper, which is close to negligible at ~0.00048 at. % at 870 °C [2]. Therefore, graphene growth is by the precipitation method since greater concentration of carbon radicals can dissolve into the nickel, and during the rapid cooling stage, precipitate out forming multilayer graphene. Furthermore, due to the higher solubility of carbon in nickel, graphene could be formed above and below the nickel surface, i.e. in between the YSZ surface and the nickel layer, upon rapid cooling. This was demonstrated by Peng et al. and Chen et al., where they found synthesis of graphene in between the insulating substrate and nickel layer, in addition to the top surface of nickel layer [3, 4]. As discovered in Chapter 5, it is important a high integrity graphene layer is obtained during the CVD process, so that the integrity of the graphene layer is less impacted during the etching process. The formation of multilayer graphene on nickel is therefore advantageous, whereby a high integrity graphene layer can be deduced sitting on the YSZ hollow fibre after the removal of the sacrificial layer with better performance.

Electroless plating is again employed to deposit the metal layer on YSZ hollow fibre. Electroless nickel plating has been carried out on hollow fibre geometry but is mainly focused on the applications of solid oxide fuel cells or hydrogen separation membranes [5-7]. Using the knowledge developed, electroless nickel plating condition was studied to meet the needs in obtaining a dense nickel sacrificial

layer on the porous YSZ hollow fibre suitable for graphene synthesis. Following the graphene growth via CVD, a thermal oxygen and nitric acid etching method were employed to remove the sacrificial layer. Finally, defects introduced during the etching method was sealed with graphene flakes, realising the final ultra-thin pristine graphene hollow fibre membrane. A schematic of the graphene hollow fibre membrane synthesis procedure using nickel sacrificial layer is shown in Figure 6.1.

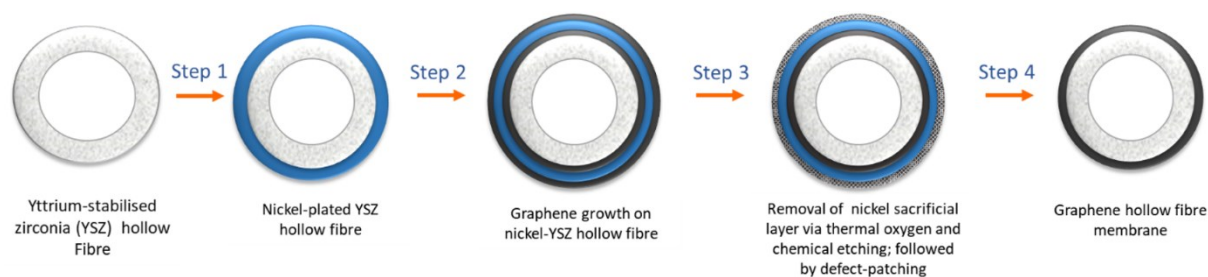


Figure 6.1. Illustration of the preparation procedure for obtaining graphene hollow fibre membrane using nickel

## 6.2 Experimental

### 6.2.1 Electroless nickel plating on YSZ hollow fibre

YSZ hollow fibres were activated and sensitised followed by electroless plating, detailed study in achieving a continuous and dense nickel layer be found in Additional Information C. Summary of the electroless nickel plating compositions investigated is summarised in Table 6.1.

Table 6.1. Composition of electroless nickel plating studied

| Compound             | Concentration mol dm <sup>-3</sup> |
|----------------------|------------------------------------|
| Nickel acetate       | 0.090                              |
| Na <sub>2</sub> EDTA | 0.011-0.0160                       |
| Lactic Acid          | 0.150                              |
| Sodium hydroxide     | 0.188                              |
| Hydrazine            | 1.00-3.30                          |

### 6.2.2 Annealing and CVD graphene growth on Ni-YSZ-HF

The plated nickel-YSZ hollow fibre was annealed at 900 °C under 5 °C min<sup>-1</sup> heating rate, at a concentration of 4:1 He:H<sub>2</sub> ratio for 2 hours. An in-situ chemical vapour deposition (CVD) process was then carried out after the annealing process. Graphene synthesis was conducted at 900 °C under atmospheric pressure with methane as the carbon precursor at 1:1 H<sub>2</sub>:CH<sub>4</sub> concentration for 20 mins. After the CVD process, the fibre was drawn out immediately from the furnace for rapid cooling. Finally, the graphene-nickel-YSZ hollow fibre (G-Ni-YSZ-HF) was obtained.

### 6.2.3 Etching of nickel sacrificial layer and post-etching defect-patching treatment

The intermediate nickel sacrificial layer must be etched to realise the final graphene layer as the selective barrier on YSZ hollow fibre. The graphene-nickel-YSZ-hollow fibre (G-Ni-YSZ-HF) was snapped in half and immersed in 1-8 M nitric acid to leach away the nickel layer, however, due to the chemical inertness of graphene, the graphene acted as a protective coating for the nickel and the nickel was unable to be leached away. Therefore, artificial defects were needed to be introduced on the top graphene layer to achieve this. The aim is to create defects on the outer graphene surface for the chemical etchant to reach the underlying nickel, leaving the bottom graphene layer successfully adhering to the YSZ hollow fibre. Various methods of cotton bud etching, oxygen plasma and thermal oxygen etching were studied followed by chemical etching to remove the sacrificial layer. For the cotton bud method, defects were created on the top graphene layer by rubbing the surface with cotton bud, followed by immersing into 8 M nitric acid. The oxygen plasma method involved placing the G-Ni-YSZ-HF inside an oxygen plasma chamber (Solarus<sup>TM</sup> Advanced Plasma System 950 system) for various time of 30 seconds to 10 mins, followed by etching in 8 M nitric acid. The final thermal oxygen etching involved placing the G-Ni-YSZ-HF inside the furnace at 1000°C under inert environment and feeding in traces of oxygen (1% oxygen in argon cylinder purchased from BOC) into the reactor. A range of 1000:1-1500:1 H<sub>2</sub>:O<sub>2</sub> concentration was used and thermally heated from a range of 180–540 seconds to achieve the artificial defects on the top graphene layer, after this, the fibre was immersed

into 8 M nitric acid for leaching. In order to ensure complete removal of the nickel sacrificial layer, the fibre is normally immersed in nitric acid for more than 1 day. Schematic of the various etching methods is shown in Figure 6.2. Post-etching defect-patching treatment was then carried out to seal any major defects using graphene flakes.

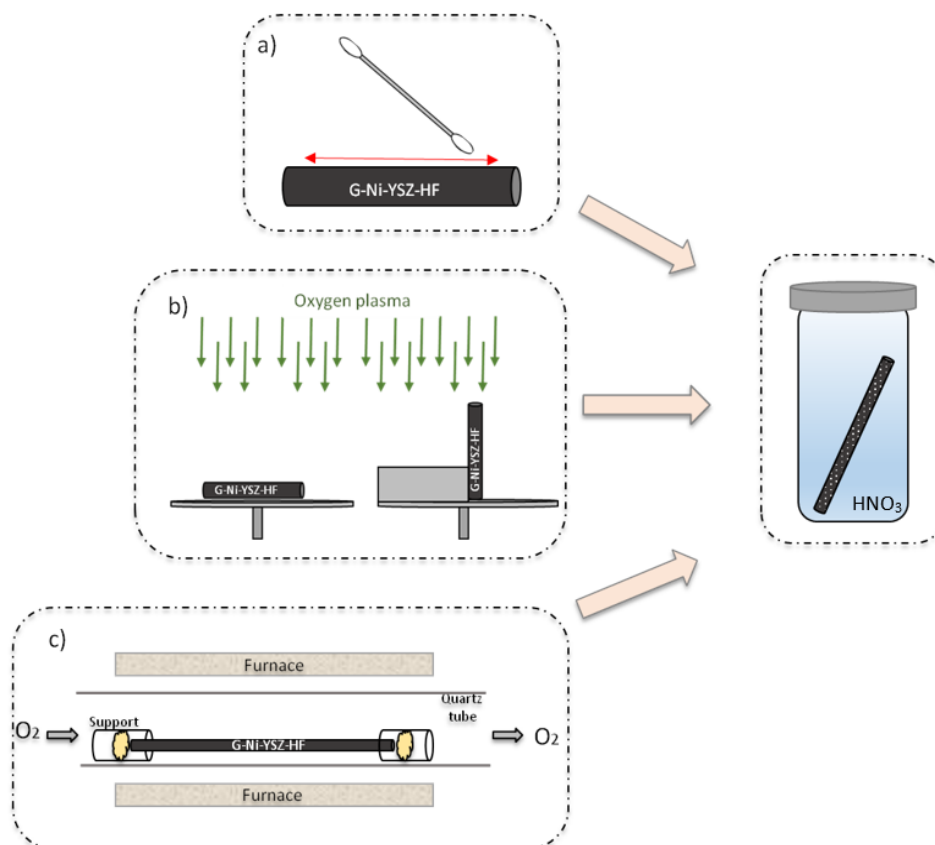


Figure 6.2. Schematic of the various etching methods used to leach away the nickel sacrificial layer, a) cotton bud method; b) oxygen plasma method; c) thermal oxygen method, followed by immersing in 8 M HNO<sub>3</sub>

#### 6.2.4 Characterisation and performance tests

SEM and Raman spectroscopy were used to characterise the hollow fibre membranes. Solvent permeation and rejection tests of the G-YSZ-HF were evaluated using dead-end filtration. The gas-tightness test was conducted in N<sub>2</sub> using a pressure-drop setup made of Swagelok VCR® fittings that has been described in the Chapter 3.7.

## 6.3 Results and discussions

### 6.3.1 Formation of nickel sacrificial layer on YSZ hollow fibre

A dense and high-quality nickel layer is paramount for high quality graphene growth. It is therefore crucial to investigate the effect of various plating conditions. In this case, the plating solution contained nickel acetate as the nickel source, sodium hydroxide as the alkaline source, hydrazine as the reducing agent, EDTA and lactic acid as the complexing agent/stabiliser. Complexing agents are added to prevent the precipitation of nickel salts and prevent the pH of the solution from decreasing too fast. While stabilisers are added to prevent the decomposition of the plating solution [8, 9]. Hydrazine was used as the reducing agent because pure nickel layer is required, and the only oxidation by-products produced are water and nitrogen. The other commonly use reducing agents are sodium hypophosphite and sodium borohydride, however, these lead to alloy deposition of nickel-phosphorous or nickel-boron, which are not desired for the graphene growth [9, 10]. Detailed study in tuning the various parameters, such as hydrazine concentration, EDTA concentration, temperature of the plating bath can be found in Additional Information C.

*Table 6.2. Electroless nickel plating composition*

| Compound             | Concentration mol dm <sup>-3</sup> |
|----------------------|------------------------------------|
| Nickel acetate       | 0.090                              |
| Na <sub>2</sub> EDTA | 0.0160                             |
| Lactic Acid          | 0.150                              |
| Sodium hydroxide     | 0.188                              |
| Hydrazine            | 3.30                               |

The electroless plating condition able to achieve a continuous and dense nickel layer is listed in Table 6.2, operating at 80 °C with hydrazine added periodically throughout a course of 6 hours. SEM images of the plated, annealed, cross-sectional area and gas tightness test of the nickel-YSZ hollow fibre

prepared using the plating condition listed in Table 6.2 are shown in Figure 6.3. The plated surface (Figure 6.3a) consists of closely packed spiked array of crystals. The formation of such spiky crystals maybe attributed to the use of hydrazine as the reducing agent, previous literatures have also reported similar structure using hydrazine as the reductant but not other reductants [11]. One other possible cause could be the coordination effect of the  $N_2H_4 \cdot H_2O$  molecule, which favours anisotropic growth [12]. Furthermore, accompanying the reduction of nickel is the formation of water and nitrogen, the release of nitrogen gas in the plating solution can disturb the nucleation and growth of the nickel crystals. At 80 °C, rapid release of nitrogen results in the growth of nickel nuclei orienting outward, along the path of the released gas, forming spiked array of crystals [13]. The annealed plated surface is shown in Figure 6.3b, after annealing at 900 °C for 2 hour under  $H_2/He$  atmosphere, the nickel atoms migrate in the crystal lattice, resulting in the decrease of dislocations and formation of dense and smoother nickel grain boundaries, which are more ideal for graphene growth. Furthermore, any impurities and oxides are removed by reducing in hydrogen under high temperature annealing. The thickness of the nickel layer obtained is shown in Figure 6.3c, with the nickel sacrificial layer

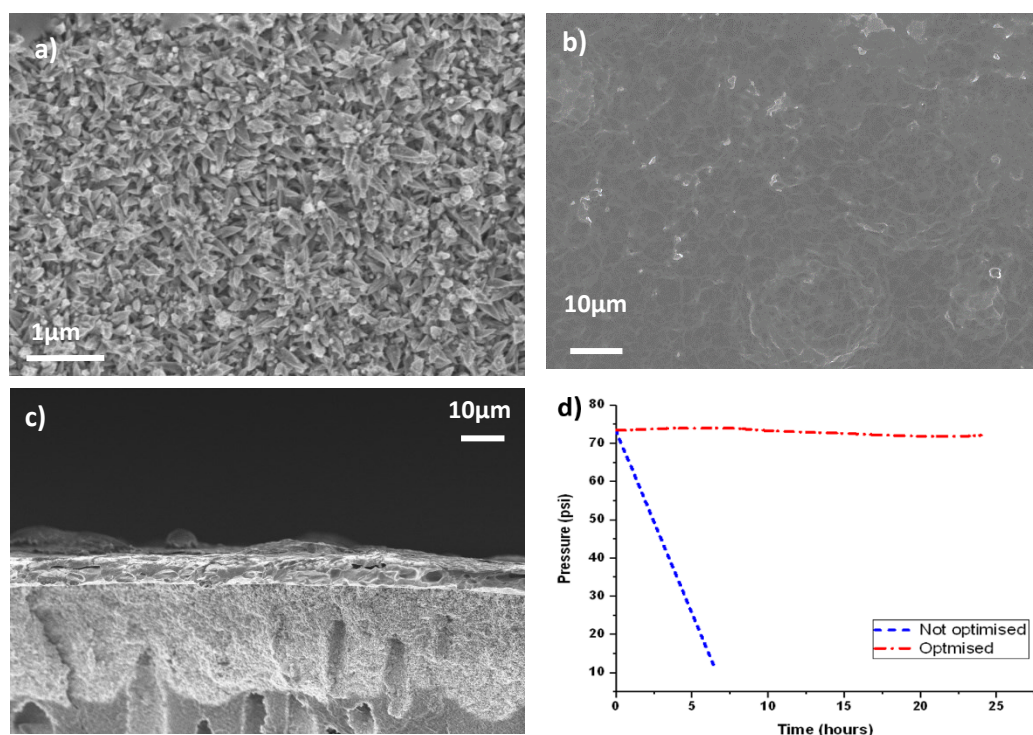


Figure 6.3. SEM images of a) plated nickel surface on YSZ hollow fibre; b) annealed nickel surface on YSZ hollow fibre; c) cross-sectional area of the annealed nickel on YSZ hollow fibre; d) gas tightness test

exhibiting a thickness of 7  $\mu\text{m}$ . In comparison to copper, nickel dewetting did not occur at annealing temperature of 900  $^{\circ}\text{C}$  due to the higher melting point of nickel. A dense and continuous nickel sacrificial layer was obtained and verified from the gas tightness test shown in Figure 6.3d, where a dense and non-dense plated fibres were compared to show the quality of the nickel sacrificial layer. For a dense nickel fibre, the chamber pressure remained stable after 1 day (Figure 6.3d), displaying  $\text{N}_2$  permeance of  $6.16 \times 10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ . According to the past literature [14], membrane is considered gas-tight when the  $\text{N}_2$  permeance is at the level of  $10^{-10} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$ , thus this indicates the absence of nickel dewetting, pinholes or defects in the current annealed nickel-plated YSZ hollow fibre. Whereas in the non-dense sample, the pressure decreased rapidly in the first 5 hours, exhibiting  $\text{N}_2$  permeance above  $4.40 \times 10^{-8} \text{ mol m}^{-2} \text{ s}^{-1} \text{ Pa}^{-1}$  indicating the low-quality nickel layer formed.

### 6.3.2 Graphene synthesis on Ni-YSZ-HF

As discovered above, nickel dewetting did not happen at 900  $^{\circ}\text{C}$ , therefore an in-situ CVD process can be carried out to realise graphene formation at 900  $^{\circ}\text{C}$ . Methane was fed into the furnace at 1:1  $\text{H}_2:\text{CH}_4$  ratio under atmospheric pressure, and after 20 mins reaction time, the fibre was rapidly drawn out of the furnace to allow rapid cooling to take place. Upon rapid cooling, the dissolved carbon atoms precipitate out to the surfaces forming graphene layers on the top and bottom of the nickel layer; solubility of carbon in Ni decreases at decreasing temperature [15]. A photograph of the graphene-nickel-YSZ hollow fibre (G-Ni-YSZ-HF) is shown in the inset of Figure 6.4a. The surface of the G-Ni-YSZ-HF exhibits a shiny outer surface indicating the formation of dense and high integrity graphene-nickel layer. Clear graphene grain boundaries can be observed from Figure 6.4a. Furthermore, good adhesion of the graphene-nickel on the hollow fibre is observed and again no nickel dewetting is seen after CVD growth at 900  $^{\circ}\text{C}$ . Raman spectroscopy was used to characterise the quality of graphene at 532 nm excitation. Figure 6.4b-d confirm the formation of multilayer graphene with the presence of G peak at  $\sim 1580 \text{ cm}^{-1}$  and 2D peak at  $2670 \text{ cm}^{-1}$ . The intensity ratio of 2D to G ratio ( $I_{2D/G}$ ) concentrates at around 0.5 highlighting the formation of multilayer graphene. Revealed by the Raman mapping in Figure 6.4c,

a continuous and high-quality graphene was obtained, demonstrated by the homogenous colour shading of  $I_{2D/G}$ . The black and yellow pixels on the mapping are caused by the roughness of the graphene-nickel layer, where the laser was not able to focus and the 2D and G bands were not able to be detected, nevertheless, the results show a homogenous coverage of high integrity graphene on the nickel-YSZ hollow fibre.

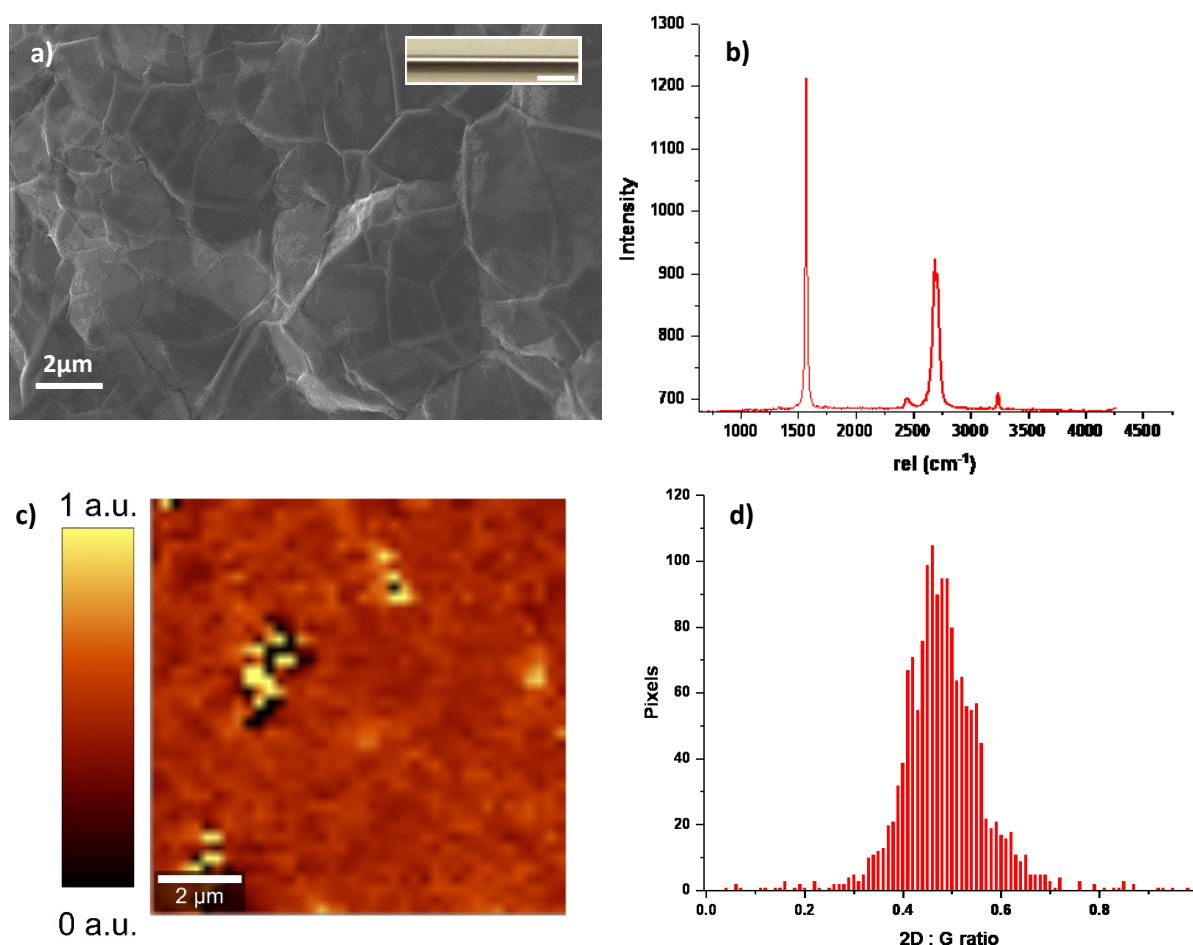


Figure 6.4. a) SEM image of G-Ni-YSZ hollow fibre surface (inset-photograph of G-Ni-YSZ, 1 cm scale); b) Raman spectra; c) Raman mapping of 2D:G ratio; d) 2D:G ratio distribution

### 6.3.3 Etching of nickel sacrificial layer

In order to achieve pristine graphene hollow fibre membrane, the dense nickel sacrificial layer must be removed for graphene to act as the selective layer supported on YSZ hollow fibre. At first, the fibre was snapped into 2 pieces, immersed in 8 M nitric acid and left to allow the etchant solution to

penetrate through the snapped edges of the G-Ni-YSZ-HF and dissolve the nickel atoms. After one week of etching, the nickel layer did not etch away. The graphene “protective coating” deemed too strong and none of the nickel could be etched. This behaviour also indicates the formation of graphene in between the YSZ surface and the nickel layer, if this graphene layer was not present, the etchant solution would have diffused into the porous YSZ support and etched the nickel layer from underneath. Artificial defects therefore need to be created on the outer graphene layer, followed by chemical etchant (8 M nitric acid) to leach away the nickel sacrificial layer, leaving the bottom graphene layer supported on YSZ as the selective layer. Three methods were used to create artificial defects on the top graphene layer before immersing into the chemical etchant.

In the first method, defects were created by rubbing the G-Ni-YSZ-HF surface with cotton bud, 8 M nitric acid was then used to etch away the nickel layer for a week. However, this method was not very promising, only some areas of the nickel were etched away because of the uneven defects created. Therefore, uniform defects must be created in order to achieve uniform removal of the nickel sacrificial layer.

This led to the use of oxygen plasma system to generate uniform defects, followed by the same chemical etching method. However, other problems arose, whether the hollow fibre was placed vertically or horizontally inside the plasma system, only the top end of the fibre was exposed to the plasma source ejected from the top. Therefore, uniform defects could not be created, and this method was also not deployed.

From the study by Agrawal et al., they have demonstrated the technique of etching pores in graphene by introducing oxygen into the CVD reactor [16]. The process is hypothesised to consists of two steps: pore nucleation, where the first carbon atom is extracted from the lattice, followed by growth, where subsequent carbon atoms are removed at the edges around the initial vacancy [16]. Furthermore, the presence of oxygen can also oxidises the graphene layer and disrupts the carbon-to-carbon bonds [17]. New functional groups of C-O and C=O bonds are formed which will enable easy defect generation of

the outer graphene layer. A similar technique was employed for the current G-Ni-YSZ-HF, the fibre was placed inside a 1000 °C reactor where traces of oxygen was fed into the reactor under vacuum condition at various H<sub>2</sub>:O<sub>2</sub> ratios for different period of time. At 1000:1 H<sub>2</sub>:O<sub>2</sub> ratio, too much defects were formed, and the leaching of nickel sacrificial layer using nitric acid became too rapid, which damaged both the top and bottom graphene layers. The ratio was thus increased to 1500:1 H<sub>2</sub>:O<sub>2</sub> and heated for 180 seconds, however, the nickel layer was unable to be leached with 8 M nitric acid. The thermal etching time was thus increased to 540 seconds. Here, the nickel layer was successfully removed, and the presence of continuous graphene layer on YSZ hollow fibre was confirmed by Raman spectroscopy (Figure 6.5). Therefore, a 1500:1 H<sub>2</sub>:O<sub>2</sub> was implemented and thermally heated for 540 seconds, followed by leaching in 8 M nitric acid to achieve the complete removal of the nickel sacrificial layer. Figure 6.5a show the graphene layer supported on YSZ hollow fibre with the nickel sacrificial layer completely removed. The morphology of YSZ hollow fibre support is clearly seen, indicating the electronic-transparent property of the obtained graphene layer. Raman spectroscopy was used to characterise the quality of the graphene layer. Figure 6.5b indicates the presence of graphene crystal lattice with the presence of 2D and G peaks. Multilayer graphene is still present as observed from the 2D to G ratios, which concentrate around 0.4. A homogenous and continuous high surface-area-to-volume ratio multilayer graphene was thus obtained and supported on YSZ hollow fibre, indicated by the uniform colour Raman mapping of the I<sub>2D</sub>/G.

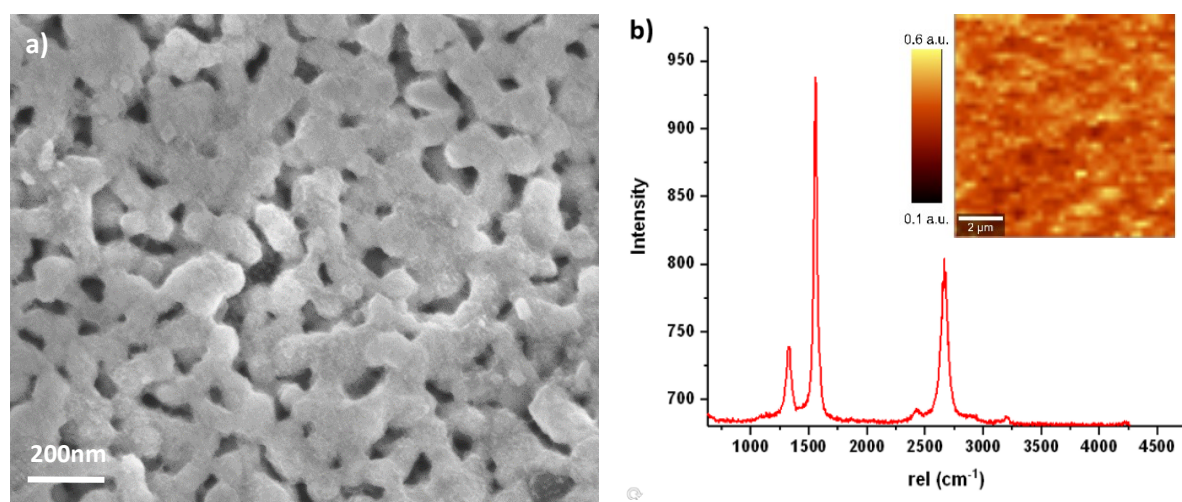


Figure 6.5. a) SEM image of G-YSZ-HF; b) Raman spectra (inset- Raman mapping of 2D:G ratio)

### 6.3.4 Post-etching defect-patching treatment

From the Raman spectra indicated by Figure 6.5b, a D peak is also found indicating the presence of defects on the graphene layer. One possible cause of these defects is due to the high temperature thermal oxygen etching and the acid leaching processes. Like Chapter 5, the G-YSZ-HF underwent post-treatment using graphene flakes to minimise the non-selective effect from these defects. As revealed in Figure 6.6a, the graphene layer supported on YSZ hollow fibre also exhibits an ultra-thin thickness even after defects were covered by graphene flakes. The underlying YSZ morphology can still be clearly observed due to the transparency of the graphene layer (Figure 6.6b).

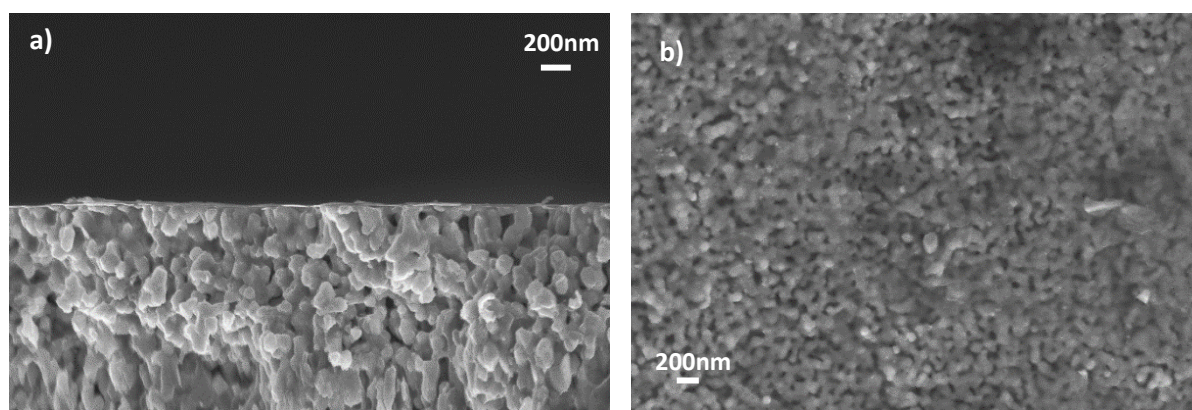


Figure 6.6. SEM images of a&b) Cross sectional view & surface of G-YSZ-HF post graphene flakes treatment

### 6.3.5 Performance of graphene membrane supported on YSZ hollow fibre

Similar to Chapter 5, the narrow space between the flakes and the graphene layer serve as intrinsic pores without the need of post pore-generation, allowing molecules to permeate through the membrane. An average methanol flux of  $2.4 \text{ LMH bar}^{-1}$  was achieved for this study. Unlike the case for copper, compaction was not observed when nickel sacrificial layer was employed. This can be explained by the existence of a higher integrity continuous graphene layer obtained, where less defects were present and needed to be sealed by graphene flakes. Hence, compaction was not observed. PEG (400-35,000 MW), PS (1300 MW) and dye rejection tests were carried out on the G-YSZ-HF. No rejection was obtained for PEG and PS, but a remarkable 98.8 % rejection was obtained with rose bengal in methanol. For the flake-patched G-YSZ-HF, the flow passage is unlikely to be the

inter-space between two perfectly flat graphene surfaces. If that was the case, the inter-space should be same as that in graphite, and the space would be too narrow for PEG and PS to pass through. In contrast, as mentioned in Chapter 5, both the CVD graphene and the graphene flakes tend to have corrugated surfaces caused by wrinkles, ripples and crumples [18]; when they are in contact, flow passages of nanometre size would be formed around the corrugations which would allow large molecules to permeate, which explains why the rejection rate was low for neutral PEG and PS molecules. On the other hand, rose bengal is negatively charged and it can be repelled by the charge associated with the edges and defects in graphene. Thus, the membrane showed the rejection of dye molecules but not polymer chains. The G-YSZ-HF was further characterised after the rejection tests. SEM and Raman spectroscopy (Figure 6.7) indicate the dye molecules did not adsorb on the graphene surface and a good integrity graphene layer was maintained even after high pressure testing at 8 bar. The presence of 2D and G peaks are still very apparent; with the intensity ratio and Raman mapping indicating the existence of homogeneous and continuous multilayer graphene supported on YSZ hollow fibre.

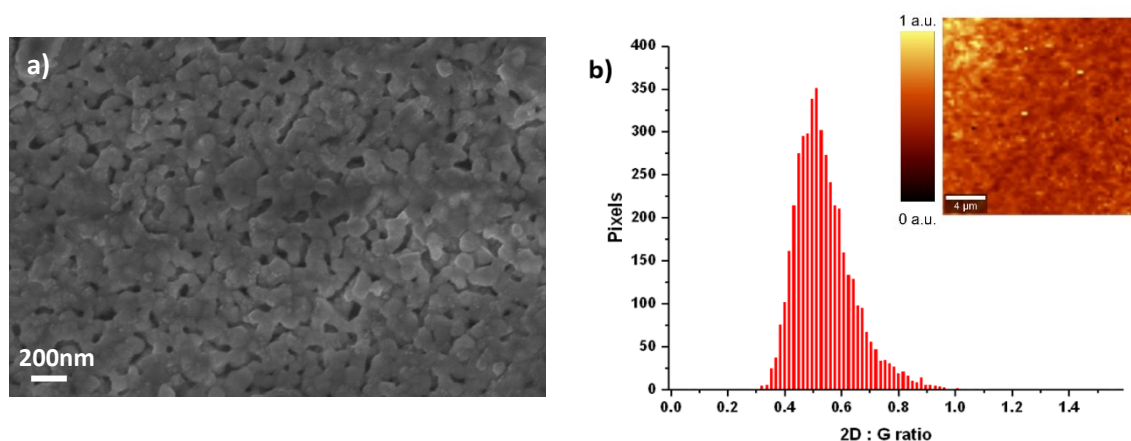


Figure 6.7. a) SEM image of G-YSZ-HF after rejection tests; b) 2D:G ratio distribution (inset- Raman mapping of 2D:G ratio) of G-YSZ-HF after rejection tests

## 6.4 Conclusion

In this chapter, nickel was proposed as the sacrificial layer for the preparation of graphene hollow fibre membrane. Unlike the case with copper, nickel dewetting was not observed during high

temperature synthesis and a continuous and dense nickel-plated hollow fibre was achieved via electroless plating. An in-situ chemical vapour deposition was carried out at 900 °C on the nickel-YSZ hollow fibre and achieved a high integrity multilayer graphene. Upon thermal oxygen and chemical etching, nickel sacrificial layer was successfully removed, leaving the pristine graphene layer supported on YSZ hollow fibre. Post-treatment was carried out using graphene flakes to cover large defects formed from the etching process. Finally, the ultra-thin pristine graphene membrane supported on YSZ hollow fibre was prepared, exhibiting a methanol flux of 2.4 LMH bar<sup>-1</sup> and a remarkable 98.8 % rose bengal rejection. Though the filtration performance still needs to be improved in future developments, this study presents a step towards successful synthesis of graphene membrane supported on micro-tubular supports with reasonable performance.

### **Note:**

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## **Additional Information C**

### **1. Study of electroless nickel plating condition**

The composition of the electroless nickel plating solution studied is shown in Table C.1 and various parameters, such as hydrazine concentration, EDTA concentration, temperature of the plating bath were investigated to achieve a dense and continuous nickel layer.

*Table C.1. Composition of electroless nickel plating studied*

| <b>Compound</b>            | <b>Concentration mol dm<sup>-3</sup></b> |
|----------------------------|------------------------------------------|
| <b>Nickel acetate</b>      | 0.090                                    |
| <b>Na<sub>2</sub>.EDTA</b> | 0.011-0.0160                             |
| <b>Lactic Acid</b>         | 0.150                                    |
| <b>Sodium hydroxide</b>    | 0.188                                    |
| <b>Hydrazine</b>           | 1.00-3.30                                |

Firstly, the effect of adding hydrazine all at once or periodically over the course of 6 hours were investigated and the concentration of hydrazine was varied from 1 M to 3.3 M. The rest of the parameters were kept constant as shown in Table C.1, with EDTA concentration at 0.016 mol dm<sup>-3</sup> and the plating temperature operating at 80 °C. After the fibre was plated, it was then transferred to high temperature furnace and was annealed at 900 °C under inert environment to remove unwanted impurities and oxides and to achieve a continuous smooth nickel layer for graphene growth.

Two experiments both operating at 3.3 M hydrazine concentration were tested first, hydrazine was added all at once at the start of one experiment, and in another it was added periodically over the course of 6 hours. Results showed when hydrazine was added all at once, the nickel deposition happened too quickly and a non-uniform layer was formed, furthermore, the rapid deposition also resulted in bad nickel adhesion to the YSZ support. Therefore, it was desired to add hydrazine gradually to obtain a good adhesion and uniform nickel layer.

Next, the effects of varying hydrazine concentration were investigated. At 1 M, 2 M and 2.8 M hydrazine concentration, the annealed nickel surface showed the presence of pinholes and porous surface, similar to the SEM image on Figure C.1a. Increasing the concentration to 3.3 M, the nickel surface finally became dense indicating that the annealed nickel layer was thick enough to cover the YSZ support (Figure C.1b). A dense and continuous nickel topology is crucial in obtaining a high-quality continuous layer; thus 3.3 M hydrazine concentration was selected.

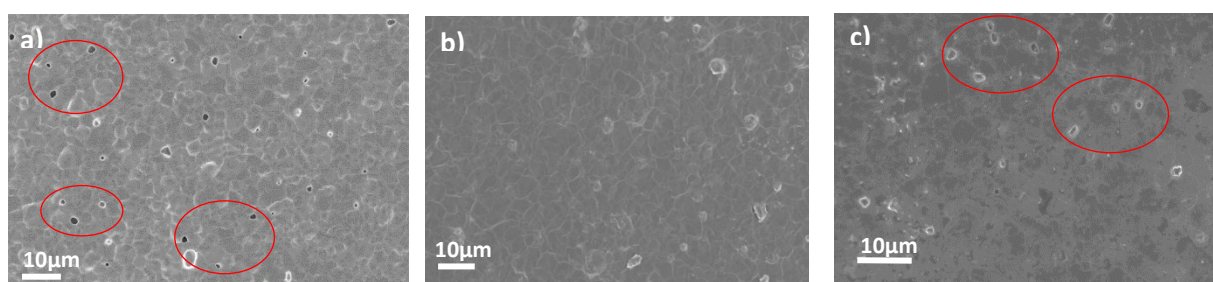


*Figure C.1. SEM images of annealed nickel surface a) 1M hydrazine at 80°C (red circles indicating the pinholes); b) 3.3 M hydrazine at 80 °C; c) 3.3 M hydrazine at 70°C (red circles indicating the pinholes)*

Afterwards, the plating temperature was explored and in the past studies of electroless nickel plating, plating temperature of 60-90 °C have been investigated [10, 19]. At low temperature, deposition rate is slow because of the endothermic reduction process, however, the plating bath is more controllable due to the slower reaction. A compromise was reached to achieve a reasonable deposition rate, meanwhile, preventing the plating solution from instability and being uncontrollable. At 70 °C, results showed that the deposition was not sufficient to cover the entire YSZ surface and pinholes were observed on the surface, shown in Figure C.1c. Whereas at 80 °C the temperature was high enough to achieve sufficient nucleation and growth of the nickel crystals, full coverage was obtained on the YSZ support (Figure C.1b). Higher temperature of 90 °C was not desired because the deposition rate can become too rapid and uncontrollable, and a non-uniform layer will form on the support surface [19]. The final parameter investigated was the concentration of complexing agent. As mentioned earlier, complexing agent is used to control the amount of free electron (nickel) and retard the precipitation of nickel plating solution [8, 9]. Concentrations of 0.011 and 0.016 M were studied, with the rest parameters kept the same as Table C.1, 3.3 M hydrazine concentration was used operating at 80 °C.

At decreased EDTA concentration, full coverage of nickel layer was not achieved (Figure C.2a), insufficient complexing agent was present to prevent the fluctuation of pH in the plating solution, resulting in decreasing of pH and pinholes forming on the surface. Gas tightness test was conducted to test the densification of the 2 fibres (Figure C.2b). The graph shows the pressure of the gas-tightness test vessel with respect to time, at 0.011 M EDTA concentration the pressure of the vessel decreased rapidly in the first 5 hours, indicating the presence of pinholes on the nickel layer, while the pressure remained stable after 1 day for the fibre plated with 0.016 M EDTA concentration.

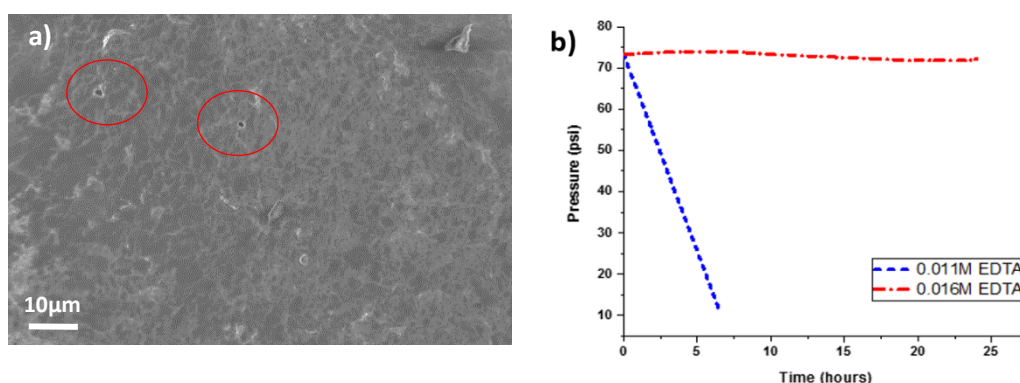


Figure C.2. a) SEM images of annealed nickel surface at 0.011M EDTA (red circles indicating the pinholes); b) gas tightness test

Hereafter, the electroless plating condition able to achieve a dense and continuous nickel layer is listed in Table C.2, operating at 80 °C using plating conditions with hydrazine added periodically throughout a course of 6 hours.

Table C.2. Electroless nickel plating condition used

| Compound              | Concentration mol dm <sup>-3</sup> |
|-----------------------|------------------------------------|
| Nickel acetate        | 0.090                              |
| Na <sub>2</sub> .EDTA | 0.0160                             |
| Lactic Acid           | 0.150                              |
| Sodium hydroxide      | 0.188                              |
| Hydrazine             | 3.30                               |

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## Chapter 7: Conclusion and future work

### 7.1 Overall conclusion

The main research objectives of this thesis are on the fabrication and applications of graphene hollow fibre membranes. Graphene-nickel hollow fibre membrane and pristine graphene hollow fibre membranes were successfully prepared and their application in liquid separation and acting as a protective coating were successfully demonstrated.

In Chapter 4, porous nickel hollow fibre membrane precursors were first prepared using the phase-inversion process. An in-situ single-stage sintering-CVD process was then carried out using methane as the carbon precursor at 900 °C. Graphene was successfully fabricated on the nickel hollow fibre surface, serving as a protective barrier for the nickel to enhance its chemical stability. High-quality multilayer graphene was formed confirmed by Raman spectroscopy and SEM. The prepared graphene-nickel hollow fibre membrane (G-Ni-HF) was exposed to concentrated nitric acid. Corrosion tests showed that the non-protected nickel hollow fibre membrane dissolved within a few hours, whereas the G-Ni-HF membrane remained intact. The prepared membrane featuring narrow pore size distribution, good chemical and mechanical robustness can be used in a variety of applications that involve harsh conditions. The G-Ni-HF membrane was then used in membrane emulsification to prepare TiO<sub>2</sub> microspheres, where a highly acidic condition is essential. Hierarchical asymmetric egg-white structure TiO<sub>2</sub> was prepared, which is distinct from the symmetric microspheres obtained by the normal emulsification method. The asymmetric TiO<sub>2</sub> microspheres also exhibit substantially improved catalytic activity to CO oxidation after impregnating with palladium catalyst.

In Chapter 5&6, another application of graphene was explored. Here, pristine graphene membranes supported on ceramic hollow fibre were prepared, which we believe to be the first-of-its-kind and its performance in liquid separation was investigated. A metal sacrificial layer approach was adopted to assist the synthesis of graphene by depositing a metallic layer on the ceramic hollow fibre using electroless plating.

In chapter 5, copper was first selected as the sacrificial layer. However, copper dewetting was observed during high temperature exposure, therefore annealing temperature was tuned to 530 °C to achieve a continuous and shiny annealed copper layer for graphene synthesis. To mitigate the dewetting behaviour, a short-duration high-temperature CVD approach was implemented, and graphene was successfully synthesised on the hollow fibre. The copper sacrificial layer was then etched in 0.1 M ferric chloride, leaving the pristine graphene layer supported on YSZ hollow fibre. Post-etching defect-patching treatment was then carried out to seal any large defects formed during the leaching process using graphene flakes. Hereafter, an ultra-thin pristine graphene membrane supported on YSZ hollow fibre was prepared. Solvent permeation was carried out; however, compaction problem was observed. The permeation flux declined after 1-hour testing. This compaction problem was caused by the use of copper, where the short-duration high temperature synthesis hindered good-quality graphene growth. Therefore, large amounts of defects were introduced, and a significant amount of graphene flakes were needed to patch the defects, resulting in the compaction problem. Therefore, alternative metal sacrificial layer was proposed. A good sacrificial layer must not dewet during high temperature synthesis and act as a good-quality metal substrate for CVD graphene growth.

This leads to the aim of chapter 6. Here, pristine graphene hollow fibre membrane was successfully prepared using nickel as the sacrificial layer. Here, nickel dewetting was not observed and following the annealing of nickel plated YSZ hollow fibre, a dense and continuous gas-tight film was formed, which is suitable for high-quality CVD graphene synthesis. Multilayer graphene was synthesised, and the nickel sacrificial layer was etched using thermal oxygen and chemical etching. Finally, the pristine graphene supported on YSZ hollow fibre was realised. Here, post-treatment was also carried out to mitigate the non-selective behaviour of the defects using graphene flakes in NMP. Due to the higher quality graphene growth, minimal amount of graphene flakes was required to patch the defect formed during the CVD and etching process, therefore compaction problem was no longer observed. The successfully prepared graphene hollow fibre membrane exhibits a methanol flux of 2.4 LMH bar<sup>-1</sup> and

a remarkable 98.8 % rose bengal rejection. This study thus presents the successful engineering of graphene membrane supported on micro-tubular supports with reasonable performance.

## **7.2 Future work**

### **7.2.1 Graphene protected porous nickel hollow fibre membranes**

Graphene acts as a protective layer for the nickel hollow fibre membrane. The protection layer can be further enhanced by growing less polycrystalline graphene. Generally, intrinsic defects are formed near grain boundaries [1], these areas are susceptible to corrosion. Ideally, synthesising large area of single crystal graphene is mostly desired [2-4], this reduces areas that are prone to external corrosion or damage. Furthermore, the employment of this graphene protected nickel hollow fibre in other application can be explored, for example, in the field of micro-membrane reactors or heat-exchangers [5]. This is especially useful for reactions which involve harsh conditions and rapid heat transfer, thus minimizing hot spot and runaway reaction making the reaction more inherently safe.

### **7.2.2 Pristine graphene hollow fibre membranes**

#### Controlled pore generation on hollow fibre geometry

Currently, reasonable permeation and rejection results were achieved with the obtained membrane. However, further flux enhancement can be realised if controlled pore generation can be carried out on hollow fibre geometry. The use of ion bombardment, oxidative etching and many pore generating processes are limited to planar surfaces. Nucleation of controlled sized pore on hollow fibre geometry is not widely explored. This should be further studied and if controlled pore generation is carried out on hollow fibre membrane, the ultimate permeation can be achieved. Agrawal et al. demonstrated the use of  $O_2$  to induce pores on graphene using controlled pressure CVD, however, further investigation is needed to precisely control the pore size and pore density formation on the graphene [6].

### Reducing number of graphene layers and minimise defects during etching

So far, multilayer graphene was synthesised on the graphene hollow fibre membrane. Higher permeation flux can be achieved if the number of graphene layers is reduced. This can be further explored by investigating the effect of carbon precursor, growth time, pressure and temperature during CVD. At the moment, graphene flakes are used to patch the defects caused from either CVD or etching. Therefore, further improvements can be made on the quality of graphene obtained from CVD and exploring ways in which defects can be minimised during the metal leaching process. By removing the needs of defect patching treatment and if controlled pore generation can be achieved, a high-performance graphene hollow fibre membrane with precise molecular cut off and ultimate permeation can be obtained.

### Scalability

At the moment, performance result is carried out on single graphene hollow fibre membrane. Greater number of graphene hollow fibre membranes can be fabricated and assembled into membrane modules for further large-scale operation and testing. For next stage of commercialisation, a lab-scale demonstration plant can be implemented to evaluate the applicability of the membrane modules in real applications.

### Other applications

Currently, the prepared graphene hollow fibre membrane is tested for liquid separation only. By developing more precisely pore controlled graphene layer, the membrane can potentially be used for gas separation. The hollow fibre geometry also offers high surface-area-to-volume-ratio which can further improve the permeability. In addition, the whole-inorganic nature of the graphene hollow fibre membrane can also be used in high-temperature applications, such as membrane reactors, where catalysts can be deposited on the graphene surface and work at high temperature.

### Other synthesis approach

Sacrificial layer assisted CVD approach was used to prepare the graphene hollow fibre membrane. This method involved electroless plating on YSZ ceramic hollow fibre, followed by annealing and CVD. Other approach in which graphene layer can be synthesised enclosing hollow fibre support can be explored. Furthermore, if electroless plating is employed, other hollow fibre substrates, except YSZ can be investigated to see if similar procedures can be carried out more effectively.

### Further liquid separation performance testing

At the moment, permeation and rejection results were carried out on dead-end filtration mode. A crossflow filtration set-up can be implemented to test the performance and rejection results. One of the main challenges observed from the performance testing was finding the right sealant material that is chemical and solvent resistant. If a better sealant material can be obtained, long-term performance test can be carried out looking into long-term stability. Further solvent permeation and dye rejection tests can be carried out to explore the effectiveness of this obtained graphene hollow fibre membrane.

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## List of Publications

1. Y. Chi, J.Y. Chong, B. Wang, K. Li, Pristine graphene membranes supported on ceramic hollow fibre prepared via a sacrificial layer assisted CVD approach. *Journal of Membrane Science*, 595 (2020) 117479.
2. Y. Chi, T. Li, J.Y. Chong, B. Wang, K. Li, Graphene-protected nickel hollow fibre membrane and its application in the production of high-performance catalysts. *Journal of Membrane Science*, (2019) 117617.
3. Y. Chi, J.Y. Chong, B. Wang, K. Li, Pristine graphene membranes supported on ceramic hollow fibre prepared via the electroless copper plated sacrificial layer approach. *In preparation*.
4. Y. Chi, T. Li, B. Wang, Z. Wu, K. Li, Morphology, performance and stability of multi-bore capillary  $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  oxygen transport membranes. *Journal of Membrane Science*, 529 (2017) 224-233.

## List of Conference Presentations

1. Y. Chi, J.Y. Chong, B. Wang, K. Li, Chemical Vapour Deposition of Graphene Protective Layer on Nickel Hollow Fibre Membranes. 14th International Conference on Inorganic Membranes, Atlanta, US, July 2016. (Oral)
2. Y. Chi, J.Y. Chong, B. Wang, K. Li, Pristine graphene membranes supported on ceramic hollow fibre prepared via a sacrificial layer approach. 15th International Conference on Inorganic Membranes, Dresden, Germany, June 2018. (Oral)
3. Y. Chi, J.Y. Chong, B. Wang, K. Li, Functionalisation of graphene with hollow fibre membranes. Euromembrane 2018, Valencia, Spain, July 2018. (Oral)

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|-------|--------------|-------------------------------------------------------------------------------------------------------------------------------------|-------------------------------|----------------------------|----------------------|------------------------|
| 17    | Figure       | Assessing biocompatibility of graphene oxide-based nanocarriers:<br>A review                                                        | Journal of Controlled Release | Elsevier                   | 22/09/2019           | 4674120788876          |
| 19    | Figure       | A roadmap for graphene                                                                                                              | Nature                        | Springer Nature            | 22/09/2019           | 4674150376622          |
| 21    | Figure       | Review of CVD Synthesis of Graphene                                                                                                 | Chemical Vapor Deposition     | John Wiley Sons            | 22/09/2019           | 4674160825685          |
| 24    | Figure       | Rapid growth of single-layer graphene on the insulating substrates by thermal CVD                                                   | Applied Surface Science       | Elsevier                   | 22/09/2019           | 4674190695917          |
| 31    | Figure       | Multilayer graphene for long-term corrosion protection of stainless-steel bipolar plates for polymer electrolyte membrane fuel cell | Journal of Power Sources      | Elsevier                   | 22/09/2019           | 4674240414424          |
| 32    | Figure       | Environmental applications of graphene-based nanomaterials                                                                          | Chemical Society Reviews      | Royal Society of Chemistry | 22/09/2019           | 4674301302116          |
| 36    | Figure       | Effective characterization of polymer residues on two-dimensional materials by Raman spectroscopy                                   | Nanotechnology                | IOP Publishing             | 27/09/2019           | 4676750048533          |
| 37    | Figure       | Water desalination using nanoporous single-layer graphene                                                                           | Nature Nanotechnology         | Springer Nature            | 22/09/2019           | 4674301414290          |
| 44    | Figure       | Graphene Oxide, Highly Reduced Graphene Oxide, and Graphene: Versatile Building Blocks for Carbon-Based Materials                   | Small                         | John Wiley Sons            | 22/09/2019           | 4674340860897          |