Molecular sorption on carbon-based porous structures: a study on water harvesting and carbon dioxide capture

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A thesis presented for the degree of
Doctor of Philosophy
of
University College London

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September 2020
Declaration

‘I, Yue Lu, confirm that the work presented in this thesis is my own. Where information has been derived from other sources, I confirm that this has been indicated in the thesis.’
Acknowledgement

First of all, I would like to express my deepest gratitude to my initial principle supervisor Prof. Zhengxiao Guo, for his valuable guidance and support on my research project. I wish him all the best for his new position at Hong Kong University. I would also like to thank my current supervisor Prof. Gopinathan Sankar for his attentive support during my final year of Ph.D study. I would like to express my very great appreciation to Dr. Srinivas Gadepelli for his valuable and constructive suggestions during the development of this research work and generous sharing of experimental techniques. I have also received a lot of support from my colleagues Dr. Tingting Zhao, Dr. Yuchen Yang, Dr. Zhuangnan Li, Dr. Yudao Qin, Juntao Li, Jian Guo, Yuting Yao, Juhun Shin and Bowen Guan. I value their kind support in lab work and appreciate them for making Ph.D. life more enjoyable. I would also like to extend my thanks to Dr. Steve Firth for technical support on sample imaging. Special thanks to Prof. Brian Derby and Prof. Julian Evans for reviewing my thesis and examine my viva. Their insightful suggestions and comments deepened my understanding of the research and improved the quality of my thesis from single word error to better structure coherent.

Last but not least, I would like to send my love to my parents and my husband. They respect my every single decision, selflessly encouraging me to keep exploring and accompany me through all the hard times. This journey would not have been possible without them.
Abstract

Carbon (CO$_2$) capture using regenerable sorbents is an effective means of mitigating green-house gas emission to the environment. The first-generation sorbents, based on liquid amines, suffer from instability, toxicity and high-energy penalty for regeneration. Solid sorbents, e.g. based on porous silica or active carbon, offer the potential of long cyclability and low cost. However, the sorption capacity is limited due to low surface area and pore volume, particularly if only physisorption mechanism dominates. The challenge and main aim of this study is to identify an effective porous carbon-based solid sorbent that can possess high capacity and low regeneration energy (hence cost) penalty.

The structures should offer enhanced physisorption (e.g. van der Waals binding at slit pores, with a binding energy $\sim$10-20 kJ mol$^{-1}$) and moderate chemisorption (e.g. binding at graphene edges, point defects or carbon-supported amine-groups, with a binding energy $\sim$20-50 kJ mol$^{-1}$) so that adsorption and desorption “window” for CO$_2$ can be narrow and at relatively low temperature. The porous structure must show high specific surface area and well-connected pores, so that the capacity can be maximised. To achieve such goals, the project first studied graphene oxide (GO) with various degrees of oxidation, ranging from $<$5 at% to $>$30 at% oxygen content, to enhance surface area and defect density; secondly, highly hierarchical porous graphene networks were derived through GO via moderate temperature thermal shock (300 °C), thermal annealing (600 °C) and/or KOH activation, to promote micropores and porosity hierarchy; and finally, for comparison and porosity improvement, another type of porous carbon structures were derived from carbonised metal-organic frameworks (MOFs), namely MOF-5 and MOF-74.

The chemical and structural properties of synthesized materials were characterised by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), transmission electron microscopy (TEM), N$_2$ adsorption-desorption isotherms (the BET method) and Raman spectroscopy. Sorption capacity and kinetics were
assessed by CO\textsubscript{2} adsorption isotherms, thermogravimetric-differential scanning calorimetry (TG-DSC) and in-house water saturation apparatus.

GO demonstrated a stacked layered structure with oxygenated functional groups such as hydroxyl, epoxy and carbonyl groups on its basal planes and edges, resulting in a hybrid structure comprising a mixture of sp\textsuperscript{2} and sp\textsuperscript{3} hybridized carbon atoms. GO is hydrophilic due to the presence of the oxygenated functional groups and the laminated structure can allow slow water diffusion into the layers. As water exist in practical cases of CO\textsubscript{2} capture, the sorption of water was studied separately and together with CO\textsubscript{2}.

From the study of highly porous GO derived exfoliated GO (exfGO), it was identified that the resulting materials possessed ultrahigh surface area and total pore volume up to 853 m\textsuperscript{2} g\textsuperscript{-1} and 6.68 cm\textsuperscript{3} g\textsuperscript{-1}. The structures were applied as solid sorbents with chemical modification by TEPA and PEHA polyamines wet impregnation to incorporate amine-based sorption sites. The solid-amine system exhibited ultrahigh selective flue-gas CO\textsubscript{2} capture of 6.16 mmol g\textsuperscript{-1} at 75 °C. The desorption occurred at 100 °C, giving a desirable narrow temperature-swing window. Further testing showed the cycling stability under simulated flue-gas stream conditions had moderate decay of ~7 wt% over 40 adsorption-desorption cycles and demonstrated stable CO\textsubscript{2} uptake ~25 wt%.

From the study on MOF carbons, it was found that the carbonisation process of MOF precursors led to loss of local metal centres and produced defective carbon structures with mainly sp\textsuperscript{2} bonding. By varying the synthesis conditions and solvents, micrometre to millimetre-sized MOF-5 crystals can be synthesized. Carbonisation process retained both meso- and macro-pores and yielded MOF carbons with high surface area up to 2237 m\textsuperscript{2} g\textsuperscript{-1} and total pore volume up to 4.6 cm\textsuperscript{3} g\textsuperscript{-1}. The resulting amine-impregnated MOF carbons achieved CO\textsubscript{2} adsorption of 4.37 mmol g\textsuperscript{-1}.

In summary, the project has developed highly porous carbon-based solid sorbents, which are stable and environmentally benign, with high specific surface area to offer a CO\textsubscript{2} adsorption capacity > 6 mmol g\textsuperscript{-1}. The binding energy is typically controlled at -50 kJ mol\textsuperscript{-1}, which allows CO\textsubscript{2} adsorption and desorption to be carried out between
25 °C and 100 °C. The developed sorbents have met the identified challenges of flue-gas conditions CO₂ capture (>50 °C, humid), high thermal stability, chemical resistance and potential for large-scale production at low-cost, as well as offering great potential for practical applications in industry. The results also show great potential for the development of high capacity carbon-based sorbents for effective pre-combustion CO₂ capture and energy storage applications.
**Impact statement**

Due to anthropogenic CO\textsubscript{2} emission over the last century, the CO\textsubscript{2} level in the atmosphere has significantly increased and is causing global climate change. It is urgent to reduce the CO\textsubscript{2} emission from the source point. According to the Intergovernmental Panel on Climate Change (IPCC), global greenhouse gas emissions must be reduced by 80% below 1990 level by 2050 to avoid dramatic consequences of global climate change. International Energy Agency (IEA) indicates that the potential for reduced CO\textsubscript{2} emissions through enhanced energy efficiency and increased renewable energy production is limited. CO\textsubscript{2} capture and sequestration (CCS) is a low-cost pathway with potential for dramatic reductions in CO\textsubscript{2} emissions within 10 to 20 years. By establishing stronger incentives favouring energy efficiency and renewable energy and by ensuring wide deployment of CCS, global CO\textsubscript{2} emissions can be reduced by approximately 70% by 2050 compared with emissions today.

One of the main CO\textsubscript{2} emission sources is the burning of fossil fuels in power plants. The PhD project aims to reduce the emission level by capturing CO\textsubscript{2} from the post-combustion flue gas by studying dry-regenerate sorbents. Carbon-based systems are particularly attractive due to their relatively high thermal stability, chemical resistance and potential for large-scale production at low cost. Materials with a wide range of interconnected pores, such as exfoliated graphene oxide (exfGO), activated graphene oxide (actGO) and metal-organic frameworks (MOFs), were synthesized using scalable methods. Specific surface area and pore volume are highly desirable properties for physisorption and chemisorption with one-step chemical modification for a solid sorbent material. The materials have achieved specific surface area and pore volume of 797 m\textsuperscript{2} g\textsuperscript{-1} and 5.88 cm\textsuperscript{3} g\textsuperscript{-1} for exfGO, 2540 m\textsuperscript{2} g\textsuperscript{-1} and 1.5 cm\textsuperscript{3} g\textsuperscript{-1} for actGO, as well as 2237 m\textsuperscript{2} g\textsuperscript{-1} and 4.70 cm\textsuperscript{3} g\textsuperscript{-1} for MOF carbons. The introduction of CO\textsubscript{2}-philic amine groups into nanoporous structures led to an enhancement in selective carbon (CO\textsubscript{2}) capture under harsh post-combustion flue gas environment of high humidity and relative high temperature ~75 °C.
Graphene oxide (GO) is hydrophilic due to oxygenated functional groups at the edges and defect region of the layered structure. Well oxidised GO can absorb up to 130% its own weight in atmospheric moisture at high relative humidity and desorb water at lower relative humidity. The material could be applied for regulating humidity levels, particularly in confined environments such as aircraft cabins and air-conditioned buildings.
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<th>Description</th>
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<tr>
<td>actGO</td>
<td>Activated graphene oxide</td>
</tr>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller theory</td>
</tr>
<tr>
<td>BJH</td>
<td>Barrett-Joyner-Halenda</td>
</tr>
<tr>
<td>CCS</td>
<td>Carbon capture and sequestration</td>
</tr>
<tr>
<td>DAC</td>
<td>Direct air capture</td>
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<tr>
<td>exfGO</td>
<td>Exfoliated graphene oxide</td>
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<tr>
<td>FTIR</td>
<td>Fourier-transform infra-red spectroscopy</td>
</tr>
<tr>
<td>GO</td>
<td>Graphene oxide</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal–organic framework</td>
</tr>
<tr>
<td>PEHA</td>
<td>Pentaethylenehexamine</td>
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<tr>
<td>PXRD</td>
<td>Powder X-ray diffraction</td>
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<td>QSDFT</td>
<td>Quenched solid density functional theory</td>
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<td>rGO</td>
<td>Reduced graphene oxide</td>
</tr>
<tr>
<td>RH</td>
<td>Relative humidity</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning electron microscopy</td>
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<tr>
<td>SSA</td>
<td>Specific surface area</td>
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<tr>
<td>STP</td>
<td>Standard temperature and pressure</td>
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<td>TEPA</td>
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Chapter 1 Literature review

1.1 Societal, technical and scientific challenges of CO₂ separation and capture

Evidence of the existence of anthropogenic climate change is increasing year by year. Therefore, preventing further temperature rise and acidification of oceans and reducing the effect of climate change have become the most urgent tasks for global policy making and regulating.¹

The main cause of climate change is greenhouse gases such as carbon dioxide (CO₂). Burning of fossil fuels has increased the concentration of atmospheric carbon dioxide (CO₂) over the last century. The 33.1 Gt of energy-related CO₂ emission reported in 2018 represents a 1.7% increase over the previous year. It also means emissions have risen in each of the first two full years since the signing of the Paris climate agreement, leaving the world far short of the 26% to 28% cut in emissions targeted by 2025.²

3600 Gt CO₂ increase in the atmosphere would heat the earth by 2 °C,³ also known as the point of no return. Measures must be taken to reduce these influences, such as reducing emissions or capturing the existing CO₂ from the atmosphere. Approaches include 1. improving energy efficiency and promoting energy conservation; 2. switching to low carbon fuels such as hydrogen gas; 3. supporting the development of renewable energy, such as solar, tidal, wind and hydropower; and 4. CO₂ capture and sequestration (CCS). Among these, CCS is considered an important strategy for meeting the CO₂ emission reduction targets.⁴

CCS is broadly recognised as having the potential to play a key role in meeting climate change targets along with other measures of reducing carbon emissions such as using renewable energies. Aiming at delivering low carbon heat and power, decarbonising industry and its ability to facilitate the net removal of CO₂ from the atmosphere. Capturing CO₂ is the first step in CCS and accounts for 70-80% of the total cost of this technology. The typical fate of CO₂ is to be sequestered, either in a
saline aquifer or, potentially, used for enhanced oil recovery (EOR). A potential alternative to the storage of CO₂ is its re-use to produce marketable compounds. The argument is sometimes made that this can both contribute to climate change mitigation and provide an attractive revenue stream. Other arguments associated with carbon storage also includes leakage of transmission pipeline or the additional emissions caused by the extraction and transportation of CO₂.¹

The International Energy Agency (IEA) and the Organization for Economic Co-Operation and Development (OECD) forecast that CCS is expected to account for the mitigation of approximately 14-20% of total anthropogenic CO₂ emissions, the CCS industry will need to be larger by a factor of 2-4 in volume terms than the current global oil industry in 2050.⁵

CCS is one of the very attractive options in the integrated assessment models (IAMs) mitigation portfolios. It offers viable solutions for tackling problems linked to greenhouse gas emission. It has a number of advantages.³,⁶,⁷,⁸ First, CCS can be integrated into existing energy systems without major amendments to the system itself. Clearly, renewable technologies become more expensive at high penetration rates as a result of the need for the infrastructure to accommodate intermittency.⁹ Furthermore, CCS is a viable option for the decarbonisation of mission-intensive industries such as cement production.¹⁰ And finally, CCS can be combined with low-carbon or carbon-neutral bioenergy to generate negative emissions.¹¹,¹²

There are three basic types of CO₂ capture: pre-combustion CO₂ capture, oxy-fuel combustion, and post-combustion CO₂ capture (PCC). In pre-combustion CO₂ capture, the fossil fuel is partially oxidised in steam and oxygen/air under high temperature and pressure to form synthesis gas, which then undergoes the water gas shift reaction to produce a hydrogen and CO₂-rich gas mixture. The CO₂ is captured, separated, transported, and ultimately sequestered, and hydrogen is used for energy production. Oxy-fuel combustion utilises pure oxygen instead of air for combustion capture, resulting in final flue gas consisting mainly of CO₂ and water.

In PCC, the fossil fuel is burnt as in conventional energy generation and the CO₂ captured from the combustion effluent gas. PCC technologies can therefore be
retrofitted to existing CO$_2$ emission sources, such as coal fired power stations, making them one of the most widely studied and used large scale CO$_2$ capture methods. PCC is considered the most economical, practical approach to reducing CO$_2$ emissions in the short to medium term.$^{13,14}$

1.2 CO$_2$ capture technologies, challenges and approaches

Anthropogenic emissions of CO$_2$ are accepted as a significant risk to global climate. Human activity is currently adding an incremental 24 Gt of CO$_2$ per year to the atmosphere, while over half of the CO$_2$ emissions are from large, industrial point sources, in which power plants are the main CO$_2$ emission source with over ten thousands Mt CO$_2$ per year.$^6$ Two ways of developing economical pathways to reduce CO$_2$ levels in the atmosphere are being considered: 1. CO$_2$ removal from post-combustion industrial point sources (i.e. flue gas capture) and 2. atmospheric CO$_2$ removal by direct air capture (DAC).$^{15}$

Implementation of DAC requires a low-cost sorbent that combines optimum uptake, kinetics, energetics, physical/chemical stability and selectivity for CO$_2$ over competing gases and vapours at atmospheric CO$_2$ concentrations. Given that CO$_2$ concentration in the air is in ppm level, DAC is the toughest to achieve of all forms of carbon capture by current technology. DAC systems typically employ solid organo-amine based chemisorbents, where amine functional groups are physically or chemically anchored to the surface of cellulose, porous silica or porous polymer networks. However, the drawback is that the sorbents normally require elevated temperature (>100 °C) for regeneration.$^{16}$

A power plant equipped with a CCS system would need roughly 10-40% more energy than a plant of equivalent output without CCS, of which most is for capture and compression. However, the net result is that a power plant with CCS could reduce CO$_2$ emissions to the atmosphere by approximately 80-90% compared with a plant without CCS.$^6$ Therefore, physisorbents that can capture CO$_2$ with high selectivity and have low recycling energy consumption are very attractive. High
selectivity allows the CO₂ component of the flue gas to be completely removed for subsequent sequestration. However, the affinity of the material toward CO₂ is also a major consideration for minimising the energy penalty of capture.

The heat of adsorption for physical adsorption ranges between -25 to -40 kJ mol⁻¹ while chemisorption has an adsorption heat of -60 to -200 kJ mol⁻¹.¹⁷ If the interaction is too strong, this leads to a high energy requirement for desorption of the captured CO₂. On the other hand, weak interactions, while lowering the regeneration cost, would suffer from low selectivity for CO₂ over other components of the flue gas. Furthermore, the material should exhibit a high stability under the conditions of capture and regeneration. Owing to the large quantities of CO₂ that need to be removed from the flue gas, the material should take up CO₂ at high density, such that the volume of the adsorbent bed can be minimised.¹⁸

To mitigate CO₂ effectively and economically, research has been directed to improve current CO₂ capture and storage technologies. Capture sorbent that can perform both adsorption and desorption is very important.³,¹⁹ Main low temperature CO₂ separation technologies include dry re-generable sorbents, filtration membranes, pressure and temperature swing adsorption.

The choice of CO₂ removal process depends on the approach to CO₂ capture either from combustion source or directly from the atmosphere. To be more specific, for CO₂ removal from the atmosphere, filtration membranes can be prepared to allow only CO₂ to pass through and separate other components from the gas mixture or the other type of adsorbent material can selectively absorb CO₂ gas only. However, the basis of these two types of materials is the membrane or adsorbent material which is made of a composite polymer bonded to a thick and non-selective layer with low cost. This method can also be applied to separate other gases such as CO₂ from CH₄ and H₂ from CO₂.

The development of ceramic and metallic membranes and polymeric membranes for membrane diffusion could produce membranes significantly more efficient for CO₂ separation than other adsorption processes.²⁰,²¹ The performance of a membrane system largely depends on the condition of gas such as low CO₂ concentration and
pressure. This is a main hurdle affecting the application of this technology to real situations.

Adsorption is an attractive technology for a number of reasons. It can be retrofitted to any power plant should the adsorption column be optimised to ensure acceptable footprint and cost. In addition, it can cover a wide range of temperature and pressure condition so that low, medium, and high temperature adsorbents can be used as well as adsorbents for both pre- and post-combustion settings can be designed. This study is focused on low temperature adsorbents for post-combustion application (<200 °C).

The separation of CO₂ from nitrogen is an essential step in power plant flue-gas purification. Flue gases typically contain 3-15% CO₂ and >70% N₂. Other components such as H₂O and O₂ which can account for 5-7% and 3-4% of the flue gas, respectively. Depending on the feedstock of the power plant, trace components such as SO₂, NOₓ, and H₂S as well as gaseous organic compounds could affect the CO₂ selectivity and also the structural stability of the adsorbents during CO₂ removal. The treatment process of flue gas includes electrostatic precipitator to remove ash and other particulates, then pass through a denitrification unit to remove NOₓ followed by desulfurization process. CO₂ capture technologies are continuously being developed and refined. In academic research, gases other than CO₂, N₂ and H₂O are normally not considered. H₂O is however considered in the gas uptake condition in this thesis. A typical CO₂ separation condition is as ~1 bar and above 40 °C.

Currently in industries, the first-generation large-scale carbon capture materials have been widely applied for fossil fuel combustion via liquid amine-based sorption processes. Aqueous organic amine-based technology is the most mature technique for post-combustion capture. Amines are dissolved into water and exhaust is being bubbled through the liquid. The amines species in various capturing sorbents react with CO₂ to form a carbamate complex which selectively removes the CO₂ from the flue gas. The reactions are as follow:
The CO₂ rich solution is subsequently pumped to the stripper where steam from the power plant is used to heat the CO₂ rich amine solution between 120 °C and 150 °C to release the captured CO₂. The process is pressurized and piped underground, the amines can then be reused. Amine scrubbing technology is based on an acid (CO₂)-base (amines) reaction leading to the formation of chemically stable species (carbamates), offering an outstanding CO₂ uptake/capture per cycle ranging between 8 and 13 wt%. However, the cost of operation is high. It imposes a large energy penalty for the back release of the captured CO₂. Aqueous amine solution has high heat capacity (3-4 J g⁻¹ K⁻¹ depending on concentration), the pumping and heating can use up to 30% of the energy produced by a coal-fired power plant, reducing its efficiency and raising its electricity price. Additionally, in this process, the employed amines degrade and hence need to be frequently replaced (2.2 kg monoethanolamine (MEA) per tonne of CO₂). Volatility of the amines also leads to significant material losses. Besides, the system suffers from a relatively high energy penalty due to limited surface utilisation and easy degradation to harmful species. In this regard, solid adsorbents with high accessible surface area, stability and appropriate molecular binding energies are very attractive to enhance the sorbent performance. Though the technology will remain competitive in the future, it suffers from problems such as high cost, toxicity, degradation and evaporation of the solvent.

Current research regarding to CO₂ capture has two main potential applications, which are post-combustion capture (PCC) of flue gas from gas-fired power plants and direct air capture (DAC). An ideal CO₂ adsorbent should satisfy some criteria to be both economically and operationally efficient for CO₂ capture from flue gas. The criteria are: 1. high adsorption capacity; 2. high CO₂/N₂ selectivity, e.g. possess basic sites on the surface such as hydroxyl or amine groups to facilitate chemical interaction with acidic CO₂ molecules; 3. moderate heat of adsorption; 4. fast adsorption/desorption kinetics; 5. chemical stability/tolerance to impurities such as...
NOx and SOx present in typical flue gas mixture; 6. mechanical stability; 7. low regeneration energy, compared with high decomposition temperature of the inorganic carbonates such as calcium oxide (CaO), magnesium oxide (MgO) and sodium hydroxide (NaOH); and 8. low sorbent costs and substantial operational cost considered such as mitigate for the loss of the solvent of liquid amine solutions.29,30

Highly stable porous materials are crucial to the applications of energy and environmental technologies, such as to enhance the performance of core devices in chemical energy storage, purification or separation of gaseous molecules and pollutant removal in water and air. The adsorptive removal of carbon by nanoporous solids is considered one of the most promising approaches to fulfilling the short-term goals of carbon capture and sequestration (CCS). Recently, several silica materials incorporating a CO2 capturing agent have emerged as dry sorbents for CO2. Silica support alone has negligible CO2 capture capacity, but dispersion, immobilization and confinement of the amine functional group inside the porous silica support can result in a stable, mass transfer efficient, less toxic and less corrosive material than the corresponding liquid amines.31 Several classes of solid materials such as cation-exchanged zeolites,32 metal organic frameworks (MOFs),33,34 amine-functionalised mesoporous silicas,35-37 porous polymeric networks,38 organic framework materials39 and porous carbon materials40,41 have stated high sorption capacity and good selectivity for CO2 from CO2/N2 gas mixture.

1.3 Mechanism of CO2 capture

In recent years, the application of immobilized amines on a high surface area solid to adsorb CO2 has proved to give very good results.42

Carbon dioxide is a non-polar, highly stable, linear molecule with an electropositive carbon atom and two electronegative oxygen atoms. Main pathways for activating CO2, either for capture or conversion, rely on a nucleophilic interaction with the electrophilic carbon atom.43 The reversibility of the capture relies on the strength of
binding, defined by the $Q_{st}$. The stronger the binding, the more energy is required to regenerate the sorbent.

$\text{CO}_2$ adsorption can take place by physisorption (van der Waals force), chemisorption (chemical bonding) or by both. Physical properties such as surface area and porosity could affect the quality and character of solid phase materials. Pore size distribution and pore volume are the main parameter of physisorption. Chemisorption measures the number of surface active-sites which are used to promote a specified catalytic reaction.

Critical parameters for chemisorption measurement are the area of the active element, metal dispersion, surface acidity, exposed proportion of the active element, etc. Chemisorption takes place in the first layer and subsequent deposition into multilayers is solely physisorptive and gradually loses the binding strength.

Typically, active alkali —$\text{NH}_2$ group possess a lone pair of electrons on N atom which undergoes nucleophilic attack on the C atom of acidic CO$_2$, resulting in carbamate formation through carboxyl group. The active H atom in carboxyl group may then form ion pairs through hydrogen bond with the nearby amine group/moisture in feed gas, and thus stabilises the chemisorption of CO$_2$.

Primary amines CO$_2$ capture mechanism relies on a process that evolves through the formation of bicarbonate ion, ammonium carbamates and carbamic acid. It is often assumed that the reactions occurring with aqueous amines also occur in gas phase due to the presence of water molecules in the flue gas. More specifically, sterically hindered primary amines react with CO$_2$ to form bicarbonate in the presence of water. This reaction path allows for the amine efficiency of 100%, i.e. 1:1 amine-CO$_2$ stoichiometry. In the case of moderately hindered amines, the reaction with CO$_2$ can form carbamate via the formation of the zwitterion. This reaction allows for a 2:1 amine-CO$_2$ stoichiometry, and an amine efficiency of 50%. Carbamates can then further react with CO$_2$ to form the relevant carbamic acid.
Figure 1. Chemisorptive reaction mechanisms of CO$_2$ with primary, secondary, or tertiary amines in dry and humid conditions.$^{1,45}$

The reaction mechanism between amino groups in polyamines and CO$_2$ is well studied. The primary and secondary amino groups form carbamates upon contact. When water molecule is present, carbamates will transform into bicarbonate during adsorption. Two amino functionalities are needed for each CO$_2$ to be adsorbed in the dry CO$_2$ capture while theoretically one amino functionality is required for a CO$_2$ molecule in a humid environment.

The CO$_2$ uptake tests in this study were carried out using dry gas streams, therefore, a double uptake amount can be expected when tested under humid environment.$^{46}$ The mechanism demonstrates that primary and secondary amines can undergo carbamate formation in dry conditions through chemisorption and carbamates formation is not possible in tertiary amine containing porous materials in dry CO$_2$ capture.

It is essential to have fast adsorption/desorption kinetics for CO$_2$ under the operating conditions. The kinetics of adsorption and desorption control the cycle time of a fixed-bed adsorption system. The overall kinetics of CO$_2$ adsorption on a functionalised solid sorbent is influenced by the intrinsic reaction kinetics of CO$_2$ with the functional group present, as well as the mass transfer or diffusional resistance of the gas phase.
through the sorbent structures. The porous support structures of functionalised solid sorbents also can be tailored, to minimise the diffusional resistance. The faster an adsorbent can adsorb CO$_2$ and be desorbed, the less of it will be needed to capture a given volume of flue gas.$^{44}$

### 1.4 Carbon capture sorbents and state-of-art developments

According to the international nomenclature, in the context of physisorption, pores are classified according to their diameters:$^{47,48}$

i. Pores with widths exceeding about 50 nm are called macropores;

ii. Pores of widths between 2 nm and 50 nm are called mesopores;

iii. Pores with widths not exceeding about 2 nm are called micropores.

The term nanopore embraces the above three categories of pores, but with an upper limit ~100 nm.

Ideally, a CO$_2$ sorbent for post-combustion CO$_2$ capture is either ultra-microporous (pore aperture similar to the steric size of CO$_2$ molecules, following physisorptive, sieving-based weakly binding mechanisms) or mesoporous with strong enough basic amines tethered on its walls (chemisorptive, strongly binding mechanisms). When CO$_2$ is at low pressure (0.15 bar, maximum), these two sorbent types can lead to high uptake with strong but reversible CO$_2$ affinity.$^{1,14,49,50}$

Gaseous molecules have a high affinity for micropores. Microporous material has higher surface area than the same amount of macroporous material, and therefore has larger CO$_2$ capacity. However, larger pores allow higher diffusion of gas inside the structure. When CO$_2$-philic functionalities are incorporated to a pore, the binding affinity of CO$_2$ molecules can be highly improved.$^{49,51,52}$ Larger pores are ideal for chemical modifications. Therefore, the porosity and chemistry of a sorbent have to be modified simultaneously to bring the best performance of CO$_2$ capture of a
sorbent material. This difficult task of constructing a perfect framework remains a significant challenge for chemists, both on the lab scale and at industrial quantities.

The mechanical strength of sorbents is of great importance. The sorbent must demonstrate microstructure and morphological stability and retain the CO$_2$ capture capacity during multi-cycling between the adsorption and regeneration steps. Microstructure and morphological stability of tailored regenerable sorbents in multicycle operation is critical to maintain high kinetics. Operating conditions, such as high volumetric flow rate of flue gas, vibration, and temperature should not cause appreciable disintegration of the sorbent particles. This could also happen via abrasion or crushing. Therefore, adequate mechanical strength of sorbent particles is critical to minimise the sorbent makeup rate and to keep CO$_2$ capture process cost-effective.

Common physical adsorbents, such as zeolites, carbons and metal-organic frameworks (MOFs), show great promise.$^{33,53}$ For example, metal organic frameworks (MOFs) with selective pore sizes would capture CO$_2$ from flue gas and release with moderate heating.$^{54}$ Polymer membranes containing MOFs or other porous solid particles can allow CO$_2$ pass through while blocking other exhaust gases such as NO$_x$ and O$_2$ are also promising sorbents.$^{39}$ Therefore, the transformation of porous graphene from creating pores to morphology design is gradually attracting more attention in recent years.

In the field of gas separation, other types of graphene-based material excluding membrane could be developed, such as graphene foam or hydrogel. Excluding two-dimensional structures, GO or exfoliated GO with high surface area and high pore volume can also be made into a 3D macroscopic graphene foam by a self-assembly of the 2D flexible graphene nano-sheets building blocks.$^{54}$ The advantages of graphene foam are that it can prevent graphene membranes from aggregating and restacking and ensures a larger specific surface area.$^{55,56}$ On the basis of 3D graphene networks, using several modification such as cross-linking with polymers should give good gas separation or adsorption results.
Metal organic frameworks (MOFs) are a promising class of sorbent materials. However, they are not typically manufactured at large scale, and are typically supplied as a powder rather than a structured adsorbent. The porous materials have high amenability to design and the flexibility with which their pores can be functionalised. Developing an understanding of the large-scale production of MOFs in a form suitable for practical application is key to moving these materials forward towards industrial deployment.

Previous researches have shown promising results and the field is constantly progressing with better performing materials. An ethylenediamine-grafted zeolite showed that it can effectively capture CO$_2$ from a wet flue gas at 40 °C and efficiently regenerated under temperature swing conditions at 130 °C for 30 minutes with cyclic stability. Grafted materials and samples impregnated with around 50% organic amount or higher, showed minor influence of the dilution of CO$_2$ in the feed gas on their CO$_2$ uptake. Soy derived heteroatom doped carbon captures 14 wt% CO$_2$ at 25 °C and 57.7 wt% at -78 °C at 1 bar pressure, with surface area of 1072 m$^2$ g$^{-1}$. By supporting aminated poly(vinyl chloride) on mesoporous silicas, a family of polymer/silica composites was synthesized, specifically ethylenediamine-treated PVC products on SBA-15 support. The adsorption capacity for CO$_2$ at maximum is 12 cm$^3$ g$^{-1}$. A highly microporous silica, synthesized by secondary sintering of fumes silica, impregnated with poly(ethylenimine) (PEI) showed high CO$_2$ adsorption kinetics and capacity. Silica has extra-large pore volume (1.8 cm$^3$ g$^{-1}$) and pore diameter (56 nm) and a thick wall (>10 nm). CO$_2$ capacities of PEI/silica are 2.44 and 3.84 mmol g$^{-1}$ respectively without and with the presence of water content and showed 10% decrease compared with the initial CO$_2$ adsorption capacity over the 14 days steam stability test.

The CO$_2$ uptake measured by gravimetric method normally uses wt% as unit while volumetric method uses mmol g$^{-1}$ or cm$^3$ g$^{-1}$. The units wt% and mmol g$^{-1}$ are convertible by dividing or multiplying the molecular weight of CO$_2$ (44.01 g mol$^{-1}$). Standard volume of 1 mmol of an ideal gas at STP is 22.414 mL (cm$^3$). The units mmol g$^{-1}$ and cm$^3$ g$^{-1}$ are convertible by dividing or multiplying 22.414.
1.5 Water adsorption of GO

Graphene oxide is a hydrophilic material with high content of oxygenated functional groups. Recent studies on the interaction of water with GO laminates have demonstrated the possibility of utilising their relatively high hydrophilicity for applications such as humidity sensor,\textsuperscript{60} fruit preservation desiccant\textsuperscript{61} and molecular sieves.\textsuperscript{62,63} The strong interaction between GO and water, fast water transport mechanism and expandable interlayer spacing make it a potential candidate for desiccant application.\textsuperscript{2,3} Previous study has observed that GO imparts high water uptake capacity of up to 0.58 gram of water per gram of GO (g g\textsuperscript{-1}).\textsuperscript{4} The precise role of the expandable interlayer spacing and functional groups in GO laminates has not been fully understood.

Graphite and reduced graphene oxide (rGO) show insignificant adsorption capability of less than 0.05 g g\textsuperscript{-1} water uptake.\textsuperscript{64} Interlayer spacing of graphite (3.4 Å) and rGO (3.7 Å) should be enough to accommodate a 2.4 Å sized water molecule but the space is filled with delocalised electron. Therefore, there exists no pore to accommodate the water molecule and thus repulses water. The hydrophobic characteristics also restrict the entry of water molecules into the pores. C\textsubscript{2}N\textsubscript{x}O\textsubscript{1-x} framework carbon with defined micro porosity has a water vapour physisorption of 425 cm\textsuperscript{3} g\textsuperscript{-1} at relative pressure of 0.9, which is equivalent to 0.341 g g\textsuperscript{-1} uptake.\textsuperscript{65} GO paper with high oxygen content has higher moisture adsorption capability. The absorbance at high humidity is significantly improved due to direct formation of multilayer water vapour in the system, which is derived from the weak interaction between the adsorbent and the adsorbate.

Current atmospheric water generators function either by chilling air below its dew point or by distilling water absorbed in concentrated brine, both of which require large energy input.\textsuperscript{66} Solid sorbents that use natural variations between daytime and night-time temperature and relative humidity (RH) to capture and release water are an alternative that requires no additional energy input.\textsuperscript{67} Water uptake from atmosphere by MOF captures 82% water by weight below 30% relative humidity and
demonstrates a cooling capacity of 400 kWh m$^{-3}$ per cycle, also a sorbent capable of creating 20 °C difference between ambient and output temperature.$^{68}$

The capture of water vapour at low relative humidity is desirable for producing portable water in desert regions and for heat transfer and storage. The understanding of water transport and water adsorption properties of GO can provide further insights towards the structural modification and next-generation applications.

### 1.6 Porosity and surface area analysis of materials

Gas adsorption is a well-established tool for the characterisation of the texture of porous solids and fine powders. Adsorption is defined as the enrichment of molecules, atoms or ions in the vicinity of an interface, specifically solid surface and outside the solid structure in a gas/solid system. Adsorption can be physical (physisorption, occurring between adsorbable gas and adsorbent) or chemical (chemisorption, forming chemical bonds). In the process of adsorption, adsorbate gets adsorbed on adsorbent. Desorption denotes the converse adsorption process, in which the amount adsorbed progressively decreases.$^{48}$

On solid surface, CO$_2$ interacts first through predominantly intermolecular forces, such as van der Waals force. If there is no chemical interaction that would favour a chemical bond, the interaction will follow simple condensation principles where layer-by-layer deposition is likely to take place. Adsorption of CO$_2$ on the pore walls is a favourable event and leads to CO$_2$ capture. This leads to a steep increase in uptake capacity until the pore is filled, for example, in a micropore. In a mesopore, two such steep curves are observed, first in the logical micropore filling behaviour but then the second, at which the remaining opening is a micropore itself. Filling that second pore is called pore condensation, a phenomenon that contributes to gas uptake significantly. In between, an equilibrium plateau of adsorption–desorption is observed.$^{1,69}$
Figure 1. 2 Layer-by-layer deposition in a mesopore.\textsuperscript{1}

Isotherm graphs are between the amounts of adsorbate adsorbed on the surface of adsorbent and pressure at constant temperature. The isotherms studied in this project are based on Brunauer-Emmett-Teller (BET) theory. BET Theory put forward by Brunauer, Emmett and Teller explained that multilayer formation is the true picture of physical adsorption.\textsuperscript{48} BET theory is used for analysis of surface area of porous structures. Gas can be adsorbed at the surface of a solid by relatively weak forces such as van der Waals forces. A monomolecular layer of gas can be attracted to the surface of the powder material during the analysis. The amount of adsorbate gas on a powder sample can be used to determine the specific surface area. The volume of gas at the surface can then be measured by a volumetric or continuous flow procedure at the temperature of liquid nitrogen (\textasciitilde195.79 °C (77 K)). The specific surface area can be calculated correspondingly by taking account the molecular cross-sectional area of N\textsubscript{2}.\textsuperscript{48}

According to Le-Chatelier principle, the direction of equilibrium would shift in that direction where the stress can be relieved. In case of application of excess of pressure to the equilibrium system, the equilibrium will shift in the direction where the number of molecules decreases in the gas phase. Since number of molecules decreases in forward direction, with the increases in pressure, forward direction of equilibrium will be favoured. Under the condition of high pressure and low temperature, thermal energy of gaseous molecules decreases, and more and more
gaseous molecules would be available per unit surface area. Due to this multilayer adsorption would occur.

Figure 1. 3 Classification of physisorption isotherms.\textsuperscript{48}

IUPAC recommends classifying physisorption isotherms into six types.\textsuperscript{48} Three isotherm types are associated with reversible adsorption: Type I, II and III. Type I isotherm is concave to the pressure axis and approaches a limiting adsorption saturation loading as the relative pressure (P/P\textsubscript{0}) approaches 1. Adsorbents displaying Type I isotherms are typically microporous with strong adsorbate-adsorbent interactions. The saturation value is controlled by the accessible pore volume. Type II isotherm is typically obtained from nonporous or macroporous materials and is characterised by unrestricted monolayer-multilayer adsorption. The Type III isotherm is essentially the inverse of the Type I isotherms. There is no identifiable monolayer formation and the adsorbed molecules are clustered around the most favourable sites on the surface of a nonporous or microporous solid. This
is resulted when the adsorbate-adsorbate interaction is much stronger than adsorbate-adsorbent interaction.\textsuperscript{48,70} The amount adsorbed remains finite at the saturation pressure as adsorbed molecules are clustered around the most favourable sites on the surface of a nonporous or macroporous solid.

Characteristic feature of the Type IV isotherm is its hysteresis loop, which is associated with capillary condensation taking place in mesopores, and the limiting uptake over a range of high $P/P_0$. The initial part of the Type IV isotherm is attributed to the monolayer-multilayer adsorption since it follows the same path as the corresponding part of a Type II isotherm obtained with the given adsorptive on the same surface area of the adsorbent in a non-porous form. Type IV isotherm is given by many mesoporous industrial adsorbents. Type IVa isotherm occurs when the pore width exceeds a certain limit, depending on the adsorption system and temperature. Type IVb is given by conical and cylindrical mesopores. The Type V isotherm is uncommon, it is related to the Type III isotherm in that the adsorbent-adsorbate interaction is weak, but is obtained with certain porous adsorbents. The Type VI isotherm, in which the sharpness of the steps depends on the system and the temperature, represents stepwise multilayer adsorption on a uniform non-porous surface. The step-height represents the capacity for each adsorbed layer.\textsuperscript{70,71} Hysteresis appearing in the multilayer range of physisorption isotherm is usually associated with capillary condensation in mesopore structures. Such hysteresis loops may exhibit a wide variety of shapes.

Analysis of the pore size distribution is carried out by applying different theories and calculations. Pore volume distribution curves are obtained by differentiation of the cumulative pore volume curves. Consequently, the shape of the distribution curve depends only upon the changes in slope of the cumulative curve within the range of pore radius values over which the differentiation is carried out.\textsuperscript{72}

Classic methods exist to determine pore size distributions, for instance: The pore size distribution analysis of a porous material is usually obtained with Barrett, Joyner and Halenda (BJH) methods or density functional theory (DFT).\textsuperscript{48} BJH method is commonly used for mesopore analysis, but it may underestimate the pore size for
narrow mesopores (for pore diameter <10 nm, the pore size can be underestimated by ~20-30%) because the curvature and enhanced surface forces are not taken into account.

DFT method captures the essential features of both micropore and mesopore filling and hysteresis and provide a more reliable assessment of the pore size distribution over the complete nanopore range. DFT method has been developed into a powerful method for the description of the adsorption and phase behaviour of fluids confined in well-defined pore structures. The configuration of adsorbed molecules in pores on a molecular level can be described and thus provides detailed information about the local fluid structure near the adsorbent surface. The fluid-solid interaction potential is dependent on the pore model. Different pore shape models (e.g. slit, cylinder and spherical geometries and hybrid shapes) have been developed for various material classes such as carbons, silicas and zeolites.

Quenched solid density functional theory (QSDFT) takes account the surface heterogeneity, significantly improving the reliability of the pore size analysis of heterogenous nanoporous carbons. BJH and DFT methods were applied where appropriate in the analysis in the experiment chapters.

The BET surface area of a nonporous, microporous or a mesoporous solid can be regarded as the ‘probe accessible area’ (i.e. the effective area available for the adsorption of the specified adsorptive) for a well-defined Type II or Type IV isotherm). Nitrogen is commonly used as the adsorptive for BET area determination at its boiling temperature, 77 K. The specific surface areas in this thesis were obtained through BET method on the desorption isotherm in the $P/P_0$ pressure region between 0.01 and 0.2. Micropore specific surface area for the pores of up to 2 nm can be obtained through QSDFT fitting to the desorption isotherm.

If a mesoporous adsorbent contains no macropores, its Type IV isotherm remains nearly horizontal over the upper range of $P/P_0$. The pore volume can be derived from the amount of vapour adsorbed at a relative pressure close to unity ($P/P_0 = 0.95$) by assuming that the pores are filled with the adsorbate in the bulk liquid state. However, if macropores are present, the isotherms are no longer nearly horizontal near $P/P_0 =$
1 and the pore volume obtained is not accurate. Pore volume is a single point total pore volume obtained at $P/P_0$ of $\sim 0.99$. It can be defined as, $V_{\text{total}} = (N_2 \text{ adsorbed at 0.99 in cm}^3 \text{ g}^{-1}) \times (N_2 \text{ liquid density at } \sim 1 \text{ bar})/ (N_2 \text{ gas density at STP})$ and is equal to $V_{\text{ads at } (P/P_0=0.99)} \times 0.001547$.

### 1.7 Research aim and objective

An effective approach to CO$_2$ capture and sequestration (CCS) is via dry regenerable sorbents, which can selectively absorb CO$_2$ gas from flue gas mixture. There are three main factors affecting solid-sorbent material for CO$_2$ capture: physisorption, chemisorption and the absorbate. The surface of the sorbent has van der Waals binding force with the gas molecules and gaseous molecules have a high affinity to micropores. Meso- and macropores is ideal for chemical modification via amine impregnation. Therefore, materials with large surface area and high pore volume with a range of micro-, meso- and macro-porosities are desirable for gas adsorption application. Certain modification such as exfoliation and KOH activation methods can be applied to carbon substrates to enhance their micro- and meso-porosity. However, the physisorption is considered a weak sorption as the heat of adsorption is $\sim$ -10 kJ mol$^{-1}$ compared with $\sim$ -50 kJ mol$^{-1}$ of chemisorption. With chemical modification of the substrates, stronger chemical bonding occurs between sorbent and absorbate. Besides, as flue gas contains water and water can affect the chemisorption. The effect of water adsorption capacity of the sorbents is also studied. In general, the aim of this PhD project is to design and synthesize a solid CO$_2$ sorbent material which could optimise gas uptake by both physisorption and chemisorption and can be repeatedly used in a harsh flue gas environment.

Hence, the project was organised in the following three chapters:

Chapter 3: Physical properties of graphene oxide (GO) were studied in this chapter. GO has stacked structure with oxygenated functional groups such as hydroxyl, epoxy and carbonyl groups on its basal planes and at its edges, making it hydrophilic in nature. The oxygen-functional groups will affect the physical properties of GO and
thus have effect on gas adsorption. GO samples with various degrees of oxidation were synthesized through improved Hummer’s method by controlling oxidising conditions. GO has laminated structure can interact with water and allow slow diffusion into the layers. Water uptake capacity of GO with various oxidation level has been measured at different moisture levels by recording gravimetric changes.

Chapter 4: From my colleague and I’s previous work, it is found that direct chemical modification on GO samples shows very low uptake under flue-gas condition due to low pore volume, which is 10 wt%. Therefore, hierarchical porous graphene networks of ultrahigh total pore volume synthesized from GO and amine modified were used for CO₂ capture. The exfoliated GO (exfGO) and activated GO (actGO) structures were derived through moderate temperature thermal shock (300 °C) and KOH activation (800 °C) from GO precursors. The thermal shock exfoliation is led by pressure build-up of volatile surface oxy-functional groups and hydrogen bonded interlamellar water molecules under sudden heat, which creates meso- and microporous exfGO. KOH activation is used for introducing micropores to solid-state materials. We also found that the exfGO and actGO samples alone without amine impregnation show very low CO₂ uptake capacities, which is <0.4 mmol g⁻¹ at flue gas condition. The uptake capacity can be potentially improved with amine modification. The solid-amine system was used as selective flue-gas CO₂ capture adsorbents tested at various temperatures. The cycling stability has also been studied by gravimetric swing tests.

Chapter 5: Another type of porous structure is metal-organic framework (MOF). MOFs consist a range of micro-, meso, and macro- porosities. MOFs (MOF-5 and MOF-74) were synthesized through solvothermal reaction of metal salts and linkers in solvent. By tuning linkers and solvent, the crystal size, total pore volume and surface area can be modified. The as-synthesized MOFs are highly sensitive to moisture and can easily break down when exposed to air. Therefore, a direct carbonisation can be applied to maintain carbon skeleton structure. Carbonisation retained both macropores and mesopores in the yield products with high surface
area and pore volume. With further chemical modification, i.e. amine impregnation, MOF carbons also achieved over 4 mmol g\textsuperscript{-1} of CO\textsubscript{2} uptake.

The physical properties of the materials were analysed using scanning electron microscopy (SEM), transmission electron microscopy (TEM), X-ray diffraction (XRD), Raman spectroscopy, Fourier transform infra-red spectra (FTIR), X-ray photoelectron spectroscopy (XPS), thermogravimetry-differential scanning calorimetry (TG-DSC) and BET surface area and pore size analyser.

In conclusion, various materials with porous structures have been studied and they have offered great potential for the design and development of complex materials as molecular sorbents. The products have the advantages of high thermal/chemical stability, high specific surface area and high functionalities. Other advantages include low cost and easy scale-up of production, can lead to potential industrial level applications.
Chapter 2 Characterisation techniques and experimental details

2.1 Instrumentation

The morphology characterisation was carried out using scanning electron microscopy (SEM, JEOL JSM-6700F) and transmission electron microscopy (TEM, JEOL JEM-2100F) on gold coated samples stuck to sample holder using carbon tape or on carbon coated copper TEM grid.

The surface elemental content was measured by X-ray photoelectron spectroscopy (XPS, Al-K-alpha, Thermo Scientific).

The phase and structure were identified by powder X-ray diffraction (PXRD, on a Stoe Stadi-P capillary geometry system, Cu-K-alpha). Samples were ground into fine powder and filled into glass capillaries under ambient conditions. The glass capillaries are made of borosilicate glass (Capillary Tube Supplies Ltd.) with outside diameter of 0.5 mm or 0.7 mm and wall thickness of 0.01 mm. The X-ray energy source is Cu-K-alpha, which corresponds to an X-ray wavelength of 1.5406 Å. Raman spectroscopy (514.5 nm laser, Renishaw InVia Raman Microscope) was carried out on hand pressed powder samples on a glass slide.

Fourier transform infrared spectroscopy (FTIR, Bruker Alpha) was performed in transmittance mode on loose powder with background correction.

The porosity and gas adsorption-desorption isotherms up to 1 bar were determined on a Quantachrome Autosorb-iQC. The specific surface area was measured from the 77 K N_2 isotherm using liquid nitrogen in a relative pressure range between 0.01 and 0.15, according to the Brunauer–Emmett–Teller (BET) method. Quenched solid density functional theory (QSDFT) slit/cylinder/sphere pores model was applied to micro-pores (<2 nm) and mesopores (≥2 nm, <50 nm) while Barrett-Joyner-Halenda (BJH) model was applied to macropores (≥50 nm). The total pore volume was estimated from the amount of N_2 adsorbed at a relative pressure P/P_0 =0.99. Note that the total pore volume at P/P_0 ≤0.994 was in good agreement with the total pore
volume obtained through the BJH method (meso-pore + macro-pore) + QSDFT method (micro-pore). The sample was degassed at either 120 °C or 180 °C overnight under dynamic vacuum prior to the actual gas adsorption measurement. The volumetric method CO$_2$ uptake at various temperatures were measured and tested by CO$_2$ adsorption-desorption isotherms.

Combined thermogravimetry-differential scanning calorimetry (TG-DSC, Setsys DTA, Setaram) up to 1000 °C measurements were carried out on a dry sample under nitrogen flow with heating rate of 3 °C per min. TG weight change was analysed after background correction with respect to the empty alumina crucible.

The volumetric CO$_2$ uptakes are shown in “mmol g$^{-1}$” while the gravimetric capacities are in “wt%”.

2.1.1 Water uptake tests

**Water uptake tests approach 1: Thermogravimetric analysis**

Samples were put into the thermogravimetric analysis (TGA) alumina sample holder and weighed, covered and put into the vacuum oven at 50 °C overnight. Prior testing, samples were taken out and weighed for the actual weight of dry samples. Moisture was supplied by pumping pure nitrogen gas through a DI water tank and connected to the TGA system. TGA data were recorded to monitor water uptake by taking the weight change at a constant temperature while supplying humid gas. The wetted gas flow created around 80% RH environment for the samples. After testing, samples exposed to humid environment were weighed again to confirm the mass increase calculated from TG data in order to avoid TGA balance system shifting. The adsorption capacities were represented by water uptake per unit weight of dry absorbent, with a unit of mg per 100 mg or %.

**Water uptake tests approach 2: Self-made apparatus measurements**

This test approach is by measuring spontaneous water uptake at ambient environment using a home-made apparatus which can control relative humidity of individual samples. A 2 mL glass vial was put inside a 10 mL sample vial, in which
water was filled to 4/5 height of the small glass vial. Another 5 mL glass vial with dry sample was put on top of the 2 mL glass vial inside the 10 mL glass vial, avoiding direct contact with water. The cap was then placed on the largest glass vial, further sealed with moisture-proof parafilm. Weight of the samples were recorded by balance weighing. Before measuring, GO samples were outgassed over 24 hours in vacuum oven. Then the dry samples were weighed and put in ambient environment to allow spontaneous uptake. Humidity was measured with a RS PRO Temperature & Humidity Datalogger, with accuracy of ±5.0% at 80% to 100% RH. The experiment started from an ambient relative humidity about 50% at 20 °C. After one day, samples were transferred to a closed environment with a cup of water in it. The evaporation of water created an environment with RH around 90% (±5%), as recorded by humidity meter.

2.2.2 CO₂ uptake measurement approaches

Two methods were applied to measure the CO₂ uptake capability of the samples. Method one is by volumetric method for single-component CO₂ uptake and method two is gravimetric method for both pure CO₂ and mixed gas capture using a mimetic flue-gas stream (consisting of 15% CO₂ in 85% N₂ and humified by bubbling through water at a flow rate of 100 ml min⁻¹).

Samples were screened with volumetric adsorption isotherms using 100% dry CO₂ and measured up to 1 bar at different temperatures between 25 °C and 75 °C (temperature maintained by using an electric heating water bath) on a Quantachrome Autosorb-iQ2. The samples were degassed at 70 °C overnight prior to the CO₂ adsorption-desorption isotherm measurement.

The gravimetric CO₂ gas uptake tests were performed with TGA under a constant gas flow of 100 ml min⁻¹ at around 1 bar. The mixed gas tests were carried out under 3 different streams of gas supplies: 1. mimetic flue-gas which is humidified (bubbled through a water bubbler) 15% CO₂ balanced with 85% N₂; 2. 15% dry CO₂ balanced with 85% N₂ and 3. humidified 100% N₂, as a reference. In each case the desorption
process was obtained under dry N\textsubscript{2} flow (100 ml min\textsuperscript{-1}) at ≈100 °C. The sorption tests were conducted at different temperatures of 30 °C, 50 °C, 65 °C and 75 °C.

The gravimetric and temperature swing cyclic CO\textsubscript{2} uptake tests were carried out by taking measurements of sample weights while changing the operating temperature and gas streams. A typical cycle starts from first heating the sample to 100 °C from room temperature under dry N\textsubscript{2} flow and remains at 100 °C until the decrease of mass becomes smooth and steady, usually over 1 hour, to allow complete desorption of water and other pre-adsorbed gas molecules. Then the temperature is slowly decreased to the designated working temperature, for example, 75 °C, 50 °C or 25 °C. When the temperature reaches and can steadily maintains at each designated temperature, the gas stream is quickly switched to mimetic flue-gas stream for recording CO\textsubscript{2} uptake. The temperature and gas flow are maintained to allow adsorption to reach a plateau, where sample saturates and attains the highest capacity. Then the sample is degassed by switching gas supply back to dry N\textsubscript{2} flow while increasing the temperature to 100 °C. This complete adsorption-desorption process is regarded as one cycle. Since the experiments involve switching between the gases manually for each adsorption and desorption process, the measurements are carried out in the daytime and the subsequent sorption process is left with no further gas supply in the night-time. The samples are allowed to naturally cool down to room temperature and ready for subsequent cycling the next day.

2.2 Experimental details

2.2.1 Chemicals

The following chemicals were used as received without further purification: synthetic graphite powder (≤20 μm, Sigma-Aldrich), potassium permanganate (≥99.0%, Sigma-Aldrich), sulphuric acid (95-97%, Sigma-Aldrich), phosphoric acid solution (≥85 wt%, VMR), hydrogen peroxide solution (34.5-36.5%, Sigma-Aldrich), hydrochloric acid (35%, Fisher Scientific and 37%, ACS reagent, Sigma-Aldrich), tetraethylenepentamine (TEPA) (technical grade, Sigma-Aldrich),
pentaethylenehexamine (PEHA) (technical grade, Sigma-Aldrich), methanol (≥99.9%, Sigma-Aldrich), potassium hydroxide, ≥85%, ACS reagent, pellets (Sigma-Aldrich), zinc nitrate tetrahydrate (Sigma-Aldrich), terephthalic acid (Sigma-Aldrich), N,N-dimethylformamide (Acros Organics), N,N-diethylformamide (Acros Organics), 2,5-dihydroxyterephthalic acid (Sigma-Aldrich), chloroform (Sigma-Aldrich), methanol (Fisher Chemicals) and deionised water (DI water, 18.2 MΩ cm⁻¹, ThermoScientific, Barnstead Easypure RoDi).

All gases used in the thesis, nitrogen (99.998%, oxygen free), carbon dioxide (99.8%) and 15% carbon dioxide in nitrogen gases were of research grade purity and supplied by BOC, UK.

2.2.2 Synthesis of graphene oxide (GO)

Graphene oxide (GO) samples used in this chapter were synthesized following the improved Hummers’ method. Graphite powder (1.0 g) was added to a cold (0 °C) 9:1 mixture of concentrated H₂SO₄/H₃PO₄ (22.5:2.5 ml) under stirring, with the solution becoming silvery-black. Whilst stirring was maintained, KMnO₄ (6.0 g) was slowly added, ensuring that the temperature of the system never rose above 5 °C using ice bath. Upon addition, the solution became deep dark green due to the formation of the oxidising agent MnO₃⁺. The solution was then left to cool back down to 0 °C while stirring. The reaction mixture was then heated to 50 °C (oil bath), covered, and left for 1 day. Upon return, the solution had turned into a brown paste, indicating complete consumption of MnO₃⁺. The paste was then diluted with DI water slowly (120 ml), turning the solution dark brown with pale lilac manganite crystals visible on the bottom of the glassware. The reaction mixture was left stirred for an hour, after which time the manganite crystals had dissolved back into the solution. 35.5% H₂O₂ (9 ml) was added to the solution, causing vigorous foaming and a colour change to bright yellow. The solution was stirred for 30 minutes at a warm phase (50 °C), and then maintained at 50 °C for an additional 30 minutes without stirring. The GO solid was separated from the liquid by centrifugation followed by decantation. The GO was then washed in dilute (3.4%) HCl acid (750 ml) to remove any remaining
salts, followed by further washing in DI water (~950 ml) until the washings were pH neutral. GO was then freeze-dried under vacuum for 7 days. A typical yield of this method can reach 150%.

2.2.3 Synthesis of thermally exfoliated graphene oxide (exfGO)

ExfGO was produced through a thermal shock process in a preheated vertical tube furnace at 300 °C. Each batch of GO sample (500 mg) was loaded into a glass tube under ambient atmosphere. Then the tube was covered with folded paper towel and loosely sealed with a metal clamp. The tube was covered in order to prevent the sample from escaping while releasing generated gases and avoid pressure build-up. The tube was then placed into the tube furnace vertically. The first exfoliation can be observed within 1-2 minutes with a sudden exploding sound and the tube filled with fluffy black powder. Glass tube was kept in the furnace for a further one minute to ensure complete reduction process. The whole process can be finished within 5 minutes. After removing the tube from furnace and allowed to cool down, the exfoliated sample was carefully collected and weighed.
2.2.4 Thermal annealing of graphene oxide

Thermal annealing was carried out by putting certain amount of exfGO in a tube furnace using a ceramic crucible under N\textsubscript{2} flow. The temperature was increased by 5 °C per minute until reaching 600 °C and was kept at 600 °C for 6 hours. The sample was then naturally cooled down to room temperature under N\textsubscript{2} flow.

2.2.5 Synthesis of activated graphene oxide (actGO)

Activated graphene oxide (actGO) was produced from thermally exfoliated GO (exfGO) through chemical activation using 7M KOH solution\textsuperscript{,74,75} 400 mg exfGO was added to in 20 ml KOH (7M) solution\textsuperscript{,76} The solution was stirred for 4 hours and left soaked for 20 hours at room temperature to ensure complete contact of the activator KOH with exfGO. Surplus solution was removed by filtration and the deposit was dried in 100 °C oven overnight. The solid was then put in a ceramic crucible and transferred into a tube furnace for thermal activation. The furnace was heated to 800 °C at a rate of 3 °C/min under N\textsubscript{2} flow and held for 1 hour. 800 °C was used as it is the optimum temperature to obtain actGO with the highest BET surface area and pore volume as indicated in the literature\textsuperscript{,77,78} Then the furnace was naturally cooled back to room temperature under N\textsubscript{2} flow. After the activation process, the sample was washed with distilled water until pH neutral and dried at 100 °C overnight.

2.2.6 Synthesis of MOFs carbons

**MOF-5 (DEF) synthesis**

18.9 g of zinc nitrate tetrahydrate and 4.05 g of terephthalic acid were dissolved in 900 ml of N, N-diethylformamide (DEF) and distributed into 3 x 500 ml ISO blue cap borosilicate glass bottles (autoclavable to 140 °C, Simax). The tightly sealed bottles were left in an oven for 48 h at 100 °C. After decanting the hot mother liquor and rinsing with DEF, the product was immersed in chloroform and dried in small sample
vials at 80 °C in vacuum oven. The sample was then stored in argon filled glove box for further use.\textsuperscript{33}

\textbf{MOF-5 (DMF) synthesis}

21 g of zinc nitrate tetrahydrate and 4.5 g of terephthalic acid were dissolved in 1 L of N, N-dimethylformamide (DMF) and distributed into 3 x 500 ml ISO blue cap borosilicate glass bottles (autoclavable to 140 °C, Simax). The tightly sealed bottles were left in an oven for 48 h at 100 °C. After decanting the hot mother liquor and rinsing with DMF, the product was immersed in chloroform and dried in small sample vials at 80 °C in vacuum oven. The sample was then stored in argon filled glove box for further use.

\textbf{Zn-MOF-74 synthesis}

10 g of zinc nitrate tetrahydrate and 2.5 g of 2,5-dihydroxyterephthalic acid were dissolved in 500 ml of N, N-dimethylformamide (DMF) and 25 ml of deionized water in a 2x 500 ml ISO blue cap borosilicate glass bottle (autoclavable to 140 °C, Simax). The tightly capped bottles were placed in an oven at 100 °C for 48 h. After decanting the hot mother liquor and rinsing with DMF, the product was immersed in methanol for 6 days, during which the methanol was decanted and freshly replenished 6 times. The product was dried in a small sample vial at 80 °C in vacuum oven. The sample is highly sensitive to moisture in the air, with decomposition occurring when exposed to the atmosphere due to the metal linker bond hydrolysis. Therefore, the MOF precursor was stored in argon filled glove box for further use.

The MOF carbons were obtained by direct carbonisation of MOF precursors. In the carbonisation process, MOF samples of 3 g each were placed in an alumina boat and transferred into a horizontal tube furnace. As the MOF samples are highly sensitive to air, the weighing and transfer processes were carried out in glove box. The furnace tube was closed with a gas feedthrough end seal and the sample area was thoroughly purged with nitrogen. The nitrogen flow was maintained throughout the reaction, lasting about 24 hours. The carbonization was carried out at 1000 °C and 1100 °C with a dwelling time of 6 h at a ramping rate of 5 °C min\textsuperscript{-1}. The obtained
carbons treated ≥900 °C were clean from impurities and were metal free as confirmed by XPS surface analysis, thus no further acid treatment was needed.

2.2.7 Chemical modification of carbon substrates

Carbon substrates introduced in previous sections were chemically modified using wet amine impregnation method. Pentaethylenehexamine (PEHA) and tetraethylenepentamine (TEPA) are long straight chain amines with high amine group density and were selected for amine impregnation in this study. The polymers were diluted to a 10 wt% solution of 1 g PEHA/TEPA per 10 ml methanol. 10 mg exfGO/actGO was carefully weighed using a 5-digit balance and put into a small glass vial. The required amount of diluted amine solution to designated ratio was directly dropped into the glass vial using a pipette. The mixture was then topped up with methanol and stirred on a shaker overnight to ensure complete mixing, as shown in Figure 4.5 a). For example, actGO was mixed with 10 wt% PEHA (1 g per 10 ml) with the ratio of 1:1; 1:2; 1:3; 1:4. Each sample contains 10 mg actGO, which means 0.1 ml, 0.2 ml, 0.3 ml and 0.4 ml of 10 wt% PEHA being added to each sample respectively. The mixture was then dried in a 60 °C oven to allow methanol to evaporate. After most methanol evaporated, the glass tube was transferred into a vacuum oven to allow further complete drying.
Chapter 1 & 2 References


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Chapter 3 Synthesis and properties of graphene oxide (GO) with various degrees of oxidation

3.1 Introduction

Graphene is a 2D atom-thick layer of carbon with extended honeycomb network structure. It has attracted extensive research interests due to its extraordinary thermal conductivity, mechanical, optical and electrical properties since 2004 when few atoms thick monocrystalline graphitic films were first prepared.\(^1\) Since their discovery, graphene-based materials have been widely regarded as promising and scalable materials to obtain desirable structures.\(^2\)-\(^5\) GO has graphene networks from graphite enriched with reactive oxygenated functional groups generated from graphite. Chemical modification of GO has been a promising route to achieve mass production of chemically modified graphene.\(^6\) GO has successful applications in various industrial fields such as electronics, conductive films, electrode materials, and composites.\(^7\),\(^8\) Graphene-based materials have good chemical and mechanical stability, which have also been considered promising as membranes due to its ultimate thinness. Separation membranes therefore can minimise transport resistance and maximize flux.\(^9\)-\(^11\) GO structures are synthesized by a top-down approach of graphite oxidation followed by chemical or thermal reduction. Thus, the achievable conductivity and porosity in the final graphene-based networks is directly related to the strengths of the oxidation of the starting graphite and the reduction (of GO) processes. Graphene-based materials have attracted great attention in the flue gas separation industry and have obtained good achievements so far, which make them very promising for further development and future usage instead of liquid amine scrubbing technologies.\(^12\)-\(^14\)

Commonly used GO synthesis methods include Hummers' method, modified and improved Hummers' method.\(^15\)-\(^17\) The differences between these methods are the types of oxidising reagents and the amount of oxidising reagent used to treat the graphite precursor. Hummers' method (KMnO\(_4\), NaNO\(_3\), H\(_2\)SO\(_4\)) is the most common
method used for preparing GO. Improved Hummers’ method excludes the NaNO₃, doubles the amount of KMnO₄, and performs the reaction in a 9:1 mixture of H₂SO₄/H₃PO₄ improving the efficiency of the oxidation process. In modified Hummers’ method, a new component K₂S₂O₈ has been introduced to the reaction system to maintain the pH value. The oxidation degree of the reaction product largely depends on the synthesis procedure. However, to the best of the author’s knowledge, no research has clearly addressed the effects of oxidising reagents on GO products. Therefore, in this chapter, the effects of reagents on GO products have been studied.

Materials that are able to reversibly absorb and desorb water from the atmosphere could provide a vital source of drinking water in water scarce areas, such as in desert regions. In recent years, water harvest from atmospheric water has attracted research interests due to climate change causing increasing aridity in certain regions on earth. GO has high potential to absorb and store water molecules owing to the oxygen-containing functional groups on its hydrophilic surface. By comparing the functional groups and intrinsic properties of GO samples obtained from various characterisation techniques, the water absorbing capacity of GO with different degrees of oxidation was studied and possible mechanisms were suggested. The moisture level of GO can also greatly affect the CO₂ capture efficiency which is studied in the later chapters. Therefore, it is important to study water adsorption capacity of GO.

It can also offer energy-efficient air conditioning. Currently, the highest water uptake that can be achieved by MOF (Co₂Cl₂ (BTDD)) is 97 wt% at relative humidity (RH) ~80%.[18] Another MOF sorbent could deliver 82 wt% below 30% RH.[19] Static water adsorption at RH > 50% of a zirconium-formate possesses working capacity of 12 wt%.[20] Water absorbing materials have various applications, for example, room humidity modifier in a closed environment and self-powered electronics.[21] An ideal water adsorption system should be powered by low grade, renewable, and abundant energy sources (e.g. solar-thermal heating). These conditions require materials with a large working capacity.[22] Besides, the asymmetric moisturizing of a two-sided GO film can induce self-charging as a moisture-electric power generator with a voltage...
output up to 2 V, which is high enough to power commercial liquid-crystal displays (LCDs) for portable electronic devices. The capability of generating power based on such a simple fabrication process holds promise for a significant reduction in the cost of existing power generation systems while opening up new extensive applications in stimuli-responsive materials, self-powered electronics and water/vapour management.\textsuperscript{21}

In general, this chapter has exploited GO properties from two aspects. The first part discussed the effects of each possible variables on the synthesis of GO, particularly the degrees of oxidation. The latter part investigated the water absorbing capability of GO with different degrees of oxidation. The water uptake property was investigated using thermogravimetric analysis (TGA), and in-house set-up for long period weight recording.

### 3.2 Results and discussion

#### 3.2.1 Synthesis of graphene oxide

Following improved Hummers' method (section 2.2.2), two of the synthesis steps were controlled as variables, one being the oxidation level and the other one is whether to add H\textsubscript{2}O\textsubscript{2}. Oxidation level was controlled by adjusting the amount of oxidising agent K\textsubscript{MnO\textsubscript{4}} to the concentrated acid and graphite powder mixture. Whether adding H\textsubscript{2}O\textsubscript{2} at the last step was to study the effect of H\textsubscript{2}O\textsubscript{2} to the oxidation degree and product morphology. The K\textsubscript{MnO\textsubscript{4}} used for each sample was from 0 wt. equivalent to 6 wt. equivalent to convert 1 wt. equivalent of graphite into GO. The samples were labelled as GO-R0, R1, R2, R2.5, R3, R4, R5, R6 and R6-no H\textsubscript{2}O\textsubscript{2} respectively according to the amount of K\textsubscript{MnO\textsubscript{4}}/H\textsubscript{2}O\textsubscript{2} added to the precursors during synthesis. From GO-R3 and above, the graphite interlayers swelled up after 3-day oxidation and turn into pastes. The magnetic stirrers were trapped in the paste with gentle wobble. Please note R2.5 sample is synthesized at a later stage to confirm the relatively large gap in properties of sample R2 and R3 such as interlayer spacing.
(Figure 3.6), Raman spectrum (Figure 3.7), FTIR spectra (Figure 3.9) and XPS spectrum (Figure 3.10).

The effects of temperature and length of oxidation on the GO have been studied previously by peer literatures and our group. Low temperature ($T= 0 \, ^\circ C$) affects the exfoliation process of producing GO while high temperature ($T= 30 \, ^\circ C$) helps the exfoliation process and single layered GO can be synthesized.\textsuperscript{23} In another study, the increasing synthesis temperature from 60 $^\circ C$ to 75 $^\circ C$ destroyed the plate-shape structure of graphene, deforming it into a defragmented shape similar to carbon black.\textsuperscript{24}

![GO synthesis with varied degree of oxidation by varying the ratios of graphite and KMnO$_4$. Photos showing GO samples from GO-R0 to GO-R6. Large photos are samples kept in 50 $^\circ C$ oil bath for three days after adding KMnO$_4$. The right corner inserts are samples at the stage after adding water and H$_2$O$_2$.](image)

From me and my colleague’s previous study, it is found that the length of oxidation stage has significant influence on the oxidation level.\textsuperscript{25} The rate of diffusion of the oxidizing agent into the graphite interlayer galleries is significantly lower than the rate of the chemical reaction itself.\textsuperscript{26} Traditionally, 24 hours of oxidation is commonly
used, but it is found that longer oxidation time can allow more complete oxidation. However, oxidation rate slows down at a near complete state after three days, further extended time period will not make large difference. Therefore, each sample prepared has been placed at 50 °C in an oil bath on hot plate for three days before finishing the oxidation.

Oxidising process is to introduce oxygen content into the graphene lattice with formation of C—O covalent bonds. GO is synthesized from bulk graphite, where individual graphene layers are closely aligned and stacked. The mechanism of GO synthesis consists of three distinct steps. The first step is conversion of graphite into a stage-1 H$_2$SO$_4$-graphite intercalation compound (GIC). This step begins immediately upon exposing graphite to the acidic oxidising medium. The layered graphite precursor has strong in-plane chemical bonds but weaker inter-layer interactions. The interlayer galleries at this stage are closely packed with H$_2$SO$_4$ molecules and HSO$_4^-$ ions. The second step is conversion of the stage-1 GIC to oxidised graphite, which is defined as pristine graphite oxide (PGO). This step involves diffusion of the oxidising agent into the preoccupied graphite galleries. This step is the rate-determining step of the oxidation process, which makes the entire process diffusion-controlled. The third step is conversion of PGO into conventional GO after exposure to water, which involves covalent sulphates and loss of all interlayer registry.

A photograph of all eight samples after drying is shown in Figure 3.2., from left to right being samples GO-R0 to GO-R6-no H$_2$O$_2$ (different label method written on sample vial). A change in colour from silvery black to black, to blackish brown and brownish yellow can be observed due to different levels of oxygenated functional groups. Each sample tube contains GO sample of same weight, with higher oxidised samples also showing higher volume.

Each sample vial is packed with same weight of GO powder with gentle tapping. The photograph shows clear sample volume and colour change in Figure 3.2. Please note the written labels on the sample vial are not corresponding to the ratio of oxidising agent.
GO oxidation is a diffusion-controlled process and the diffusion of the oxidising agent into the preoccupied graphite galleries process depends on the size of the graphite flakes. Therefore, for the same source of graphite with a range of sizes, small flakes are oxidised significantly faster than large flakes. While the edge-to centre propagation speed is the same for small and large flakes, the percentage of the entire unoxidized region is significantly reduced for small flakes than large flakes.

![Figure 3. 2. Digital photographs of the as-synthesized GO samples of different degrees of oxidation.](image)

Considering the mesh size and structural characteristics of graphite precursor from different sources, the oxidation degree of the as-synthesized graphene oxide may vary. In general, highly crystalline graphite powders are harder to oxidise than the more disordered ones. It is also worth noting that manganese content in KMnO$_4$ is never detected in the water-washed GO samples by XPS. This suggests that manganese does not form any stable functionalities on the GO basal planes.

### 3.2.2 Physical properties

The samples were labelled as GO-R0, R1, R2, R3, R4, R5, R6 and R6-no H$_2$O$_2$ respectively according to the amount of KMnO$_4$/H$_2$O$_2$ added to the precursors during synthesis. In this set of experiments, GO-R6 was synthesized using standard improved Hummers' method in large batch of 20 g graphite powder, obtaining 29.7 g GO with a yield of 148.5%. The large batch was made to test the lab-scalability of
GO synthesis. In previous experiments, GO samples were repeatedly made in smaller batches of 2 g or 5 g under similar conditions using the same graphite source. Interestingly, small batch products have more desirable physical properties than the larger-scale samples such as higher oxygen content, surface area and pore volume. It is predicted that large batch synthesis may encounter incomplete stirring due to limited selection of experiment apparatus. A comparison of main properties between samples are listed in the Table 3.1 below. Small batch GO with modification was used for a set of experiments as solid-state CO$_2$ absorbents in the previous study.\textsuperscript{25}

Most properties of small batch synthesized GO are more desirable as solid sorbents than the large batch GO in terms of oxidation level (refer to Table 3.1). However, in order to be consistent with the experiment conditions with other samples in this set of experiments and minimise the system error of characterisation techniques, the large batch made GO is used for comparison in this chapter.

### Table 3.1 A comparison of physical properties between small batch and large batch synthesized GO and exfGO using the improved Hummers’ method.

<table>
<thead>
<tr>
<th>Properties</th>
<th>Small batch GO</th>
<th>Large batch GO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Interlayer spacing</td>
<td>9.2 Å</td>
<td>7.8 Å</td>
</tr>
<tr>
<td>Carbon/oxygen content</td>
<td>68.7 at%/ 31.3 at%</td>
<td>68.71 at%/ 31.29%</td>
</tr>
<tr>
<td>% mass change at 500 °C</td>
<td>57.5%</td>
<td>53.7%</td>
</tr>
<tr>
<td>Total pore volume of exfGO</td>
<td>6.10 cm$^3$ g$^{-1}$</td>
<td>5.22 cm$^3$ g$^{-1}$</td>
</tr>
<tr>
<td>Specific surface area of exfGO</td>
<td>830 m$^2$ g$^{-1}$</td>
<td>643 m$^2$ g$^{-1}$</td>
</tr>
</tbody>
</table>

The morphology of various oxidised GO samples was characterised by SEM technique (Figure 3.3). As-synthesized samples, in powder form, were directly stuck onto a metal sample holder using carbon tape. Since GO has C/O ratio of 2:1, it is considered non-conductive therefore does not have enough electron conductivity. Gold coating was performed under argon gas purge in order to increase the surface conductivity and make details visible to the scanning microscope under high magnifications.
Figure 3. SEM micrographs of samples GO-R0 to R6 with different degrees of oxidation with 2000x to 5000x magnifications.
A set of SEM micrographs for GO-R0 to R6 samples is shown in Figure 3.3. The as-purchased graphite powder used as precursor is bulk flake with specification of particle sizes ≤20 µm. GO-R0 sample, followed the process of improved Hummers’ method without addition of oxidising agent, does not have apparent changes to structure and appears to be thick bulk particles similar to graphite powder as seen in literature. The edges of graphite is more vulnerable than the centre, which the oxidation process follows an edge-to-centre reaction propagation. The edges of GO synthesized with addition of strong oxidising agent are visibly opened to large voids and are randomly aggregated and crumpled. For GO-R2 onwards, the edges of GO become less ordered and graphene layers at the edges expanded, showing the edges of the graphite have encountered acid attacking and undergone an oxidation process. The reduced flake size of GO-R0 to GO-R6 compared to graphite flakes is predicted to be partially caused by mechanical stirring of the solution using magnetic bar under long duration of three days. The addition of defects can also breakdown the structures. GO-R3 and latter samples do not have visible difference in structure by SEM characterisation, all displaying highly agglomerated wrinkled structure.

The GO exfoliation process is associated with an exothermic reaction, where a highly enhanced exothermicity occurs at the decomposition point of GO. A relatively higher exothermicity is observed for the highly oxidised samples compared with the less oxidised samples during the exfoliation process, GO-R3 to R6 caused small exploding sound while GO-R0 to R2 were quiet during the whole process. The release of heat with TG heating confirmed the observation as shown in Figure 3.16. Besides, products appeared to be fluffier for highly oxidised samples, both from naked eye observation and SEM imaging (Figure 3.4).
Figure 3. 4. SEM micrographs of exfoliated samples exfGO-R0 to R6 with different degrees of oxidation.
Since the GO structure incorporates surface oxygenated functional groups and hydrogen bonded interlamellar water molecules, the sudden volatility of these labile species leads to a pressure build-up between the graphene sheets. Therefore, a highly oxidised GO sample always leads to a high degree of exfoliation, and visibly larger pores and voids. The degree of oxidation of GO precursor had large effect on the development of porosity. The SSA and the total pore volume were linearly increased with respect to the oxidation of sp² (C=C) carbon into C=O/C—O/COO. Highly oxidised GO showed large pore networked GO layers after thermal exfoliation. For exfGO samples, there are no obvious change in morphology between GO-R0 and R1 while R2 has little expansion, but the difference is still negligible. For R3 and R4, the interconnected structure of exfGO starts to appear. With higher oxidation degree, exfGOs can achieve more complete exfoliation therefore higher expansion.

The surface morphology of as-synthesized GOs with different degrees of oxidation was examined using TEM. All samples were prepared by ultrasonication in water to allow uniform dispersing. Then the solution was dropped onto the square mesh copper TEM grid. The sonication treatment can be regarded as a further reduction and exfoliation process.

All samples displayed sheet-like morphology with different degrees of transparency. This is due to the different number of layers present in the stacked structure. Sample GO-R0, R1 and R2 contains less oxygenated functional groups, of which the exfoliation into monolayers or few layered structures was limited. Therefore, the transparency of these samples is lower than other samples. With the increase in oxidation level, higher amount of oxygenated functional groups allows them to be exfoliation into few-layered structure, therefore GO-R4 to R6 samples appears to have high transparency.
Figure 3. 5. TEM micrographs of GO samples GO-R0 to GO-R6 with different degrees of oxidation.

XRD analysis was used to characterise the crystalline structure of as-synthesized GO samples. XRD patterns of GO with different oxidation ratios are shown in Figure 3.6. The interlayer spacing of GO is calculated according to the Bragg’s law and the calculated values are listed in the Table.3.2. With the increasing degree of oxidation by adding higher ratio of oxidising agent, the interlayer spacings have a generally increasing trend, from 3.4 Å to 8.3 Å. The increasing interlayer spacing of the GO samples suggests that different levels of oxygen containing groups were attached to the graphite lattice.
Pristine graphite has a typical 2θ at 26.7°, which corresponds to 3.35 Å d-spacing. The GO-R0 sample exhibited a sharp diffraction peak centred at 2θ at 26.4°, corresponding to the (002) graphite plane composed of well-ordered graphene with an interlayer spacing of 3.37 Å. R1 sample’s peak slightly shifted to lower 2θ compared with graphite due to acid attack caused interlayers to expand slightly. When oxidising agent KMnO₄ is added to the system, it can substitute the acid penetrated through the graphene layers.

With the addition of higher weight equivalent but still insufficient KMnO₄, for example, GO-R1 and R2, the 2θ becomes wider and less noticeable. The broadening at 26.18° and 22.46° are due to the lattice distortion that occurs in the graphite lattice stacking due to mild oxidation. This is because incomplete oxidation causes some regions of graphite have better oxidation than other regions, leading to less crystalline structure.

Table 3. 2. Main peaks of GO and corresponding interlay spacings. Copper K-alpha source was used as the energy source, with a wavelength of 1.5406 Å. An average value of 2θ has been taken for three measurements of each sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ (°)</th>
<th>d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-R0</td>
<td>26.420</td>
<td>3.4</td>
</tr>
<tr>
<td>GO-R1</td>
<td>26.180</td>
<td>3.4</td>
</tr>
<tr>
<td>GO-R2</td>
<td>22.460</td>
<td>4.0</td>
</tr>
<tr>
<td>GO-R2.5</td>
<td>11.360</td>
<td>7.8</td>
</tr>
<tr>
<td>GO-R3</td>
<td>11.585</td>
<td>7.6</td>
</tr>
<tr>
<td>GO-R4</td>
<td>11.255</td>
<td>7.9</td>
</tr>
<tr>
<td>GO-R5</td>
<td>11.405</td>
<td>7.7</td>
</tr>
<tr>
<td>GO-R6</td>
<td>11.285</td>
<td>7.8</td>
</tr>
<tr>
<td>GO-R6 (no H₂O₂)</td>
<td>10.655</td>
<td>8.3</td>
</tr>
</tbody>
</table>

The interlayer distance between GO-sheets is represented by d-spacing, calculated from the 2θ position of (001) peak, positioned around 11°. Interlayer distance with
less oxidised sample is calculated from the 2θ position of (002) peak, positioned above 20°.

From Figure 3.6, the peak intensity of GO-R1 sample has a large drop compared with GO-R0. There are many factors affecting the relative intensity of the spectra. One may due to the multiplicity of Bragg planes. The number of identically spaced planes cutting a unit cell in a particular hkl family is called the plane multiplicity factor. For low symmetry systems, the multiplicity factor is low. Therefore, this indicates the oxidation has led to a less bulk disordered structure of the precursor, while not giving much change to the interlayer spacings. Correspondingly, from Raman spectra in Figure 3.8, the 2D Raman peak indicating stacking of graphene layers also became less visible from R0 to R1 samples. The spacing starts to largely expand from GO-R2 to ~4 Å.

From GO-R2, the peak starts to shift towards lower 2θ with a broad peak around 22°, giving a larger interlayer spacing of 3.95 Å. The peak of R2 has low intensity compared with other samples. At this stage, oxidation reaction occurred but insufficient KMnO₄ was supplied to the reaction, resulting in incomplete oxidation.

It is suggested that there is highly disordered crystalline structure caused by co-existence of high amount of oxidised and non-oxidised sheets. These changes came from the heterogeneous nature of the oxidised graphite comprised of both sp² domains from graphite and the sp³ domains from oxidised graphite.

Up to this point, the sample possesses more graphitic domains and less oxidised domains. Sample R2.5 shows a typical peak of GO at around 11° as well as a broad peak at around 21.5°. It has peaks located in both well oxidised region and non-oxidised region, indicating an overall near sufficient supply of oxidising agent.
Figure 3. 6. PXRD patterns of the GO with different degree of oxidation. Copper K-alpha source was used as the energy source, with a wavelength of 1.5406 Å.

With further increase of oxidation level (GO-R3 to R6), relatively low peaks at 11.5° 2θ appear instead of the peaks around 22°-26° 2θ, corresponding to the diffraction of the (001) GO plane in the c-axis and interlayer separation ≈8 Å.

GO-R3 to R6 samples have similar interlayer spacing, which means the effect of oxidising agent on the interlayer spacing expansion do not have greater change from R3 and above. Interestingly, as confirmed by XRD, sample GO-R6 no H₂O₂ has 0.46 Å interlayer spacing increase compared with GO-R6. It is predicted that H₂O₂ has a great effect on the interlayer spacing of GO. The addition of H₂O₂ quench stops the oxidation reaction and therefore a contraction of graphene layers. As graphite transforms to GO by oxidising agent diffuse into the preoccupied graphite galleries.²⁶ Without addition of H₂O₂ can allow water to slowly dissolve and wash out the impurities without disturbing the layers.

Exfoliated GO losses its crystalline structure and becomes amorphous during the exfoliation process. Therefore, they do not show any characteristic peaks in the detected region and are not discussed in this section.
Raman spectroscopy was used to characterise GO through analysing the vibrational information obtained from the Raman spectrum. It can provide information about the presence of sp²-sp³ hybridization, the chemical impurities, doping, defects, crystal disorder, edge structure, number of graphene layers and curvature, etc.\textsuperscript{27,30} Raman spectra of samples with different oxidation degrees are shown in Figure 3.8.

The Raman spectra of GO have two typical peaks, G band and D band. The D band and G band are related to the vibrations of sp³ and sp² carbon atoms domains respectively.\textsuperscript{26} The G band is located at \(\sim 1580\ \text{cm}^{-1}\) and is caused by the in-plane bond stretching vibrations of the sp² C—C bond in graphitic materials. It is visible in all sp² carbon systems.\textsuperscript{31} It is weak in a single graphene sheet but increases in intensity with the increase in number of layers.

The D band located at \(\sim 1350\ \text{cm}^{-1}\) arises from presence of defects in the graphite material such as bond-angle disorder, bond-length disorder, vacancies and edge defects.\textsuperscript{26,28}

All samples exhibit two remarkable peaks at around 1350 cm\(^{-1}\) and 1580 cm\(^{-1}\) corresponding to the well-defined D band and G band, respectively. From sample R0 to R3, the G band shifts from 1580 cm\(^{-1}\) to higher frequencies (blue shift) by 9 cm\(^{-1}\) from graphite to disordered graphene structures, which are 1585 cm\(^{-1}\), 1588 cm\(^{-1}\) and 1589 cm\(^{-1}\) respectively. It is also observed that R1 and R2 samples' G band peaks are not symmetric and have a small shoulder at higher Raman frequencies. This is due to the mixing of unreacted ordered graphite structure and oxidised disordered graphene sheets.
Figure 3. 7. Comparison of Raman spectra at 514 nm for GO with different degrees of oxidation acquired from selected areas. a) and c) Raman spectra show prominent G band peak at ~1580 cm\(^{-1}\) and D band at ~1360 cm\(^{-1}\); b) and d) spectra around 2D~2700 cm\(^{-1}\) which indicates number of layers.

The second-order Raman feature, namely 2D band, can be found at around 2710 cm\(^{-1}\) for sample R0. The 2D band at ~ 2700 cm\(^{-1}\) is regarded as the secondary Raman feature, which is very sensitive to stacking along the c-axis and the number of stacking of graphene layers.\(^{29}\)

Raman spectra can be used to determine the number of layers for multilayer graphene by the shape, width and position of the 2D peaks. With increasing number of stackings, the band becomes broader as shown in Figure 3.7, this feature can only be observed in samples of R0 and R1. From R2 and above, the doublet is not obvious. Therefore, the Raman spectra indicate the sample has more disordered
and randomly arranged graphene sheets with increased oxidation degrees.\textsuperscript{32,33,34} Samples with a higher oxidising ratio (R4, R5, and R6) have similar Raman spectra, with D band at 1350 cm\textsuperscript{-1} and G band at 1590 cm\textsuperscript{-1}.

Figure 3. 8. Comparison of Raman spectra at 514 nm for exfGO from different oxidation degree GO acquired from selected areas. a) and c) Raman spectra of exfGO with prominent G band peak at ~1580 cm\textsuperscript{-1} and D band at 1360 cm\textsuperscript{-1}; b) and d) spectra around 2D~2700 cm\textsuperscript{-1} which indicates number of layers. The spectra were normalised with respect to D peak.

Raman spectra of exfGO samples are similar to GO’s, which also represent a highly disorder state of the samples. The structure order 2D Raman peak at around 2700 cm\textsuperscript{-1} is also hardly noticeable.
Table 3. Raman $I_D/I_G$ values of sample GO and exfGO-R1 to R6.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$I_D/I_G$</th>
<th>Sample</th>
<th>$I_D/I_G$</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-R0</td>
<td>0.07</td>
<td>exfGO-R0</td>
<td>0.36</td>
</tr>
<tr>
<td>GO-R1</td>
<td>1.05</td>
<td>exfGO-R1</td>
<td>0.63</td>
</tr>
<tr>
<td>GO-R2</td>
<td>0.97</td>
<td>exfGO-R2</td>
<td>1.08</td>
</tr>
<tr>
<td>GO-R2.5</td>
<td>0.81</td>
<td>exfGO-R2.5</td>
<td>/</td>
</tr>
<tr>
<td>GO-R3</td>
<td>0.87</td>
<td>exfGO-R3</td>
<td>0.79</td>
</tr>
<tr>
<td>GO-R4</td>
<td>0.86</td>
<td>exfGO-R4</td>
<td>0.80</td>
</tr>
<tr>
<td>GO-R5</td>
<td>0.84</td>
<td>exfGO-R5</td>
<td>0.76</td>
</tr>
<tr>
<td>GO-R6</td>
<td>0.83</td>
<td>exfGO-R6</td>
<td>0.80</td>
</tr>
<tr>
<td>GO-R6 no H$_2$O$_2$</td>
<td>0.83</td>
<td>exfGO-R6 no H$_2$O$_2$</td>
<td>0.76</td>
</tr>
</tbody>
</table>

The intensity ratio of D and G peak can be used as an indicator of materials’ disorder. Quantification of disorder is usually analysed by the $I_D/I_G$ intensity ratio between the disorder-induced D band and the G band (Figure 3.7-3.8). It reflects the ripples, edges, charged impurities, presence of domain boundaries, and other characteristics of the materials. For edges, the intensity of the D peak depends on the edge structure; it is weak at the zigzag edge and strong at the armchair edge.\textsuperscript{35}

A higher ratio of $I_D/I_G$ normally shows a more disordered graphene structure. GO-R1 and R2 has the most disorder, while fully oxidised samples have similar disorder. This could be due to the breaking of crystallites with initial oxidation resulting in the formation of defect, disorders, sp$^3$ hybridization and changes in crystallinity. Also, GO-R1 and R2 samples’ solution did not turn into paste like other GO samples with swelling GO layers. The magnetic stirrer can easily keep stirring continuously for 3 days, breaking large flakes into small bits. Comparing GO and exfGO samples, except R0 and R2, all other samples have decreased disorder. This may due to the areas selected for testing are limited, exfGO are chaotic in a more macroscopic view.

FTIR is used to characterise the functional groups of sample structures through atom vibrations, as shown in Figure 3.9. The oxygen containing groups have a broad
absorption band at around 3420 cm\(^{-1}\) assigned to hydroxyl group O—H stretching. The absorption peak at 2920 cm\(^{-1}\) is represented by the stretching mode of C—H groups. The absorption peak at 1590~1620 cm\(^{-1}\) and 1720 cm\(^{-1}\)~1740 cm\(^{-1}\) are C═C (sp\(^{2}\)) carbonyl moiety functional groups and C═O stretching of carboxylic respectively. These are two typical peaks of GO. C═O peaks indicate the oxidation degree of graphene oxide.

![FTIR spectra of a) GO-R0 to GO-R6 with different degrees of oxidation and b) exfGO samples.](image)

**Figure 3. 9.** FTIR spectra of a) GO-R0 to GO-R6 with different degrees of oxidation and b) exfGO samples.

Highly oxidised samples, GO-R4 to R6 have stronger C═O peaks than less oxidised samples. In the fingerprint region between 250 cm\(^{-1}\) and 1400 cm\(^{-1}\), the two absorption peaks at around 1380 cm\(^{-1}\) and 1040 cm\(^{-1}\) are assigned to the C—O stretching vibrations. Sample GO-R0 does not have any obvious peaks, indicating the sample is not oxidised. This is also due to the less expanded carbon layers, which water molecules cannot get into. For samples GO-R1 and GO-R2, C═O peaks become visible, indicating limited oxidation of carbon. Samples with higher oxidation degrees have all fingerprint peaks and the result is consistent with XPS surface analysis.\(^{36}\) After thermal exfoliation, the original GO has <15% remaining oxygen and a huge amount of C—C bond have been destroyed due to the formation of CO\(_2\)/CO, therefore exfGO samples do not show much information from the spectra. The O—H bond disappears after thermal shock compared with GO samples, caused
by the removal of O—H and formation of H₂O. The overall decrease in oxygen content is consistent for all samples as confirmed by XPS surface analysis.

XPS surface analysis is essential for analysing the degree of oxidation of the materials. It detects the elemental composition of the top few nanometres surface of the sample. It is assumed that the sample is even throughout the bulk and GO has been fully exfoliated in this study. Elemental compositions for all GO and exfGO samples are summarised in the Table 3.4 below. The trace amount of silicon from impure graphite precursor or system contamination in all samples is either not found or below 1% and is therefore eliminated in the table.

Table 3.4. XPS surface elemental analysis of GO and exfGO samples. An average value is obtained from the spectra measured at three random spots on each sample.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (at%) in average</th>
<th>O (at%) in average</th>
<th>O/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-R0</td>
<td>95.2</td>
<td>4.8</td>
<td>0.05</td>
</tr>
<tr>
<td>GO-R1</td>
<td>86.0</td>
<td>14.0</td>
<td>0.16</td>
</tr>
<tr>
<td>GO-R2</td>
<td>80.0</td>
<td>20.0</td>
<td>0.25</td>
</tr>
<tr>
<td>GO-R2.5</td>
<td>71.4</td>
<td>28.6</td>
<td>0.40</td>
</tr>
<tr>
<td>GO-R3</td>
<td>70.8</td>
<td>29.2</td>
<td>0.41</td>
</tr>
<tr>
<td>GO-R4</td>
<td>69.4</td>
<td>30.6</td>
<td>0.44</td>
</tr>
<tr>
<td>GO-R5</td>
<td>69.3</td>
<td>30.7</td>
<td>0.44</td>
</tr>
<tr>
<td>GO-R6</td>
<td>68.7</td>
<td>31.3</td>
<td>0.46</td>
</tr>
<tr>
<td>GO-R6 (no H₂O₂)</td>
<td>70.5</td>
<td>29.5</td>
<td>0.42</td>
</tr>
<tr>
<td>exfGO-R0</td>
<td>95.5</td>
<td>4.5</td>
<td>0.05</td>
</tr>
<tr>
<td>exfGO-R1</td>
<td>87.2</td>
<td>12.8</td>
<td>0.15</td>
</tr>
<tr>
<td>exfGO-R2</td>
<td>85.4</td>
<td>14.6</td>
<td>0.17</td>
</tr>
<tr>
<td>exfGO-R3</td>
<td>87.5</td>
<td>12.5</td>
<td>0.14</td>
</tr>
<tr>
<td>exfGO-R4</td>
<td>87.0</td>
<td>13.0</td>
<td>0.15</td>
</tr>
<tr>
<td>exfGO-R5</td>
<td>88.4</td>
<td>11.6</td>
<td>0.13</td>
</tr>
<tr>
<td>exfGO-R6</td>
<td>87.1</td>
<td>12.9</td>
<td>0.15</td>
</tr>
<tr>
<td>exfGO-R6 (no H₂O₂)</td>
<td>87.7</td>
<td>12.3</td>
<td>0.14</td>
</tr>
</tbody>
</table>
With the increase of oxidising agent to 2.5 wt. equivalent, O/C ratio has a successive increase from 0.05 to 0.4. Most oxygen atoms are bonded to the graphite surface and edges and propagate to the centres, thus the graphite interlayers are expanded when oxidised. Increased oxidation content is consistent with XRD showing the samples have gradually enhanced layer spacings. The exfoliation of GO samples is identified with the reduction of atomic oxygen content, from 31.29% to 12.93%.

In the XPS C 1s fitting spectra shown in Figure 3.11 of GO-R0 to R2 samples, a peak corresponding to C—C stretching at 284.5 eV dominants indicating rare existence of oxygenated functional groups. With increasing of oxidation level, the relative intensity level of C—C peak due to the sp² carbon bond in graphite gradually decreases and the intensity of hydroxyl, carboxyl and epoxy functional groups increases.

Figure 3. 10. XPS C 1s fitting of various degree oxidation GO.
From GO-R2.5 and above, the combined intensity of C—OH and O—C═O functional groups are stronger than C—C groups. These are clear evidences that the oxidation process has introduced these oxygenated functional groups into the graphite system. The hydroxyl and carboxyl on further oxidation have led to the formation of epoxide groups, which results in the increased interlayer spacing, as seen in the XRD results (Table 3.2). The formation of epoxide groups signifies the increase in interlayer spacing and oxidation of graphitic oxide into GO. It also assisted the complete exfoliation of GO into exfGO.

Figure 3.11. XPS C 1s fitting of exfGO-R0 to R5 with various oxidation degrees.

The percentage of oxidation is estimated by deconvolution of the C 1s peak into three peaks representing the C═C/C—C, hydroxy l C—O/C—OH and carboxylic C═O/COO. The increased oxidation degree of GO samples from GO-R0 to GO-R6 is confirmed by an enhancement in the relative increase of the concentration of
C—O/C—OH and C═O/COO atomic percentage at the expense of graphitic C═C/C—C atomic percentage (at%), as seen in Table 3.5.

Table 3.5. XPS carbon functional groups analysis of GO and exfGO samples. The spectra were measured at three random spots on surface of each sample to obtain an average value. The atomic percentage of each functional groups is estimated from the C 1s peaks.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C═O/COO— (288.5-289) eV</th>
<th>C—O/C—OH (287-287.7) eV</th>
<th>C═C/C—C (284.7-285.5) eV</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-R0</td>
<td>11.3</td>
<td>20.4</td>
<td>68.3</td>
</tr>
<tr>
<td>GO-R1</td>
<td>18.8</td>
<td>26.5</td>
<td>54.7</td>
</tr>
<tr>
<td>GO-R2</td>
<td>12.4</td>
<td>31.4</td>
<td>56.2</td>
</tr>
<tr>
<td>GO-R2.5</td>
<td>14.2</td>
<td>36.0</td>
<td>49.8</td>
</tr>
<tr>
<td>GO-R3</td>
<td>10.8</td>
<td>48.0</td>
<td>41.2</td>
</tr>
<tr>
<td>GO-R4</td>
<td>15.1</td>
<td>44.5</td>
<td>40.4</td>
</tr>
<tr>
<td>GO-R5</td>
<td>11.5</td>
<td>46.0</td>
<td>42.5</td>
</tr>
<tr>
<td>GO-R6</td>
<td>13.8</td>
<td>44.8</td>
<td>41.4</td>
</tr>
<tr>
<td>GO-R6 no H₂O₂</td>
<td>11.1</td>
<td>49.0</td>
<td>39.9</td>
</tr>
<tr>
<td>exfGO-R0</td>
<td>13.9</td>
<td>21.4</td>
<td>64.7</td>
</tr>
<tr>
<td>exfGO-R1</td>
<td>20.4</td>
<td>15.9</td>
<td>63.7</td>
</tr>
<tr>
<td>exfGO-R2</td>
<td>21.4</td>
<td>18.6</td>
<td>60.0</td>
</tr>
<tr>
<td>exfGO-R3</td>
<td>18.2</td>
<td>21.5</td>
<td>60.3</td>
</tr>
<tr>
<td>exfGO-R4</td>
<td>31.4</td>
<td>13.7</td>
<td>54.9</td>
</tr>
<tr>
<td>exfGO-R5</td>
<td>31.4</td>
<td>12.0</td>
<td>56.6</td>
</tr>
<tr>
<td>exfGO-R6</td>
<td>31.3</td>
<td>11.1</td>
<td>57.6</td>
</tr>
<tr>
<td>exfGO-R6 no H₂O₂</td>
<td>31.7</td>
<td>11.8</td>
<td>56.5</td>
</tr>
</tbody>
</table>

After exfoliation, the C═C contents of highly oxidised samples experience a significant increase, by ~15%. The relative amounts of hydroxyl C—O/C—OH and carboxylic C═O/COO groups have changed. GO has more hydroxyl groups than carboxylic groups, while exfGO has more carboxylic groups. This is because
carboxylic groups are more stable than hydroxyl groups. During the exfoliation process, the labile hydroxyl groups have broken the bonds.

The N$_2$ adsorption-desorption isotherms (77 K) of GO samples are shown in Figure 3.12. The specific surface area and pore volume of samples were derived from the isotherms. Though oxidation has caused addition of oxygen content into the system and caused expansion of layers, GO still has relatively low specific surface area below 100 m$^2$ g$^{-1}$ and pore volume below 0.1 cm$^3$ g$^{-1}$. Calculated SSA and pore volume of the samples are shown in Table 3.6.

Figure 3. 12. N$_2$ adsorption-desorption isotherms (at 77 K) of as-synthesized GO. All samples show negligible uptake thus show negligible porosity.

After thermal exfoliation, the N$_2$ adsorption amount of exfGO-R3 to R6 have a dramatic increase, exceeding 3500 cm$^3$ g$^{-1}$. Correspondingly, exfGO-R0 to R1 remains low with a slight increase to $<100$ cm$^3$ g$^{-1}$. exfGO-R0 to R2 show negligible uptake thus negligible porosity. These samples were plotted separately in Figure 3.13 right to allow clearly distinguish in a smaller Y-axis range. Samples were outgassed overnight at 80 °C for GO samples and 120 °C for exfGO samples.
Table 3. 6. List of BET specific surface area and pore volume of GO and exfGO samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET SSA (m² g⁻¹)</th>
<th>Total pore volume at P/P₀ of ≤0.994 (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-R0</td>
<td>18</td>
<td>0.08</td>
</tr>
<tr>
<td>GO-R1</td>
<td>19</td>
<td>0.12</td>
</tr>
<tr>
<td>GO-R2</td>
<td>20</td>
<td>0.11</td>
</tr>
<tr>
<td>GO-R3</td>
<td>23</td>
<td>0.05</td>
</tr>
<tr>
<td>GO-R4</td>
<td>62</td>
<td>0.08</td>
</tr>
<tr>
<td>GO-R5</td>
<td>50</td>
<td>0.09</td>
</tr>
<tr>
<td>GO-R6</td>
<td>99</td>
<td>0.11</td>
</tr>
<tr>
<td>GO-R6 no H₂O₂</td>
<td>29</td>
<td>0.07</td>
</tr>
<tr>
<td>exfGO-R0</td>
<td>17</td>
<td>0.09</td>
</tr>
<tr>
<td>exfGO-R1</td>
<td>22</td>
<td>1.40</td>
</tr>
<tr>
<td>exfGO-R2</td>
<td>23</td>
<td>1.20</td>
</tr>
<tr>
<td>exfGO-R3</td>
<td>551</td>
<td>4.51</td>
</tr>
<tr>
<td>exfGO-R4</td>
<td>598</td>
<td>4.35</td>
</tr>
<tr>
<td>exfGO-R5</td>
<td>643</td>
<td>5.22</td>
</tr>
<tr>
<td>exfGO-R6</td>
<td>592</td>
<td>4.22</td>
</tr>
<tr>
<td>exfGO-R6 no H₂O₂</td>
<td>578</td>
<td>4.72</td>
</tr>
</tbody>
</table>

Pore size distribution of GO and exfGO are shown in Figure 3.14 and Figure 3.15. The pores of GO-R0 to R2 samples are mainly distributed in the microporous range while GO-R3 to R6 samples have pores in the mesopore range.
Oxidising process has led to intercalating oxygenated functional groups thus increase in pore sizes. When thermal exfoliation is carried out, the removal of functional groups in the forms of CO$_2$/CO causes expansion between layers and create large pores and voids, leading to enhanced specific surface areas (~600 m$^2$ g$^{-1}$) compared to original GO.

Figure 3. 13. N$_2$ adsorption-desorption isotherms (at 77 K) of exfoliated GO and b) shows the enlarged scale of exfGO-R0 to R2.

Figure 3. 14. Porosity characteristics of GO samples. QSDFT (micro- to mesoporous region) fitting derived pore size distribution (line data on left Y-axis) and cumulative pore volume (dashed data on right Y-axis) curves.
GO with higher oxidation degree are expected to have larger expansion in pore sizes. Pore sizes of exfGO-R0 to R2 extended the range from 1 nm~10 nm to 1 nm~14 nm while exfGO-R3 to R6 have highly hierarchical extended structure with pores distributed across the micro-meso- and macro-porous regions, as shown in Figure 3.15. The porosity characteristics of the samples are further supported by SEM and TEM micrographs.

![Graph showing porosity characteristics of exfGO samples](image)

Figure 3.15. Porosity characteristics of exfGO samples with QSDFT (micro- to meso-porous region) fitting derived pore size distribution (line data on left Y-axis) and cumulative pore volume (dashed data on right Y-axis) curves.

The decomposition behaviour of GO has been investigated using thermogravimetric analysis (TGA). Selected samples were weighed and put into a small alumina crucible with gentle pressing without prior degassing and covered with a matching alumina lid. Samples were loaded at ambient environment and the weight of sample was recorded while the temperature rose from room temperature (25 °C) to 500 °C at rate of 3 °C min⁻¹ under nitrogen flow. TGA graphs show weight profile of powder samples as variation of temperature. Slow increase of temperature at a rate under 6 °C min⁻¹ does not cause the exfoliation process of GO. Therefore, the sample volume in the small crucible does not have visible difference before or after heating. Evaporation of water or combustion of certain elements would occur when the heating temperature exceeds its ignition temperature. The resultant TGA curve was plotted by % mass change against time, indicating the final residue percentage of
the sample. A blank run using empty alumina crucible was taken to correct the background effects.

Figure 3.16. a) TGA diagram of GO samples with different degree of oxidation at heating rate of 3 °C per minute. TGA signal indicates about 50% mass loss at the decomposition point of well oxidised samples. b) DSC curves show sudden exothermic reaction occur during the decomposition of samples process.

Pristine graphite is stable below 600 °C. GO-R0 has <5% oxygen content, which is stable below 500 °C in the TGA temperature range, similar to the thermal behaviour of graphite. Therefore, it does not show any visible mass loss in the test. The TGA curves of GO shown in Figure 3.16 a) can be regarded as sample weight decreased through four stages. Stage I is from 25 °C to 100 °C, where no obvious change occurs in sample weight. Sample weight starts to decrease as the temperature exceeds 100 °C. A shallow slope occurs from 100 °C to 150 °C, which is regarded as Stage II. The loss of mass is due to hydroxyl group being oxidised to the corresponding carboxyl group in this temperature range. Water molecules absorbed at the surface or trapped between the graphene layers are also slowly evaporated. The higher decrease of highly oxidised sample shows they have higher water adsorption capacity. At Stage III at around 180 °C to 260 °C, a sharp drop in mass occurs due to decomposition of labile oxygen-containing functional groups, such as alcoholic hydroxyl, carboxyl, carbonyl and epoxy groups, yielding CO and CO₂. The
decomposition is because the single bond between carbon and oxygen of the hydroxyl group is weaker than the double bond between carbon and oxygen of the carboxyl group.³⁷ At Stage IV, the weight change slows down, showing a relatively stable state after oxygen-containing functional groups are removed. The remaining weight at this stage is mainly carbon skeleton of GO. Well-oxidised samples can lose more than half of its original weight. After TGA, GO samples GO-R0 to R6 reveals a gradual change in the final residue mass. The samples display a good trend of final weight loss amount at 500 °C, which is highly consistent with their degrees of oxidation. Samples R0 to R6 have final weight losses of 0%, 4.8%, 10.8%, 46.6%, 49.2%, 49.6%, 53.7% and 50.0%, respectively. Highly oxidised samples show ~50% weight loss due to consumption of carbon skeleton by oxygen at high temperature.

Table 3.7. Weight comparison of each GO sample after thermal exfoliation treatment or TGA tests. Each GO thermal exfoliation batch is 500 mg in powder form.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Weight after thermal exfoliation (mg)</th>
<th>% weight loss by thermal exfoliation</th>
<th>% weight loss by TGA At 500 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-R0</td>
<td>496.2</td>
<td>0.8</td>
<td>0</td>
</tr>
<tr>
<td>GO-R1</td>
<td>476.4</td>
<td>4.7</td>
<td>4.8</td>
</tr>
<tr>
<td>GO-R2</td>
<td>385.7</td>
<td>22.9</td>
<td>10.8</td>
</tr>
<tr>
<td>GO-R3</td>
<td>220.5</td>
<td>55.9</td>
<td>46.6</td>
</tr>
<tr>
<td>GO-R4</td>
<td>195.3</td>
<td>61.0</td>
<td>49.2</td>
</tr>
<tr>
<td>GO-R5</td>
<td>196.5</td>
<td>60.7</td>
<td>49.6</td>
</tr>
<tr>
<td>GO-R6</td>
<td>203.0</td>
<td>59.4</td>
<td>53.7</td>
</tr>
<tr>
<td>GO-R6 (no H₂O₂)</td>
<td>196.7</td>
<td>60.7</td>
<td>50.0</td>
</tr>
</tbody>
</table>

The Table 3.7 above shows the weight of exfGO collected after thermal exfoliation of each GO sample at 300 °C. GO structure incorporates surface oxygenated functional groups and hydrogen bonded interlamellar water molecules. ExfGO samples show low oxygen content (~10%) confirmed by XPS (table 3.4). The sudden volatility of these labile species leads to a corresponding weight loss of samples.
After thermal shock, exfoliated sample was collected and weighed. However, certain product sticks to the glass tube or paper towel, which is hard to collect. Therefore, the product weight loss is higher than that of by TGA and has an error range of ±3% by estimation. From Table 3.6 above, weight loss measured by TGA and by direct exfoliation shows similar trend.

![Graph](image)

Figure 3.17. a) TGA curves and b) DSC curves of GO-R3 and R5 samples at heating rate of 3 °C per minute

The differential scanning calorimetry curves show that the decomposition of GO is exothermic. The decomposition of labile oxygen-containing functional groups, such as carboxyl groups and epoxide groups, causes sudden release of energy. The highly exothermic nature of well oxidised samples leads to the explosive nature of decomposition. Initially, sample of >9 mg was packed by pressing in a 70 µl TGA crucible. Highly oxidised samples exfoliated causing a sudden loss in mass and certain amount of exfGO escaped from crucible into the chamber (Figure 3.17). Since the amount of energy released is represented by the area under peak, it can therefore be concluded that the exothermic heat is enhanced with increased degree of oxidation of GO.

### 3.2.3 GO water uptake properties

The laminated structure of GO can have interactions with water molecules which enables GO to possess excellent water uptake. Through observation from previous
experiments such as degassing treatment and thermogravimetric test, it is found that GO with different degrees of oxidation has varying water uptake. It is suggested that the expandable interlayer spacings and functional groups in GO laminates may affect the property. Therefore, the water adsorption capacity of GO with different degrees of oxidation has been studied using two approaches in this section. A possible mechanism of water adsorption of the material is also suggested. Suggested water adsorption mechanisms in GO follow the steps of (i) physisorption in the form of layers and clusters and (ii) capillary condensation.

GO sheets consist of a large number of pinhole defects resulted from the oxidation synthesis process, which allow water molecules to pass through freely. There are two main water transport pathways through GO laminates, which are through (i) pinhole defects, that circumvent the need for water to travel the entire lateral dimension of individual sheets and/or (ii) regions arising from imperfect stacking in the laminates. Hydrophilic polar functional groups such as alkoxy groups and water molecules trapped in between layers have attraction to water molecules.

Figure 3. 18. TGA curves of water uptake of GO-R0 to R6 samples. Moisture was supplied by pumping nitrogen gas through a DI water tank. Sample weight change was recorded by TGA. Tested at room temperature between 22 °C and 25 °C.
Table 3.8. Water uptake by weight % of GO samples at various degrees oxidation measured by TG using humid nitrogen gas at room temperature. Data corrected with balance weighing data and background test. The uptake % was calculated with reference to the dry sample weight.

<table>
<thead>
<tr>
<th>Sample</th>
<th>GO-R0</th>
<th>GO-R1</th>
<th>GO-R2</th>
<th>GO-R3</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG water uptake %</td>
<td>3.5</td>
<td>5.8</td>
<td>20.5</td>
<td>40.4</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>GO-R4</th>
<th>GO-R5</th>
<th>GO-R6</th>
<th>GO-R6 no H₂O₂</th>
</tr>
</thead>
<tbody>
<tr>
<td>TG water uptake %</td>
<td>53.6</td>
<td>46.3</td>
<td>65.6</td>
<td>52.0</td>
</tr>
</tbody>
</table>

The cyclic capability of GO-R6 sample was tested by a humidity swing test at constant room temperature. The sample absorbed water when humidified nitrogen gas was supplied, as showed in the blue region in Figure 3.19. When switched to dry gas, water moisture was desorbed. Subsequent water adsorption cycles were not allowed for saturation, but it is found that the initial water adsorption rate for each cycle is similar. This test shows that the water adsorption-desorption process is a reversible reaction for GO samples.

Figure 3.19. Water uptake cycling test using TGA with temperature being maintained at 25 °C. Adsorption and desorption of water were achieved by humidity swing of supplied gas at constant temperature.
The migration of water molecules from the edge to the centre is an extremely slow process. TGA measurement has several limitations when recording long-period measurements in this application. TGA equipment is placed in a non-temperature regulated lab, where daily temperature difference of the lab can be over 10 °C. Water vapour accumulated during daytime inside the TG chamber condense overnight.

The condensed water droplet may drop onto the sample holder during the next test. Therefore, the true water uptake by sample itself cannot be guaranteed over a long range of testing time period. Besides, another limitation is that the maximum humidity that can be achieved by TGA is about 80% RH. Generally, adsorption increases with the concentration in the adjacent fluid.\textsuperscript{39} Therefore, the potential of adsorption has been largely limited by the relative pressure. In order to optimise the performance, a self-assembled apparatus was designed.

In order to reach maximum humidity (100% RH) at room temperature, a new simple setup (Figure 3.20) has been designed to allow water vapour to saturate and reach equilibrium state at room temperature. Samples were placed in the setup for overnight and carefully weighed for the mass change the following day. Multiple readings for each sample were taken during the whole measuring period of two months. The samples gradually reached saturation in 30-day period under 100% RH humidity environment.

At low humidity, functional groups such as hydroxyl and carboxyl groups on the edges of GO flakes begin to adsorb water molecules. Thereafter, water penetrates through GO laminates, forming a monolayer of water on the surface of GO platelets.\textsuperscript{40,41} By further increase of humidity, multilayer adsorption of water molecules begins. Water uptake is observed significantly higher and quicker than in low humidity environment when switched to high humidity. The adsorption capacities were represented by water uptake per unit weight of GO absorbent and has a unit of mg 100 mg\textsuperscript{-1}, which is equivalent to wt%.
Figure 3. 20. A self-made simple apparatus set up for water uptake measurement under 100% RH environment.

The significant increase before reaching the near saturation point is possible due to water molecule condensation in capillary pores of meso-porous materials. Water molecule penetration slows down when one layer of water molecules forms on each GO flake, because the intercalation of water and swelling-up of the laminates requires energy to overcome not only the van der Waals force between GO layers but also the hydrogen bonding of GO-water interface. Friction-free water transport could be achieved in non-oxidised sections of GO nano-channels. Samples with low oxidation degrees do not show high water uptake even at high humidity. This is due to the less oxidised sample bearing fewer functional groups and small interlayer spacing, therefore maintain weak interaction with water vapour. GO-R0 only has <10% water uptake at 100% RH for 30 days.

Increasing the oxidation level of GO increases the hydrophilic functional group contents by enlarging the interlayer space of GO. GO-R6 has the largest interlayer spacing, which allows water molecules to easily permeate and diffuse along the nano-capillaries. Suggested water adsorption mechanisms in GO follow the steps of initial physisorption in the form of layers and clusters is followed by capillary condensation. And the results clearly indicate that samples with high oxygen content have higher moisture adsorption capability.
Figure 3. 21. Room temperature (20-22 °C) water uptake of GO with various oxidation degrees measured over a period of 53 days. The relative humidity was kept at ~50% RH for 13 days then escalated to 100% RH.

The water adsorption capacity of graphite is extremely low as there are no functional groups at the surface and only very small interlayer spacings. Therefore, it has weak interaction with water vapour. Suggested water adsorption mechanism is that hydrophilic functional groups at the surface and edges of GO nanoplatelets first adsorb water molecules. Then the already existing water molecules will attract more water from the environment. Slow migration of water molecules then occurs from edges to centre between the interlayer gaps. This is an extremely slow process and the sample weight can keep increasing continuously for 30 days. GO-R6 sample could absorb water up to 1.3 times of its own weight. GO-R4 and above samples can also absorb water content of their own weights.

Upon removing the samples from the 100% RH environment and placing them in ambient environment (20 °C, ~50% RH) for five days, the weight of the samples decreased, but still higher than the level where it has reached before putting into the 100% humidity environment. This could be due to water trapped between the layers cannot easily escape. The trend of water adsorption uptake in GO is consistent with
their oxidation degrees, highly oxidised GO can adsorb more water than less oxidised ones.

The rate of water adsorption is not only depending on the speed of water entering open GO pores but also controlled by the rate of water transport inside GO laminates. A humidity swing has been observed. When the ambient environment relative humidity decreased, the weight of the sample decreased correspondingly to the saturation level at that humidity. Besides, if dry gas is supplied to the system, the moisture will be taken away, leaving the testing sample dry again. This could allow easy regeneration of GO adsorbents.

Figure 3. 22. Water uptake measurement under 84% RH humidity for 20 days.

To repeat the experiment, selected samples made from the same batch were placed in saturated potassium chloride solution. The humidity fixed points of binary saturated aqueous solution of KCl could give a stable relative humidity of 85.11% ± 0.29% at room temperature (20 °C when the experiments were carried out). Initial water adsorption rate is fast, highly oxidised sample can reach over 30 wt% in one day. The final sample water adsorption uptake is consistent with previous 100% RH tests.
Figure 3.23. FTIR graph of a) GO samples with different degrees of water content; b) left axis: alcohol O-H stretching intensities, right axis: carboxylic O-H stretching intensities against water content; c) GO with different degree of oxidation soaked in water.

The moisture adsorption of GO with different amounts of oxygen-containing functional groups were characterised using FTIR. GO structure does not undergo physical changes when adsorbing moisture. Therefore, water adsorbed can be removed by heating up GO powder.

In addition to the typical GO peaks from Figure 3.9, samples with certain amount of water show gradual change of water characteristics. Liquid water has three vibration modes which are symmetric stretching (3490 cm\(^{-1}\)), asymmetric stretching (3280 cm\(^{-1}\)) and bending of the covalent bonds (1644 cm\(^{-1}\)) as shown by the FTIR spectrum of water. Increased strength of hydrogen-bonding at ~1600 cm\(^{-1}\) will result in an
increased intensity due to the increased dipoles. All the vibrational bands in liquid water are made up from contributions of different components from water molecules in different hydrogen-bonded environments, lower frequency components are attributed to water molecules with stronger hydrogen bonds and higher frequency components have weaker hydrogen bonds. Therefore, water content has a great effect on the intensity of the spectra, as confirmed by Figure 3.23. Variations in the environment around each liquid water molecule and accumulating of the number of hydrogen bonds give rise to considerable line broadening with vibration shifts in a hydrogen-bonded-donating water molecule.

From Figure 3.23 b), by fixing the invariant graphene absorption band around 2000 cm\(^{-1}\), the relative intensity of alcohol O—H stretching (~3250 cm\(^{-1}\)) and carboxylic acid O—H stretching (~2750 cm\(^{-1}\)) were plotted. Liquid water is plotted as 100% water content while saturated GO is plotted as 99% water content. The alcohol O-H stretching suggests loosely attached water molecules increases with the increase of water content in GO samples. As for carboxylic O-H stretching, water molecules form hydrogen bonding with oxygen functional groups on the GO edges and surfaces. Therefore, there is corresponding increase in the intensity with higher water uptake capacity through accumulated hydrogen bonding. Water does not show this peak.

The pristine defect-less region of GO without oxygenated functional groups is hydrophobic, which can be regarded as a friction-less region that allows water molecules to flow freely and achieve ultra-fast flow velocity. GO can continuously suck water in due to this water depleted region and the capillary force between the layers. Also, the hydrogen bonding between the water molecules in the region allows free energy to be much lower than that of the water outside the region, which consequently reduces the energy barrier for water molecules entering the layers.

The oxygenated hydrophilic groups tend to interact strongly with water molecules. Interestingly, some studies believe the carboxyl groups at the edges of flakes and the hydroxyl groups at defect pores may block and reduce the water flux. Meanwhile some studies show hydrophilic groups are also capable of promoting water permeation, specifically the carboxyl groups at the edges of flakes and the
hydroxyl groups at defect pores.\textsuperscript{50} This is because hydrogen bonding can be formed between the —OH groups from GO and water molecules, resulting in ideal entropic conditions for water to either enter nano-channels or pass through defect pores.\textsuperscript{50} In addition, oxygen-containing groups in amorphous regions possess a large content of distorted sp\textsuperscript{3} C—O bonds, resulting in nano-wrinkles and defect pores in GO flakes which offer initial passages through which water can diffuse into GO.\textsuperscript{51,52,53}

### 3.3 Conclusions

GO was synthesized using an improved Hummers' method with different degrees of oxidation. The formation of various oxygenated functional groups at different stages of oxidation and their influence on the chemical and structural analysis were investigated. The enhanced layer spacing of GO samples is confirmed by XRD, increased concentration of epoxy (–C–O–C–), hydroxyl (–C–OH) and carboxylic (–C–O–OH) groups on the graphene basal plane and edge by XPS and Raman spectroscopy, and excess mass-loss and exothermicity during the decomposition in thermal reduction by TG-DSC. The morphological studies using SEM and TEM showed a sheet-like morphology in all stages of oxidation.

The GO structure is tenable by varying the oxidation level and therefore can be purposely synthesized according to the demand. Through experiments carried out in this chapter, the concept that oxygenated functional groups could promote water adsorption has been verified. With the increasing degree of oxidation in GO samples, the water adsorption capacity is significantly improved. Well oxidised GO can suck up to 130\% of its own weight in atmospheric moisture at high relative humidity and desorb water at lower relative humidity. Suggested water adsorption mechanisms in GO follow the steps of initial physisorption in the form of layers and clusters and is followed by capillary condensation. The material could be applied for regulating humidity levels, particularly in confined environments such as aircraft cabins and air-conditioned buildings. Graphene oxide also has good hydrolytic stability, which is stable in water and could be simply dried either by oven heating or preferably by freeze drying.
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Chapter 4 Highly porous carbon substrates derived from graphene oxide (GO) for CO₂ capture

4.1 Introduction

Graphene-based materials have attracted great interests in a wide range of research applications. Since their discovery, graphene-based materials have been widely regarded as promising and scalable materials to obtain desirable structures. A wide range of graphene related materials have been synthesized for potential applications in electronics, energy storage, catalysis, gas sorption, storage, separation and sensing.¹⁻⁴ Among these applications, selective sorption of CO₂ from power plant flue gas is of critical importance in mitigating greenhouse gas emissions.

Current commercially available technologies for CO₂ separation is through liquid amine scrubbing.⁵ The basic process is to allow CO₂ being absorbed from a fuel gas or combustion gas near ambient temperature into an aqueous solution of amine-based polymers. The amine solution is regenerated by stripping with water vapour between 100 °C and 120 °C. Water is then condensed from the stripper vapour, leaving pure CO₂ that can be compressed to 100 to 150 bars for geologic storage. The minimum work requirement to separate CO₂ from coal-fired flue gas and compress CO₂ to 150 bars is 0.11 MWh (3.96×10⁸ J) per tonne of CO₂.⁵ Cost is a main driving force in CO₂ capture technologies. The sorbent regeneration step is the most energetically demanding and expensive component of the overall CO₂ capture process, prompting the development of new sorbent materials with lower regeneration temperatures.⁶

Aqueous amines provide relative strong binding to CO₂, considerably lower than the carbonates of alkali/earth alkali metals, which allows relatively easy regeneration and requires less regeneration energy. Considering pros and cons of the potential replacements, amine impregnated porous solid sorbents emerge as the most promising replacement to liquid amine sorbents. The major advantages of porous
Solid sorbents are 1. easy handling, 2. fast diffusion, and 3. adjustable sorbent chemistry. Speed of recovery is closely related to the ease of regeneration and both are directly proportional to the binding energy. A significant advantage of a solid sorbent is its easy recovery and regeneration.

Sorbents for flue gas capture application include both physisorbent and chemisorbent materials, it has been suggested that physisorbent materials such as zeolites, activated carbons, or metal-organic frameworks (MOFs) typically perform poorly at low CO₂ partial pressures, offering very small CO₂ uptake and low CO₂ selectivity. Various solid sorbents have been examined in the past decade for CO₂ adsorption. For example, monolithic silica as hierarchical pore structure to support amine impregnation. and MOF derived, low-cost support for TEPA/PEI. For chemisorption to occur under dry conditions, two amine groups must be capable of freely interacting with a single CO₂ molecule. This results in the formation of a covalent bond between the species. Physical adsorption only requires an electrostatic interaction between the pore surface/amine site and CO₂ species. In the cases where amine groups are not packed densely enough to allow chemisorption to occur, physical adsorption dominate. Resulting capacities could be far lower than expected since chemisorption is the desired capture mechanism in supported amine sorbents.

Solid carbon structures mostly have been treated at temperature over 300 °C, which exhibit good thermal stability. Therefore, the thermal stability of the solid sorbents is largely dependent on the amine used for chemical modifications. In this project, two amine-based polymers pentaethylenehexamine (PEHA) and tetraethylenepentamine (TEPA) were chosen for their relatively high amine density and thermal stability. Both TEPA and PEHA are straight chain amine-group rich polymers, where TEPA has five amine groups and PEHA has six amine groups per chain. The flash point and boiling point for TEPA and PEHA are 163 °C and 175 °C, 340 °C and 350 °C respectively.

The reaction mechanism for amino groups and CO₂ is well studied, where primary and secondary amines can form carbamate groups with CO₂. Tertiary amines do no
react with CO$_2$, therefore, straight chain amines rather than branched amines were chosen for this purpose. PEHA has a slightly longer chain compared with TEPA due to one more set of amine group, and is therefore more thermally stable due to the increase of melting temperature, molecular weight and force of intermolecular forces.

![Molecular structures of PEHA and TEPA](image)

Figure 4. 1. a) Molecular structure of pentaethylenehexamine (PEHA), Mw = 232.37 (Sigma-Aldrich); b) Molecular structure of tetraethylenepentamine (TEPA), Mw = 189.3 (Sigma-Aldrich).

Different carbon nanostructures have applications as CO$_2$ adsorbents due to their unique surface morphology. GO shows high affinity to amine-based polymers as there are oxygen functional groups on its basal planes and edges. When amine chains attached to the surface of GO, the remaining amine groups can perform gas adsorption capability of acidic gas such as CO$_2$. Though the reaction is favourable, synthesizing porous structure with large pore volume and high specific surface area remains a challenge.

Theoretical amine loading in the substrate material by wet impregnation method is determined by the pore volume of the substrate and density of the chosen amine:

\[
\text{Amine loading on solid substrate (g g}^{-1}\text{)} = \text{specific pore volume of solid sorbent (cm}^3\text{ g}^{-1}\text{)} \times \frac{1}{\rho \text{ polyamine (cm}^3\text{ g}^{-1})}
\]

Through the above relationship, the pore volume of the substrate material is of great importance to achieve maximum CO$_2$ capacity. Therefore, searching for a material with high porosity has been a constant goal in the research area. Open pores (cavity or channel communicating with the surface of a particle) and voids (space or interstice between particles) both contribute to the porosity of a material.

Porosity is defined as the ratio of the total pore volume to the volume of the particle or agglomerate. It is commonly introduced to the solid-state materials by two
methods. One is during the synthesis of the porous material, and the other one is by using sacrificial templates or porogens that are thermally activated. In this chapter, both methods have been applied to GO for obtaining highly porous substrates.

From previous study, direct amine loading triethylenetetramine (TETA) on as-synthesized GO without exfoliation or activation shows a maximum CO$_2$ capacity of only 10 wt% with very slow uptake kinetics at 75 °C under flue-gas conditions.$^{19}$ Direct amine impregnation on GO does not show satisfying results. Nevertheless, with a one or two further processing steps, the performance can be improved significantly.

In general, hierarchical hyperporous networks with ultrahigh total pore volume obtained from GO through various modifications have been demonstrated in this chapter.

### 4.2 Results and Discussion

#### 4.2.1 Synthesis of thermally exfoliated graphene oxide (exfGO)

ExfGO was synthesized following a thermal exfoliation process as described in section 2.2.3. A typical yield of thermal exfoliation of graphene oxide is less than 40%. Since the GO structure incorporates surface oxygenated functional groups and hydrogen bonded interlamellar water molecules, the sudden volatility of these labile species leads to a pressure build-up between the graphene sheets. The pressure causes a sudden expansion of layer spacings, which can be described as exfoliation. The thermal exfoliation process can cause significant volume expansion of the sample, as shown in Figure 4.2.
The GO in the left bottle expanded to the volume of the right bottle after being thermally exfoliated. The exfoliation process is an exothermic reaction. When the tube was heated up, GO exfoliated while releasing large amount of energy. Therefore, by this process, a highly oxidised GO sample always leads to a high degree of exfoliation.\textsuperscript{19}

4.2.2 Synthesis of activated graphene oxide (actGO)

ActGO was synthesized by KOH activation as described in section 2.2.4. The obtained sample weighed about 10\% of the original GO and 20-30\% of exfGO. The volume of actGO was significantly decreased as compared with exfGO due to increased density. Micropores were largely introduced in the process and meso- and macro-pores significantly reduced, showing reduction in volume of the sample, as shown in Figure 4.3. The decrease in pores of actGO was caused by the drastic shrinkage and restructuring of the wrinkled graphene.
The activation process requires strict experiment conditions control. A few batches of activation delivered extremely low yield due to an unnoticeable crack on the furnace tube. During the activation process, the carbon structure was burnt out at high temperature due to air leaked into the chamber. The yield was far lower than expected due to excessive consumption of carbon structure. The white product was crystallised KOH covered unburnt exfGO.
4.2.3 Chemical modification of carbon substrates

Note that for more brief expression, the 1:1, 1:2, 1:3 and 1:4 are expressed as 1x, 2x, 3x and 4x in the latter report. The samples were labelled according to the amine loading with respect to the exfGO/actGO. For example, the loading of 60 mg TEPA for 10 mg exfGO sample was represented by exfGO+6 x TEPA. The group of samples are noted as amine@exfGO.

Figure 4. 5. a) Left to right: actGO (30mg each) mixed with PEHA in the ratio of 1:1, 1:2, 1:3, 1:4 and 1:5, solid substrate was mixed with diluted amine solution and topped with methanol to allow complete mixing; b) vacuum oven dried sample ready to be collected and tested (not the same batch as a).

Amine loading is directly controlled by the pore-structure and volume of the host materials. Maximum CO$_2$ capture capacities are directly governed by sample porosity to facilitate high amine loading, though excessive amine loading, much higher than the pore volume equivalent, does not show favourable CO$_2$ capture properties. This is due to the complete pore filling or increased bulk amine in the large or macro-pores, smeared out active surface area for adsorption and diffusion of CO$_2$, and thus reduces the amine efficiency for CO$_2$ capture. It will not only cause serious pore blockage and CO$_2$ diffusion resistance but also give rise to instability of regeneration performance. For example, GO has low surface area and pore volume as compared with exfGO and actGO. If to modify it with polyamines, the potential for amine loading is very low and can result in sticky product with low or no
CO$_2$ uptake capability even with a 1:1 ratio of amine loading. Also, adsorption-desorption cycle leads to certain amine leaching. This problem may be solved if a proper supporting material can be developed. As stated before, the material should have the properties of high specific surface area and high pore volumes in order to provide more sites to load amine and bind within the connected pore networks.$^{14}$

ActGO powder has large surface area due to large amount of micropores. The amine added fills the spaces and connects the GO particulates. Higher ratio of amine added will result in stickier product. The 3x and 4x samples (Figure 4.5 b) left two samples) were obviously stickier than the 1x and 2x samples (Figure 4.5 b) right two samples).

### 4.2.4 Physical properties

Five batches of GO samples GO-D, GO-E, GO-M, GO-Y and GO-Z used in this chapter were synthesized following the improved Hummers' method as described in section 2.2.2. With the varying conditions such as the amount of precursor per batch, synthesis room temperature, storage length and condition and other possible human errors, there are certain differences in chemical properties among the as-synthesized samples.

Minor difference in properties between each sample can somehow affect the CO$_2$ uptake properties. The overall performance of each sample shows the chemical modification of porous substrates is a promising approach for post-combustion CO$_2$ capture. The GO thermal exfoliation process is associated with an exothermic reaction, where an increase in the heating rate leads to a highly enhanced exothermicity at the decomposition point of GO. GO structures incorporates surface oxygenated functional groups and hydrogen bonded interlamellar water molecules. The sudden volatility of these labile species leads to a pressure build-up between the graphene layers. To be more specific, 40 MPa pressure can be generated at 300 °C. It is predicted that pressure as low as 2.5 MPa is enough to exfoliate a GO platelet.$^{21}$
SEM was used to examine the surface morphology and porosity development characteristics of the samples. An obvious change in morphology can be observed among GO and exfGO samples. The oxygen content in GO reduced from >30\% to \approx14\% in exfGO. As carbon structure are partially lost, the obtained products had increased number of defects throughout the structure. The synthesis method and oxidising agent ratio were same for all GO-D, GO-E, GO-M, GO-Y and GO-Z samples and was the same with GO-R6 in Chapter 3. The XPS surface elemental analysis shows all samples have oxygen content above 30 at\% (Table 4.3). Therefore, SEM images did not show significant difference between the exfoliated samples. SEM images of exfGO samples showed highly networked structure, indicating all samples were properly exfoliated by the method.

Figure 4. 6. SEM micrographs of GO, exfGO and annealed exfGO samples. From top row to bottom row: SEM micrographs of GO-Z, exfGO-Z and exfGO-Z@600°C6h samples, three micrographs in each row are for the same sample.
Thermal annealing treatment modifies the surface morphology of materials with temperature and time. Annealing at 600 °C for 6 hours lead to further removal of remaining oxygenated functional groups with consumption of carbon backbones. The SEM images do not show obvious difference between exfGO and annealed exfGO samples as SEM could not detect inside the pores.

The annealing effect is more effective characterised using BET method and XPS, which shows an increase in specific surface area (SSA) and pore volume as well as decreased oxygen contents. GO-M is the least oxidised GO sample studied in this chapter, the exfoliation is less complete, as shown in Figure 4.7. It is visible that some graphene layers are closely stacked instead of fully exfoliated. A high degree of exfoliation shows large interconnected pore networks. The size of the pore structure is directly associated with the oxidation of the precursor GO samples, where exfGO-M and exfGO-E have the most obvious difference.

Figure 4.7. SEM micrographs of top row: exfGO-M and bottom row: exfGO-M@600°C6h samples.
Figure 4. SEM micrographs of amine impregnated exfGO-Z samples with the same 6.5x loading ratio. Top row: PEHA loading; bottom row: TEPA loading.

Same amount of TEPA and PEHA were loaded into the exfGO structure. The topological polar surface area of TEPA and PEHA are 88.1 Å$^2$ and 100 Å$^2$ respectively.$^{16,17}$

As the molecular structure/chain length of PEHA is larger/longer than TEPA, PEHA is less able to enter the micro- to meso pores, which leads to a coating-like morphology.

The pore structures of all exfGO samples are highly hierarchical, where macro-pores lead to meso-pores and the meso-pores leads to micro-pores. The pores are interconnected, resembling a “kirigami” style structure. The topological polar surface area of TEPA and PEHA are 88.1 Å$^2$ (0.88 nm$^2$) and 100 Å$^2$ (1 nm$^2$) respectively. With these sizes of molecules, the amines can accommodate at mesopores and macropores easily. Due to ultrahigh pore volume, exfGO can accept high amount of amine impregnation without surface wetting, i.e. clogging the pores and becoming sticky. SEM can also confirm that there are still void spaces for a 7.0 g g$^{-1}$ TEPA loading exfGO-E sample. With highly loaded samples, the exfGO pores were filled...
up by amine polymers, where micro- and meso-pores were less distinguishable. Higher amount of amine impregnation showed less exposed pores.

An intermediate product of activation process was examined. With overnight soaking in KOH solution, exfGO has lost its characteristic multilayer hierarchical porous structure. At this stage of the activation process, lots of creases and crinkles are created, while aligned pores are less visible. The carbon structure remains as large interconnected sheets and is not consumed by oxygen yet.

Figure 4. 9. SEM micrographs of top row: exfGO-E; middle row: exfGO-E+6.5xTEPA and bottom row: exfGO-E+7xTEPA samples.
Figure 4. 10. SEM micrographs of actGO precursor. The micrographs were taken on the intermediate stage sample excess KOH solution in exfGO was filtered out before activation with furnace.

After KOH activation treatment at 800 °C, the flakes of GO became smaller and more evenly sized. With higher magnification to 10,000x, actGO could be found in a flaky structure with wrinkles and kinks at the surface. Comparing the images of actGO and actGO+2x PEHA samples in Figure 4.11, it is found that micro-pores and inter-spacing of actGO are filled with polymers. The surface becomes smooth with extremely decreased SSA to 16 m² g⁻¹ and pore volume of 0.03 cm³ g⁻¹ obtained by N₂ isotherms (Table 4.4). However, large holes are not filled, therefore, could still have certain gas adsorption ability.
Figure 4. 11. SEM micrographs of top row: actGO and bottom row: actGO+2xPEHA samples.

Figure 4. 12. TEM micrographs of GO-Z sample. The transparency of the structure was affected by the thickness of structure.

The surface morphology of GO and exfGO was analysed using high resolution TEM (HR-TEM) and selected area electron diffraction (SAED). The samples show thin
sheet-like morphology with different transparencies. This is due to the different number of layers in the stacked structure of GO. The TEM samples were prepared by dispersing powder form sample in water using ultra-sonication to make a very dilute solution. The sonication broke GO structure into thin layers and therefore the minor differences between each GO samples are not obviously distinguishable by TEM images. GO-Z sample is used to represent the series of GO samples.

Figure 4.13. TEM micrographs and diffraction pattern of exfGO-Z sample.

Figure 4.13 shows highly interconnected graphene networks. As the exfoliation process gives GO monolayers or few-layered structure, the transparency is also increased. exfGO displays a ‘flower-like’ interconnected layered structure. The diffraction pattern was used to characterise the crystallinity of nanosized materials. It is observed that the diffraction pattern of exfGO does not show any diffraction spots but concentric rings. This is a typical pattern for materials with no long-range order in the atomic lattice and revealed the polycrystalline nature of the nanosheets. As for thermal annealed sample, the edges of reduced GO layers are more obvious due to increased defect sites. A significant change in morphology occurred to actGO, instead of flower-shaped layers, bulk flakes with numerous micropores was
observed. This shows the KOH activation process introduced large amount of micropores into the system.

Figure 4. 14. TEM micrographs of exfGO@600°C6h sample.

Figure 4. 15. TEM micrographs of actGO sample.

The crystalline structure of the samples can be examined using powder X-ray diffraction (PXRD). Pristine graphite precursor has a typical characteristic 2θ peak
at 26.7°. The five GO samples do not show this peak, indicating the graphite precursor has been uniformly oxidised by improved Hummers’ method.

The $2\theta \approx 10^\circ$ corresponds to the diffraction of (001) GO plane in the c-axis and interlayer spacing $\approx 8$ Å. The increasing interlayer separation of the GO samples suggest that different levels of oxygen containing groups were attached to the graphite lattice during oxidation. High oxidation samples show enhanced layer spacing. GO-D has the largest interlayer spacing among these samples while GO-M is the least expanded sample, with interlayer spacings of 8.9 Å and 7.9 Å respectively.

![XRD pattern of a) GO and b) exfGO samples. The spectra from 15 to 35° 2$\theta$ degrees of GO samples in a) are omitted due to no characteristic peak.](image)

A comparison GO interlayer spacings comparison is listed in Table 4.1. After thermal exfoliation, the characteristic peaks of GO around 10° disappeared and the XRD spectra do not show any characteristic peaks. This indicates that exfGO is amorphous after thermal exfoliation, losing its crystalline structure.
Table 4. 1. XRD 2θ values and d-spacings of different batches of GO. Cu K-alpha source is used as the energy source, with a wavelength of 1.5406 Å.

<table>
<thead>
<tr>
<th>Sample</th>
<th>2θ (°)</th>
<th>d-spacing (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-D</td>
<td>9.940</td>
<td>8.9</td>
</tr>
<tr>
<td>GO-E</td>
<td>9.965</td>
<td>8.9</td>
</tr>
<tr>
<td>GO-M</td>
<td>11.135</td>
<td>7.9</td>
</tr>
<tr>
<td>GO-Y</td>
<td>10.745</td>
<td>8.2</td>
</tr>
<tr>
<td>GO-Z</td>
<td>10.265</td>
<td>8.6</td>
</tr>
</tbody>
</table>

Quantification of disorder in GO samples is usually analysed by the $I_D/I_G$ intensity ratio between the disorder-induced D band and the G band listed in Table 4.2. A higher ratio of $I_D/I_G$ normally shows a more disordered graphene structure. After thermal annealing at 600 °C, all samples show increases in $I_D/I_G$ values, indicating an increase in disorder due to further loss of carbon skeleton structure.

Figure 4. 17. Raman spectra of exfGO samples and thermal annealed exfGO samples.
Table 4. 2. Raman $I_D/I_G$ ratios of exfGO and thermal annealed exfGO.

<table>
<thead>
<tr>
<th>Sample</th>
<th>exfGO-D @600°C6h</th>
<th>exfGO-E @600°C6h</th>
<th>exfGO-M @600°C6h</th>
<th>exfGO-Y @600°C6h</th>
<th>exfGO-Z @600°C6h</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_D/I_G$</td>
<td>0.857</td>
<td>0.786</td>
<td>0.910</td>
<td>0.841</td>
<td>0.709</td>
</tr>
</tbody>
</table>

XPS technique was used to characterise and analyse the surface elemental compositions of prepared samples. All surface elemental analysis is summarised in the Table 4.3. The surface oxygen contents of the materials went through significant changes along the synthesis route graphite-GO-exfGO-actGO from 5%, >30%, <15% to ~7%. Since the GO structure incorporates surface oxy-functional groups and hydrogen bonded interlamellar water molecules, the sudden volatility of these labile species leads to a pressure build-up between the graphene sheets. The exfoliation of GO can be identified with the reduction of oxygen content, typically to ~10 at% from ~30 at% in GO precursors. Graphite and actGO both have similar surface elemental composition and showed extremely low O 1s content.

The elemental composition of graphite and actGO are similar, but they have great morphology difference, as shown in Figure 4.11 and 4.15 TEM micrographs.
The percentage of oxidation is estimated by deconvolution of the C 1s peak into three peaks representing the C═C/C―C, hydroxyl C―O/C―OH and carboxylic C═O/COO. After exfoliation, the C═C contents of highly oxidised samples experience a significant increase, by ~15%. The relative amounts of hydroxyl C―O/C―OH and carboxylic C═O/COO groups have changed. GO has more hydroxyl groups than carboxylic groups, while exfGO has more carboxylic groups. This is because carboxylic groups are more stable than hydroxyl groups. During the exfoliation process, the labile hydroxyl groups have broken the bonds. All batches of GO experienced similar changes.
Figure 4. 19. XPS C 1s spectra of GO and exfGO samples with fittings.

Figure 4. 20. C 1s XPS spectra of amine-impregnated exfGO samples and comparative O 1s spectra (bottom right).
Surface elemental analysis was carried out on chemical modified samples before and after CO$_2$ cycling test to determine the change occurred during cycling.

Amine is bonded to carbon substrate by interacting with the surface oxygen functional groups. The hindered oxygen functional groups lead to decreases in O content. Amine impregnation also introduces large amount of N into the system, contributed by —NH$_2$ group. With higher ratio of amine impregnation, the N content as detected by XPS increased. The higher the N content, the higher the theoretical CO$_2$ uptake capacity.

After cycling test, the nitrogen content decreased by certain amount, indicating the degradation and/or decomposition of amine after adsorption-desorption process. For exfGO-M impregnated samples, there was no loss of N after cycling test. However, the relative ratio of O/C changed, indicating CO$_2$ molecules were adsorbed during the tests, forming carbamates.
Table 4. 3. XPS surface elemental analysis of GO, exfGO, actGO and amine impregnated exfGO before and after CO$_2$ cycling test. The spectra were recorded at multiple spots on each sample and an average value was taken. The atomic percentage for C, N and O were estimated from the C 1s, N 1s and O 1s peaks in the survey spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (at%) in average</th>
<th>N (at%) in average</th>
<th>O (at%) in average</th>
<th>O/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-D</td>
<td>67.3</td>
<td>/</td>
<td>32.7</td>
<td>0.49</td>
</tr>
<tr>
<td>exfGO-D</td>
<td>88.0</td>
<td>/</td>
<td>12.0</td>
<td>0.14</td>
</tr>
<tr>
<td>exfGO-D+2xTEPA</td>
<td>75.6</td>
<td>11.7</td>
<td>12.7</td>
<td>0.17</td>
</tr>
<tr>
<td>exfGO-D+4xTEPA</td>
<td>73.4</td>
<td>18.1</td>
<td>8.5</td>
<td>0.12</td>
</tr>
<tr>
<td>exfGO-D+4xTEPA-cycling</td>
<td>73.9</td>
<td>14.1</td>
<td>12.0</td>
<td>0.16</td>
</tr>
<tr>
<td>exfGO-D+6xTEPA-cycling</td>
<td>73.1</td>
<td>18.0</td>
<td>8.9</td>
<td>0.12</td>
</tr>
<tr>
<td>exfGO-D+6xTEPA-cycling</td>
<td>76.1</td>
<td>12.5</td>
<td>11.4</td>
<td>0.15</td>
</tr>
<tr>
<td>GO-E</td>
<td>66.3</td>
<td>/</td>
<td>33.7</td>
<td>0.51</td>
</tr>
<tr>
<td>exfGO-E</td>
<td>88.2</td>
<td>/</td>
<td>11.8</td>
<td>0.13</td>
</tr>
<tr>
<td>exfGO-E+4xTEPA</td>
<td>77.2</td>
<td>12.7</td>
<td>10.1</td>
<td>0.13</td>
</tr>
<tr>
<td>exfGO-E+5xTEPA</td>
<td>75.3</td>
<td>15.6</td>
<td>9.1</td>
<td>0.12</td>
</tr>
<tr>
<td>exfGO-E+5xTEPA-cycling</td>
<td>76.3</td>
<td>13.7</td>
<td>10.0</td>
<td>0.13</td>
</tr>
<tr>
<td>GO-M</td>
<td>67.4</td>
<td>/</td>
<td>32.6</td>
<td>0.48</td>
</tr>
<tr>
<td>exfGO-M</td>
<td>86.5</td>
<td>/</td>
<td>13.5</td>
<td>0.16</td>
</tr>
<tr>
<td>exfGO-M+3xTEPA</td>
<td>77.5</td>
<td>14.1</td>
<td>8.4</td>
<td>0.11</td>
</tr>
<tr>
<td>exfGO-M+3xTEPA-cycling</td>
<td>75.5</td>
<td>15.0</td>
<td>9.5</td>
<td>0.13</td>
</tr>
<tr>
<td>GO-Z</td>
<td>67.0</td>
<td>/</td>
<td>33.0</td>
<td>0.49</td>
</tr>
<tr>
<td>exfGO-Z</td>
<td>84.9</td>
<td>/</td>
<td>15.1</td>
<td>0.18</td>
</tr>
<tr>
<td>actGO</td>
<td>93.1</td>
<td>/</td>
<td>6.9</td>
<td>0.07</td>
</tr>
<tr>
<td>Graphite precursor</td>
<td>95.1</td>
<td>/</td>
<td>4.9</td>
<td>0.05</td>
</tr>
</tbody>
</table>
The specific surface area and pore volume of samples were derived from N₂ adsorption-desorption isotherms. By comparing the N₂ adsorption amount at relative pressure of ~0.99, all annealed exfGOs indicate considerable enhancement in the porosity than exfGO. For example, through thermal annealing, higher surface area of 853 m² g⁻¹ and total pore volume of 6.68 cm³ g⁻¹ was achieved by the sample exfGO-Z@600°C compared with 797 m² g⁻¹ and 5.88 cm³ g⁻¹ of exfGO-Z. This can be explained by further removal of C—O as well as C—C at high temperature, resulting in enhanced defect sites and porous structure. A total pore volume of over 5 cm³ g⁻¹ in exfGO samples can be consistently achieved by exfGO-D/E/Y/Z four batches. The development of hyperporosity is directly proportional to the enhanced oxidation of sp² C═C to form C═O/COO as concluded from our previous study.¹⁹ Higher degrees of oxidation can result in higher degrees of exfoliation, and correspondingly high pore volume and high specific surface area. While amine loading is directly controlled by the pore-structure and pore volume by the substrate material, high ratio of amine impregnation can also be achieved by exfGO samples.

Figure 4. 22. N₂ adsorption-desorption isotherms at 77 K of a) exfGO and b) exfGO@600°C6h samples.

High sensitivity Quantachrome Autosorb iQ2 was used to measure the N₂ adsorption-desorption isotherms. Samples were outgassed overnight at 120 °C for exfGO and actGO and 80 °C for amine impregnated samples. SSA and pore volume
were calculated using the system software. \( \text{N}_2 \) at 77 K on carbon (slit/cylinder/sphere pores) QSDFT adsorption equilibrium model had been applied.

Table 4. 4. List of BET specific surface area (SSA) and pore volume of exfGO and actGO samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET SSA (m(^2) g(^{-1}))</th>
<th>Total pore volume at P/P(_0) of ≤0.994 (cm(^3) g(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>exfGO-D</td>
<td>746</td>
<td>6.14</td>
</tr>
<tr>
<td>exfGO-E</td>
<td>722</td>
<td>5.50</td>
</tr>
<tr>
<td>exfGO@600C6h-E</td>
<td>795</td>
<td>6.84</td>
</tr>
<tr>
<td>exfGO-M</td>
<td>367</td>
<td>2.71</td>
</tr>
<tr>
<td>exfGO@600C6h-M</td>
<td>412</td>
<td>3.74</td>
</tr>
<tr>
<td>exfGO-Y</td>
<td>559</td>
<td>4.46</td>
</tr>
<tr>
<td>exfGO@600C6h-Y</td>
<td>637</td>
<td>5.61</td>
</tr>
<tr>
<td>exfGO-Z</td>
<td>797</td>
<td>5.88</td>
</tr>
<tr>
<td>exfGO@600C6h-Z</td>
<td>853</td>
<td>6.68</td>
</tr>
<tr>
<td>actGO-1</td>
<td>2540</td>
<td>1.50</td>
</tr>
<tr>
<td>actGO-2</td>
<td>2156</td>
<td>1.76</td>
</tr>
<tr>
<td>actGO-1+1xPEHA</td>
<td>25</td>
<td>0.06</td>
</tr>
<tr>
<td>actGO-1+2xPEHA</td>
<td>16</td>
<td>0.04</td>
</tr>
<tr>
<td>actGO-1+3xPEHA</td>
<td>2</td>
<td>/</td>
</tr>
</tbody>
</table>

Notes: BET-SSA is a surface area obtained through BET method on the desorption isotherm in the P/P\(_0\) pressure region between 0.01 and 0.2.

\( \text{V}_{\text{total}} \) is a single point total pore volume obtained at P/P\(_0\) ~0.99. The relationship is defined as, \( \text{V}_{\text{total}} = (\text{N}_2 \text{ adsorbed at 0.99 in cm}^3 \text{ g}^{-1}) \times (\text{N}_2 \text{ liquid density at ~1 bar STP})/ (\text{N}_2 \text{ gas density at STP}) \). Which is equal to \( \text{V}_{\text{ads}} \) at (P/P\(_0\) = 0.99) \times 0.001547.
The highly hierarchical pore sizes and their distributions across the micro-, meso- and macro-porous ranges of the samples can be derived from the qualitative behaviour of \( N_2 \) adsorption-desorption isotherms, shown in Figure 4.23. Pore size distribution in the range 0 to 200 nm were obtained using DH (Dollimore and Heal) desorption isotherms while the micropore distribution in the range 0 to 5 nm were obtained using QSDFT desorption isotherms. DH method assumes cylindrical pore geometry and is suitable for estimate meso-pores (>3 nm) and macropores (>50 nm).

QSDFT method has pore shape models applied to slit/cylinder/sphere geometry and is best applied to nano- and meso-pores (≤50 nm).\(^{23}\) The \( N_2 \) isotherms of exfGO samples belong to type II isotherms with a sharp hysteresis at high relative pressure, which indicate highly hierarchical pore sizes and unsaturated condensation of \( N_2 \) in microporous networks of a plate-like geometry. The majority of the meso-porosity is distributed in the range 3 to 50 nm, which accounts for more than 75% of the total pore volume. The porosity characteristics of the samples are further supported by SEM and TEM micrographs (Figure 4.6-4.9 and Figure 4.12-4.14).

The increased oxidation degrees can also be confirmed by enhanced layer spacings (by powder X-ray diffraction, PXRD), increased concentration of epoxy (\( -\text{C}—\text{O}—\text{C}— \)), hydroxyl (\( -\text{C}—\text{OH} \)) and carboxylic (\( -\text{C}—\text{O}—\text{OH} \)) groups on the graphene basal planes and edges (by XPS and Raman spectroscopy) and excess mass-loss during the decomposition in thermal reduction (by TGA).

The annealing process can lead to increase of defects in the exfGO pore structure. This is due to the formation of \( \text{CO}_2/\text{CO} \) by consuming \( \text{C}—\text{C} \) bonds at high temperature. The BET SSA and pore volume can thus have certain improvements after thermal annealing at 600 °C, for example, 797 m\(^2\) g\(^{-1}\) to 853 m\(^2\) g\(^{-1}\) and 5.88 cm\(^3\) g\(^{-1}\) to 6.68 cm\(^3\) g\(^{-1}\) respectively for exfGO-Z.
Figure 4. 23. First column: \( \text{N}_2 \) adsorption-desorption isotherms at 77 K of exfGO samples and annealed exfGO samples; middle column: their derived pore size (line data on the left Y-axis) and cumulated pore volume (dotted data on the right Y-axis) distribution using desorption isotherm model and right column: derived pore size (line data on the left Y-axis) and cumulated pore volume (dotted data on the right Y-axis) distribution using QSDFT desorption isotherm model.
Both batches of actGO demonstrated similar pore size distribution as shown in inset of Figure 4.22 a). There is negligible amount of mesopores and macropores. Dominant micropores have pore sizes of 3.56 nm and 4.67 nm. The pore volumes of these two batches of samples are 1.5 cm$^3$ g$^{-1}$ and 1.76 cm$^3$ g$^{-1}$, surface areas are up to 2540 m$^2$ g$^{-1}$ and 2156 m$^2$ g$^{-1}$ respectively, which are higher than GO precursors. The porosity of PEHA@actGO samples experienced dramatic decrease to 0.063 cm$^3$ g$^{-1}$, 0.035 cm$^3$ g$^{-1}$ and even unmeasurable with 1x, 2x and 3x amine impregnation. KOH activation created numerous pores in the micro size range. Long chain PEHA cannot get into the pores and cover the surface of actGO, as confirmed by SEM micrographs in Figure 4.11.

Thermogravimetric analysis (TGA) was used to determine the residue content by heating up samples from room temperature ($\approx$25 °C) to 800 °C/1000 °C with constant heating rate of 3 °C min$^{-1}$ under dry pure N$_2$ flow around 1 bar. TGA curves shown in Figure 4.25 and 4.26. displayed the change of samples’ weight in wt% with temperature. The drops in weight show the loss of component or functional groups of the tested sample.
Figure 4. 25. Thermogravimetric decomposition plots of a) GO and amine-based polymer samples and b) amine impregnated exfGO samples from 25 °C to 1000 °C with background correction.

All samples were systematic background corrected using a blank run to eliminate system shift errors. The first sign of weight drops for GO samples occurs around 100 °C, which is loss of water content as well as hydroxyl groups. The second drop indicates that GO samples start to decompose from around 180 °C due to removal of oxygenated groups including hydroxyl, epoxy, and carboxyl functional groups as well as partial carbon atoms on the graphene basal planes. The residue weights of different batches of GO showed a slight difference ranging 7.5 wt% from the highest to the lowest. GO sample with the highest O content as confirmed by XPS, i.e. GO-D has higher weight loss than the sample with lower O content of sample GO-M. This means that highly oxidised samples have greater loss in weight due to loss of oxygenated functional groups.

Amine-based polymers TEPA and PEHA were also tested using TGA. The polymers start to decompose at 150 °C followed by a significant drop at around 300 °C, indicating break-down of structures. Therefore, it is confirmed that amine-impregnated sorbents have thermal stability up to 150 °C, which is suitable for the applications where the sorbents are regenerated at 100 °C. PEHA is more stable
than TEPA at temperature below 300 °C and has lower final weight. This is because PEHA has higher molecular weight than TEPA thus better thermal stability.

Amine impregnated exfGO samples TEPA@exfGO combined the TGA characteristics of both exfGO and the polymer. They follow the pattern that water loss around 100 °C, then decomposition of polymers over 150 °C and subsequent decomposition of carbon structure at 300 °C. This demonstrates that higher amine loading amount results in a higher loss in weight after heating over 250 °C. It can also indicate correct loading amount of polymers by weight residue change pattern.

Figure 4. 26. Thermogravimetric decomposition plots of a) actGO and b) amine impregnated actGO samples with background correction.

ActGO was thermally activated at 800 °C, therefore a dry actGO sample does not show weight loss in the range of 25 °C to 600 °C and is stable below 800 °C. All chemical modified actGO samples were background corrected using actGO TGA curve. Samples with higher amine loading show greater mass change. For a 3 mmol g\(^{-1}\) loading, the residual weight is around 25 wt% of the original sample weight. Correspondingly, with the same ratio of impregnation, PEHA samples have more residue weight than TEPA samples due to longer backbone chain, shown in Figure 4.26.
4.2.5 TEPA/PEHA modified actGO for CO₂ capture

Gravimetric adsorption data were obtained for actGO with 1x and 2x PEHA at 25 °C, 50 °C, 75 °C, and 100 °C for 15% CO₂ and wet/ dry N₂ as shown in Figure 4.27. Samples do not show adsorption when dry N₂ gas flow is supplied at any testing temperature. However, when wet N₂ gas is supplied at 25 °C, considerate amount of moisture is adsorbed (30 wt% at 5 hours) for 2xPEHA sample as seen from Figure 4.27 b). For the same sample in 5-hour timescale, 75 wt% uptake for wet CO₂ gas and 50 wt% dry CO₂ gas are obtained. The CO₂ and amine group reaction mechanism indicates that moisture can enhance the CO₂ adsorption, ideally double amount of dry CO₂ uptake can be achieved.

There are limiting factors that affects the actual gas uptake such as the surface area exposed to gas, gas flow supply or temperature. The same 2x PEHA sample shows 7.5 wt% at 50 °C and 2.5 wt% at 75 °C in dry CO₂ gas flow. Samples do not show gas uptake at 100 °C. Similarly, a ~9 wt% uptake is obtained for 1xPEHA actGO sample at 25 °C.

The CO₂ uptake at low temperature (25 °C) of 1x, 2x and 3x TEPA@actGO have uptake of 5 wt%, 15 wt% and 32 wt% respectively, which show increasing trend with higher loading. However, the loading amount cannot be increased any higher as the sample starts to become sticky with excessive amine loading. The stickiness indicates either the pores are fully filled by amine polymers or the pores are too small to allow large molecules to enter.

For 2xTEPA impregnated samples, a maximum of 15 wt% gas uptake was achieved at 25 °C, 2 wt% at 50 °C and 2 wt% at 75 °C for dry gas flow, directly read from Figure 4.27 d). The amine-CO₂ interaction is an exothermic reaction, which tends to occur at relative low temperature. Though physical adsorption is particularly important to contribute to the gas uptake, chemisorption is the desired property. However, with the surface coating modification, the micropores are blocked and cannot get access to gas flow, therefore hinder physical adsorption. In realistic CO₂ capture environment, the flue gas has temperature around 75 °C.
Figure 4. 27. Gravimetric gas uptake of chemical modified actGO samples, a) 2xPEHA measured in different conditions, b) TEPA modified at 25 °C and c) 2xTEPA measured at different temperatures.

Note that the flue-gas uptakes were carried out with 15% CO₂ mixed 85% N₂ gas bubbled through water at a flow rate of 100 ml min⁻¹. Uptake measurements were carried out after a degassing at 100 °C for 60 minutes and uptake in wt% calculation is regarding to the dry sample weight after degassing.
The BET isotherms for actGO are typical Type III adsorption isotherms, for which monolayer gas adsorption formation is missing. It also indicates unrestricted multilayer formation process. This is because lateral interactions between adsorbed molecules are strong in comparison with interactions between the adsorbent surface and adsorbate. Hypothetically the potential existing oxygen-containing functional groups are capable of CO$_2$ adsorption. However, the evaluation of the role of oxygenated functional groups has been rarely reported and underestimated.\textsuperscript{25}

The attached oxygen atoms could gain extra electrons from the nearby carbon atoms and thus act as Lewis bases that donate electrons to acidic carbon atoms of CO$_2$ molecules.\textsuperscript{26} They can also induce more polarity into carbon frameworks and thus enhance the initial adsorption of CO$_2$ molecules at low pressure range. —COOH and —OH groups particularly have a positive influence on the CO$_2$ adsorption.\textsuperscript{27} actGO has extremely low oxygen content (O/C ratio of 0.074) after thermal annealing at 800 °C, particularly low in hydroxyl and carboxyl groups. Though microporous gained through the process could enhance the microporous pore volume, it compromised the oxygen content that could also attract CO$_2$ molecules.

Since adsorption is a spontaneous process and decreases in translation freedom of molecules, physisorption tends to occur at low temperature. actGO shows negligible
amount of gas adsorption at 75 °C. Therefore, the CO₂ gas uptake performance for actGO samples is better at low temperature, i.e. at room temperature. For amine loaded 1xPEHA sample, the BET SSA is 25 m² g⁻¹ with pore volume of 0.063 cm³ g⁻¹. Microporous adsorption dominates at low pressure range <0.2 bar. In order to quantify the CO₂ uptake in a CO₂/N₂ mixture gas with composition close to flue gas (15%/85%), BET measurements of CO₂ adsorption-desorption isotherm value are taken at 0.15 bar. At relative pressure 0.15, 2.75 mmol g⁻¹ (25 °C) 4.6 mmol g⁻¹ (50 °C) and 3.4 mmol g⁻¹ (75 °C) CO₂ uptake are obtained.

In general, actGO shows certain CO₂ uptake capabilities attributed to both microporous physisorption as well as chemisorption. Amine impregnation does not show ideal uptake amount as the chemisorption ability cannot be maximised with low amount impregnation. ActGO has intrinsic gas adsorption property but is not an ideal material as a substrate for amine impregnation application. Therefore, the modified actGO is prone to physisorbsent, which is more suitable for low temperature applications and is not ideal towards this application.

4.2.6 TEPA/PEHA modified exfGO for CO₂ capture

In the case of CO₂ capture, obtaining high CO₂ uptake capacities by using sorbent-based materials under flue-gas conditions remains a challenging task. Many sorbent materials show good CO₂ uptake capacities only at 0 °C/25 °C or for dry CO₂. For example, porous sorbents including zeolites, MOFs and activated carbons (shown in the previous section in this chapter) do not show desirable selective CO₂ uptake under humid conditions and/or at >50 °C. This is a major obstacle for the implementation of carbon capture and storage.

Thermal exfoliated GO is a highly hierarchical meso-and macro-porous graphene network. exfGO samples are amine impregnated using the same wet impregnation method as actGO. The exceptional meso-and macro-porosity in exfGO samples can facilitate a large amount of amine impregnation to achieve an extremely efficient solid-amine based CO₂ capture system. A high amine impregnation of >6 mmol g⁻¹
is readily attained in exfGO samples (solid-amine@exfGO), where amine loading is directly controlled by the pore-structure and volume of the host material. The exfGO structure can accept such high loading without sign of surface wetting. These uptakes are further confirmed under the simulated flue-gas stream.

CO₂ adsorption-desorption isotherms were measured at various temperatures as shown in Figure 4.29. Only adsorption regions are plotted and used for determining the CO₂ capacity of the samples. The isotherms have adsorption branches mainly in type I and type II shape. Most adsorption curves in the sample collections do not start from 0 mmol g⁻¹ at low P/P₀. This is associated with the filling of micropores is commonly found in micro-mesoporous carbons. This has proven that the micropores of the materials took part in the adsorption of CO₂ molecules.

The CO₂ uptake is considerably enhanced with the high pore volume host substrates which host high amount of TEPA/PEHA. A summary of CO₂ uptake capacity of each sample is shown in Table 4.5. Note that exfGO-D+6xTEPA (Figure 4.29 d)) shows three negative readings on the CO₂ isotherm towards the high relative pressure region, this is due to the number of samples used for volumetric uptake. Volumetric adsorption at temperatures higher than ambient conditions require sufficient amounts of sorbents to show non-negative uptake values.⁷
Figure 4. 29. Volumetric CO$_2$ (100%, dry) uptake capacity of the TEPA@exfGO and PEHA@exfGO samples in a) exfGO-D+2xTEPA, b) exfGO-D+4xTEPA, c) exfGO-E+TEPA, d) exfGO-D+TEPA, e) exfGO-E/Z+PEHA and f) exfGO-M+TEPA. Each plot shows exfGO samples with same/ different TEPA loadings at different temperatures.
The total pore volumes of chemical modified samples are obtained through N$_2$ adsorption-desorption isotherms. The isotherms belong to Type III isotherms which are typical for macroporous material, showing the sample remains macroporous after amine loading. The adsorption amount at the saturation pressure $P/P_0 \sim 0.99$ is corresponds to the pore volume of solid. Therefore, it can be directly read from the plot that increased amine loading leads to greatly reduced pore volume of the exfGO samples.

In order to quantify the CO$_2$ uptake in a CO$_2$/N$_2$ mixture gas like flue gas (15%/85%), BET measurements of CO$_2$ adsorption-desorption isotherms value are taken at 0.15 bar. The quantities of CO$_2$ and N$_2$ adsorbed at 0.15 and 0.85 bar are divided by the partial pressure ratio (0.15/0.85). For some samples, the highest uptake occurs at higher partial pressure, which means better performance can be achieved when the samples are applied under higher CO$_2$ concentration or higher pressure.

ExfGO samples alone without amine impregnation show very low CO$_2$ uptake capacities of $<1$ mmol g$^{-1}$. The CO$_2$ uptake is considerably enhanced with the high pore volume host substrates. An exceptionally high CO$_2$ capture capacity of 6.16 mmol g$^{-1}$ has been obtained by 6.5xTEPA on annealed exfGO at a practical temperature of 75°C under CO$_2$ pressure of 0.15 bar.
Table 4. Porosity and volumetric CO$_2$ (100%, dry) isotherm uptake at 0.15 bar of TEPA impregnated exfGO samples, measured at different temperatures 25 °C, 40 °C, 50 °C, 60 °C and 75 °C.

<table>
<thead>
<tr>
<th>TEPA@exfGO Sample</th>
<th>Total pore volume (cm$^3$ g$^{-1}$)</th>
<th>Uptake temperature (°C)</th>
<th>CO$_2$ uptake (mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dx2TEPA</td>
<td>0.75</td>
<td>25</td>
<td>0.67</td>
</tr>
<tr>
<td>Dx2TEPA</td>
<td>0.75</td>
<td>40</td>
<td>0.99</td>
</tr>
<tr>
<td>Dx2TEPA</td>
<td>0.75</td>
<td>50</td>
<td>0.89</td>
</tr>
<tr>
<td>Dx2TEPA</td>
<td>0.75</td>
<td>60</td>
<td>0.62</td>
</tr>
<tr>
<td>Dx2TEPA</td>
<td>0.75</td>
<td>75</td>
<td>0.35</td>
</tr>
<tr>
<td>Dx4TEPA</td>
<td>0.13</td>
<td>25</td>
<td>1.17</td>
</tr>
<tr>
<td>Dx4TEPA</td>
<td>0.13</td>
<td>40</td>
<td>2.22</td>
</tr>
<tr>
<td>Dx4TEPA</td>
<td>0.13</td>
<td>50</td>
<td>2.65</td>
</tr>
<tr>
<td>Dx4TEPA</td>
<td>0.13</td>
<td>60</td>
<td>2.59</td>
</tr>
<tr>
<td>Dx4TEPA</td>
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<td>75</td>
<td>2.08</td>
</tr>
<tr>
<td>Dx6TEPA</td>
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<tr>
<td>Dx6TEPA</td>
<td>0.04</td>
<td>75</td>
<td>2.61</td>
</tr>
<tr>
<td>Mx3TEPA</td>
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</tr>
<tr>
<td>Mx3TEPA</td>
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<td>60</td>
<td>3.83</td>
</tr>
<tr>
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<td>4.89</td>
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<td>0.06</td>
<td>75</td>
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<td>/</td>
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<tr>
<td>EAx6.5TEPA</td>
<td>/</td>
<td>75</td>
<td>6.16</td>
</tr>
</tbody>
</table>
Table 4. 6. Porosity and volumetric CO₂ (100%, dry) isotherm uptake at 0.15 bar of PEHA impregnated exfGO samples, measured at different temperatures 25 °C, 40 °C, 50 °C, 60 °C and 75 °C.

<table>
<thead>
<tr>
<th>PEHA@exfGO Sample</th>
<th>Total pore volume (cm³ g⁻¹)</th>
<th>Uptake temperature (°C)</th>
<th>CO₂ uptake (mmol g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ex4PEHA</td>
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<tr>
<td>Ex4PEHA</td>
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<td>60</td>
<td>0.72</td>
</tr>
<tr>
<td>Ex5PEHA</td>
<td>0.52</td>
<td>75</td>
<td>4.83</td>
</tr>
<tr>
<td>Ex5.6PEHA</td>
<td>0.22</td>
<td>60</td>
<td>5.22</td>
</tr>
<tr>
<td>Ex5.6PEHA</td>
<td>0.22</td>
<td>75</td>
<td>5.56</td>
</tr>
<tr>
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<td>60</td>
<td>0.72</td>
</tr>
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<td>60</td>
<td>0.92</td>
</tr>
<tr>
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<td>0.72</td>
</tr>
<tr>
<td>Zx5PEHA</td>
<td>/</td>
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<td>3.86</td>
</tr>
<tr>
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<td>75</td>
<td>4.52</td>
</tr>
<tr>
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<td>0.09</td>
<td>75</td>
<td>4.50</td>
</tr>
<tr>
<td>Zx6.5PEHA</td>
<td>0.09</td>
<td>75</td>
<td>4.46</td>
</tr>
</tbody>
</table>

Note that the maximum CO₂ capture capacities are directly governed by sample porosity to facilitate high amine loading. However, excessive amine loading (higher than the pore volume equivalent) do not show favourable CO₂ capture property. This is due to the complete pore filling or increased bulk amine in the large or macropores, and thus reduces the amine efficiency for CO₂ capture due to the smeared out active surface area for adsorption and diffusion of CO₂, inhibiting the mass transport.
4.2.7 Stability of \( \text{CO}_2 \) capture sorbents

Apart from the issue of \( \text{CO}_2 \) capture capacities for both flue-gas and pure \( \text{CO}_2 \), the stability of amine impregnation is another main concern for the practical usage for this type of sorbents. One of the main drawbacks of liquid amine scrubbing technique is the volatility of amines during the adsorption-desorption cycles. In order to overcome this problem, amines with long molecular chains were chosen for this purpose. These polyamines can be easily stabilised with a strong confinement effect in the large meso-pores of the exfGO consisting of considerable surface oxygen. The \( \text{CO}_2 \) capacity stability was carried out by performing several cycles of adsorption and desorption. Note that the flue-gas uptakes are carried out with 15% \( \text{CO}_2 \)+ 85% \( \text{N}_2 \) gas bubbled through water at a flow rate of 100 ml min\(^{-1}\) unless specified, and all the desorption runs under flowing dry \( \text{N}_2 \) at 100 °C for 60 min.

It is also worth noting that the uptake weight percent is directly read from the cycling diagram. The highest and lowest point of each cycle involves immediate quick fluctuation due to unstable gas supply during switching of gases, which are not the actual weight. The lowest point is taken by the actual lowest weight after degassing at 100 °C while the highest point is the saturation/ near saturation weight after gas adsorption at designated testing temperatures. The difference between the highest and lowest points is thus the weight change (in percentage regarding to dry sample weight) caused by gas adsorption.

For the exfGO-D+6xTEPA cycling diagram (Figure 4.31 top), the first three cycles are tested under humidified \( \text{CO}_2 \) at 75 °C, 65 °C and 50 °C, obtaining uptake amount of 23 wt%, 25 wt% and 30.5 wt%, respectively. The next three cycles are tested under wet \( \text{N}_2 \) gas flow, which give low uptake of moisture by 2, 3 and 5 wt% at 75 °C, 65 °C and 50 °C respectively. Samples show negligible uptake capacity (<5 wt%) for humidified \( \text{N}_2 \) without \( \text{CO}_2 \) at 75 °C which is a desirable property in a flue gas environment. The next cycle is tested at 25 °C. When humidified \( \text{N}_2 \) gas flow is initially supplied, the moisture uptake is 35 wt%. After reaching the saturation uptake with humidified \( \text{N}_2 \), a rapid \( \text{CO}_2 \) uptake kinetics and saturation in 10-15 minutes can be observed (switching the gas from \( \text{N}_2 \) to \( \text{CO}_2 \) under same flow and temperature).
This accounts for a true CO₂ uptake value of >20 wt%. Thus, a rapid CO₂ uptake in the amine grafted solids at or near room temperature is highly possible by simple pre-humidification of the solid-amine system.

Figure 4. 31. Gravimetric temperature swing flue-gas uptakes of exfGO-D+6xTEPA (top) and exfGO-E+5xTEPA (bottom) samples, measured at different temperatures on continuous cycles over 70 h and 26 h operation. The CO₂ uptake in wt% is indicated on the left Y axis by blue line. The temperature is indicated on the right Y axis by red line.

The following cycles repeat the previous gas switching test at 50 °C and 70 °C, obtaining an initial 5 wt% or 2 wt% moisture uptakes followed by a rapid ~15-20 wt% CO₂ uptake. The next cycle allows the sample to saturate in humidified CO₂ at 25 °C
overnight, giving a significant 62 wt% increase by absorbing water and CO$_2$. The last 6 cycles are tested at 50 °C, 60 °C, 70 °C, 75 °C, 80 °C and 88 °C (not in order) under dry CO$_2$ flow, giving uptakes of 22 wt%, 16 wt%, 13 wt%, 13 wt%, 10 wt% and 5 wt% respectively. This trend shows strong evidence that the gas uptake is best fulfilled at lower temperature.

Similarly, the exfGO-E with 5xTEPA loading (Figure 4.31 bottom) is tested using the same procedure. The first four cycles are tested at 60 °C, 75 °C, 50 °C and 30 °C under humidified CO$_2$ flow, obtaining uptakes of 28 wt%, 27 wt%, 31 wt% and 67 wt% total weight gain. Each cycle includes two steps, firstly applying humidified N$_2$ flow until reaching saturation and then quickly switching to humidified CO$_2$ flow. The initial moisture uptakes are 3 wt%, 2 wt%, 10 wt% and 23 wt% at 60 °C, 75 °C, 50 °C and 30 °C, followed by a rapid CO$_2$ uptake by 23 wt%, 22 wt%, 23 wt% and 27 wt%. Pre-humidified solid-amine system can show equally good but significantly quicker adsorption of CO$_2$ molecules.

exfGO-E with 4x TEPA and 7x TEPA impregnation (Figure 4.32) are tested using the cyclic temperature swing measurements between 75 °C and 100 °C under the same flue-gas condition respectively. After 20 cycles and 35 hours continuous testing, 4x TEPA only shows a loss of uptake capacity by 2 wt%, from 13 wt% to 11 wt%. 7 x TEPA shows a total loss of uptake by 7 wt% after 41 cycles over 100 hours operation, from 26 wt% to 19 wt%.

The capacity loss over the first 20 cycles is 2.5 wt%, which is similar to the 4xTEPA sample. The latter 20 cycles involve a capacity loss of 4.5 wt%. This shows that the amine impregnation becomes less stable over the cycling measurements. Heavier loaded sample also suffers from higher capacity loss. Such working capacity and cycling stability of TEPA@exfGO are among the top performance of current reported literatures on TEPA@carbon$^{14}$, TEPA@silica$^{28}$, TEPA@clay$^{29}$ and PEI@silica$^{30}$ between 20 to 50 regenerating cycles under similar conditions.$^{31-33}$ The loss of capacity is a gradual process, primarily due to the leaching of amines in successive temperature swing desorption runs at high temperature, e.g. at 100 °C. The decay is commonly found in CO$_2$ sorbents. The irreversible CO$_2$ sorption property is
generally associated with structural rearrangement during temperature cycling, attributed to sintering effect leading to loss of surface area and sorption sites or reactive sites.\textsuperscript{34}

![Gravimetric temperature swing flue-gas uptakes of exfGO-E+4xTEPA (top) and exfGO-E+7xTEPA (bottom) samples, measured at different temperatures on continuous cycles over 36 h and 100 h operation. The CO\textsubscript{2} uptake in wt\% is indicated on the left Y axis by blue line. The temperature is indicated on the right Y axis by red line.](image)

Figure 4. 32. Gravimetric temperature swing flue-gas uptakes of exfGO-E+4xTEPA (top) and exfGO-E+7xTEPA (bottom) samples, measured at different temperatures on continuous cycles over 36 h and 100 h operation. The CO\textsubscript{2} uptake in wt\% is indicated on the left Y axis by blue line. The temperature is indicated on the right Y axis by red line.
Figure 4. 33. Gravimetric temperature swing flue-gas uptakes of annealed exfGO-E+6.5xTEPA (top) and annealed exfGO-Z+6.5xTEPA (bottom) samples, measured at different temperatures on continuous cycles over 70 h and 20 h operation. The CO₂ uptake in wt% is indicated on the left Y axis by blue line. The temperature is indicated on the right Y axis by red line.

The 6.5 mmol g⁻¹ TEPA impregnated 600 °C annealed exfGO-E sample (Figure 4.33) shows an initial CO₂ working capacity of 28 wt% for flue-gas investigated using cyclic temperature swing measurements, between 75 °C and 100 °C for adsorption and desorption respectively. The capacity after 20 cycles is about 22 wt%. After 28 cycles of continuous operation for 70 hours, the sample still exhibits a CO₂ capture working
capacity of 20 wt%. It is reported that 2.2 kg monoethanolamine (MEA) is required to capture 1000 kg of CO₂ for current industrial liquid amine scrubbing due to degradation. By introducing the solid sorbent system, it is estimated that 1 kg exfGO+6.5xTEPA sorbent (exclude reusable substrate) could adsorb 1066 kg CO₂ according to the cycling tests in Figure 4.33. Besides, the lower regeneration temperature (~130 °C to 100 °C) could also save considerate amount of energy by solid sorbents.

The same amount of amine impregnation 6.5 mmol g⁻¹ in 600 °C annealed exfGO-Z shows less initial CO₂ uptake, which is 23 wt% for the first cycle and reduced to 19 wt% after 8 cycles. Though annealed exfGO shows improvements in BET SSA and total pore volume, the oxygen functional groups has largely decreased during the process. There is no significant improvement compared with unannealed exfGO substrate. The CO₂ adsorption ability is a trade-off between the physical properties such as SSA, pore volume, element compositions and amine loading capacity.

exfGO-M has the lowest pore volume among the five exfGO samples. With 3xTEPA loading, the maximum CO₂ uptake capacity reached 18 wt% at 75 °C, shown in Figure 4.34. The sample measurements were disrupted after the first 8 hours, and the sample was taken out from TGA chamber and reloaded after around 10 days. An obvious decay in performance can be observed and the uptake decays to a relative stable performance of 10 wt%.

exfGO-D+4xTEPA shows CO₂ uptake of 17.5 wt% at 75 °C, 25 wt% at 50 °C, 30 wt% at 40 °C, 50 wt% at 30 °C and ~40 wt% at a repeating cycle at 30 °C. The increasing uptake amount with lower temperature shows good agreement that adsorption tends to occur at low temperature. The second cycle which does not show clean line at 30 °C has strong signal disturbance affecting TG by ambient environment.

In general, the hyperporous exfGO samples exhibit remarkable cyclic working flue-gas CO₂ capacity. The enhanced working capacity and stability of the solid amine@exfGO are directly attributed to the well-impregnated amine within the oxygen-rich pores of ultrahigh pore volume. Another important advantage of using the carbon-based substrate is the heat dissipation capability. As CO₂ interaction with
amines is an exothermic reaction, the carbon support can quickly dissipate the heat and reduce the change of volatilization of amine.\textsuperscript{35}

Figure 4. 34. Gravimetric temperature swing flue-gas uptakes of exfGO-M+3xTEPA (top) and exfGO-D+4xTEPA (bottom) samples, measured at different temperatures on continuous cycles over 70 h and 80 h operation. The CO\textsubscript{2} uptake in wt\% is indicated on the left Y axis by blue line. The temperature is indicated on the right Y axis by red line.

Exceptional functional performances have been achieved by meso- and macro-pore rich exfGO networks with ultrahigh total pore volumes. The material system is facile and repeatable to make using thermal shock exfoliation process. The solid-amine@exfGO samples can be favourably considered for an efficient column
separation in a breakthrough method. The volumetric densities of these samples can be modified between 0.3 and 0.6 g cm\(^{-3}\), depending on the strength of exfoliation and amine loading to achieve desirable permeation or diffusion selectivity.

### 4.3 Conclusions

In this chapter, a simple yet efficient thermal exfoliation method has been applied to as synthesized GO to achieve ultrahigh specific surface area and pore volume. The superior properties of exfGO makes it an ideal substrate material for amine impregnation, with application to CO\(_2\) capture from flue gas.

The meso- to macro-pore volume governed CO\(_2\) capture and the capacitive energy storage performance of these structure are illustrated via stability and cyclic working CO\(_2\) capture in solid-amine@exfGO. Such samples exhibit an ultrahigh selective flue-gas CO\(_2\) capture of ~30 wt\% at 75 °C and a very long cycling stability under simulated flue-gas stream conditions. Specifically, the solid amine@exfGO system, which is the first material of its kind to use a GO based porous structure for solid-amine impregnation, exhibits such extraordinarily stable working CO\(_2\) capture capacities of ~25 wt\% for a flue-gas stream. The simple exfoliation method described in this work is clearly a viable technique not only for scaling-up, but also for reducing the cost of synthesis and therefore materials production.

To summarise, a solid-amine system for efficient CO\(_2\) capture was developed and displayed exceptional CO\(_2\) cyclic uptake stability. The exfGO shows an ultrahigh hierarchical pore volume of 6.68 cm\(^3\) g\(^{-1}\) and high surface area of 853.2 m\(^2\) g\(^{-1}\). The results also suggest that the high capacity solid-amine-based sorbents for CO\(_2\) scrubbing can be obtained by designing substrates with high pore volume. The long-term and high-temperature stability can be further enhanced with the incorporation of the more stable long chain and high molecular weight polyamines. Furthermore, the control over CO\(_2\) uptake and release is attainable with fine modifying of pore structures of the host carbon.
Chapter 4 References


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Chapter 5 Amine impregnated nanoporous carbons derived from MOF-5 and MOF-74 for CO₂ capture

5.1 Introduction

In this chapter, the synthesis and characterisation of highly hierarchical porous carbons derived from metal-organic frameworks (MOFs) for CO₂ capture are discussed.

Metal-organic frameworks (MOFs) are crystalline porous materials with periodic network structures that are different from inorganic porous materials and general organic complexes. The rigidity of both inorganic materials and the flexible nature of organic materials give them a great development potential in modern materials research. Owing to the versatility of precursor building blocks and the possibility for chemical functionalisation of coordination space, MOFs offer a broad perspective for rationally designing and fine modifying their structure and chemical properties of the pore surface.¹ MOFs have applications on adsorptive removal of SO₂ and NO₂ for clean air, purifying breathing air,² bifunctional oxygen electrocatalysis,³ water-gas shift catalysis,⁴ MOF glass⁵ and etc.

It is essential for cost-effective gas separation to possess properties such as large adsorption capacity, stability over repeated adsorption-desorption cycles, fast kinetics and favourable thermodynamics. The large number of structures that can be obtained by changing either the organic linker or the metal endows MOFs with a high versatility for modifying not only pore size and surface area but also adsorption enthalpy, which is a main factor determining preferential gas adsorption, and hence separation from gas mixtures.⁶

Control and optimisation of pore geometry, size, volume and surface area are crucial to achieve efficient CO₂ capture at pre- or post- combustion power stations. MOF materials with pore volume higher than 1 cm³ g⁻¹ are suitable for gas storage, CO₂ separation/purification and for effective post-combustion carbon capture.⁷ MOF’s
gas selectivity is measured using CO\textsubscript{2} adsorption-desorption isotherms at various temperature. Given their rich pore property, the hyperporous carbons are also potential candidates for further pore optimisation/functionalisation for energy storage, e.g. as electrode materials and methane storage.

Porous MOFs have permanent nanoscale cavities and open channels offering congenital conditions for small molecules to access and, therefore, exhibit a potential for use as a template to synthesize nanoporous carbon materials.\textsuperscript{6} Xu et al. demonstrated the application of MOF-5 for the preparation of nanoporous carbons as a sacrificial template in 2008.\textsuperscript{6} They introduced furfuryl alcohol (FA) into the micropores of MOF-5 by a vapor phase approach. After carbonization at 1000 °C in Ar atmosphere, nanoporous carbon with a very high specific Brunauer–Emmett–Teller (BET) surface area of 2872 m\textsuperscript{2} g\textsuperscript{-1} was obtained. However, at a lower temperature of 800 °C, the resultant carbon exhibited a much lower BET surface area of 417 m\textsuperscript{2} g\textsuperscript{-1}. Later, the same group also reported the carbonization of ZIF-8 with FA.\textsuperscript{7}

Porous carbon structure was synthesized from MOF precursors through several steps: (i) formation of the original templates, (ii) filling the carbon precursors into mesopores, (iii) converting the precursors into solids, and (iv) removal of the original templates. Because most of the content in MOFs is organic, porous carbon can be prepared by direct pyrolysis of MOFs/PCPs without additional inclusion of carbon sources. Yamauchi and co-workers investigated the effect of direct carbonization temperatures of ZIF-8 on several structural properties in 2012.\textsuperscript{8} By applying the appropriate carbonization temperature, both high surface area and large pore volume were realized. In comparison, direct conversion through single-step carbonisation/pyrolysis of MOFs is a straightforward pathway.

Latter work suggested nanoporous carbons displaying hierarchical pore structures could be formed by direct carbonization of MOF-5 and pore characteristics of MOF-derived carbons can be modified by selecting suitable MOFs with isoreticular structures.\textsuperscript{9} Zn cations in the framework of the MOF-5 can be reduced and vaporized away at carbonization temperature above 900 °C.\textsuperscript{10} However, the MOF-derived
carbon materials reported so far generally contained large cracks and/or voids due to insufficient amounts of carbon sources and anisotropic shrinkage of MOF structures.\textsuperscript{11}

Since then, MOF-derived porous carbon materials have gained significant attention as emergent porous materials in diverse fields. And have led to the development of a permanent adsorbent which have properties of high carbon dioxide capacity, high selective adsorption for CO\textsubscript{2} capture and physicochemical and hydrothermal stabilities.\textsuperscript{9,12,13} Mg-MOF-74 represents a benchmark for solid adsorbents exhibits the best capacity of 35.2 wt\% (8 mmol g\textsuperscript{-1}) at 1 bar and 298 K. The solid adsorbents should have a capture capacity at least matching the working capacity of amine scrubber 2-4 mmol g\textsuperscript{-1} at working conditions.\textsuperscript{14}

MOF-5 is composed of [Zn\textsubscript{4}O(−COO)]\textsubscript{6} SBUs and benzene-1,4-dicarboxylate (BDC) linkers in a primitive cubic lattice (pcu) topology. MOF-5 is thermally stable to approximately 300 °C.\textsuperscript{8} The porous structure remains after removing the solvent. However, it is not water stable and thus cannot survive long after exposure to humid air. For applications that depends on their chemical stability, such as gas storage and separation, air-sensitive MOFs are often less cost effective than those with inferior performance but stable in air.\textsuperscript{9} The components of MOF-5 showing the abstraction of the [Zn\textsubscript{4}O(−COO)]\textsubscript{6} SBU as an octahedron, the BDC linker as a rod, and their assembly into the pcu net shown here in augmented form.\textsuperscript{10}

Figure 5. 1. a) Schematic crystal structure of MOF-5. b) Schematic structure of M-MOF-74 (M: Zn, Co, Ni, Mg).\textsuperscript{2}
MOF-5 (Zn₄O[BDC]₃) shows a relatively high porosity with cubic framework nanopore cages around 1.2 nm. It is inexpensive and relatively easy to synthesize in large quantities, e.g., at room temperature by stirring or a solvothermal method with the precursors (Zn nitrate salt and benzenedicarboxylic acid) and solvent (N, N'-diethylformamide). However, MOF-5 is not well received for the gas storage specifically due to its low molecular binding energy and uptake capacity.

Importantly, it is highly sensitive to moisture and other flue gas containing acidic gases, which leads to degradation and complete collapse of the porosity. Therefore, a readily synthesized MOF-5 structure is further exploited to obtain a porous carbon that is much more stable and highly robust. MOF-5 is directly carbonised at 1000 °C/1100 °C to obtain a stable MOF carbon structure. The pore size and its distribution can be modified by size control of MOF crystals. Therefore, by changing the solvent of synthesizing MOF-5 from DMF to DEF, larger crystal size and higher pore volume were achieved.

The vulnerability of MOFs typically lies in the lability of ligand-metal bonds. According to ligand field theory, because Zn²⁺ is a transition metal ion with d¹⁰ electron configuration, it experiences no ligand field stabilization energy overall. Thus, its ligand environment is controlled primarily by steric factors. This favours a tetrahedral environment but is not heavily destabilised when this environment is disturbed during ligand exchange.

Facile ligand exchange allows the formation of a crystalline framework with high surface area and favours the formation of larger single crystals, allowing for more precise structural characterisation through single crystal XRD. However, it also lowers the chemical stability of the resulting MOF, as easily exchanged carboxylates will be displaced by water or other nucleophiles, and if too many of the linking carboxylates are displaced, the framework will collapse. Even the bond strength is high, the MOF is not chemically stable if the energy if the energy barrier for ligand substitution is low. In general, MOFs with SBUs consisting of tetrahedral Zn²⁺ are not chemically stable. However, MOFs containing Zn²⁺ in a different coordination
environment, such as MOF-69, have been shown more stable than those with purely tetrahedral Zn$^{2+}$ ions.\textsuperscript{16,17}

Several MOF-5 derived carbons with different BET surface areas and total pore volumes can be found in literatures (Appendix Table S1), ranging from 1391 m$^2$ g$^{-1}$ to 2372 m$^2$ g$^{-1}$ depending on synthesis procedures and conditions.

Zn-MOF-74 [\([\text{Zn}_2(\text{DHBDC})(\text{DMF})_2 \cdot (\text{H}_2\text{O})_2]\) DHBDC= 2,5-dihydroxy-1,4-benzenedicarboxylic acid] has a 3D hexagonal rod structure.\textsuperscript{18} Oxygen abundant Zn-MOF-74 was selected as the precursor for the MOF carbon structure. Zn-MOF-74 carbonisation process above 1000 °C is accompanied with Zn structure decomposition. The resulting metal-free carbon structure has many defects created by the evaporated metallic Zn. The oxygen content in the Zn-MOF-74 structure can promote the formation of large number of gaseous products during the carbonisation process, creating favourable pores.\textsuperscript{19}

In this chapter, MOFs were synthesized and carbonised to obtain stable porous structures for CO$_2$ capture at high temperature, up to 75 °C. Highly hierarchical porous MOF carbons with simultaneously high surface area (up to 2237 m$^2$ g$^{-1}$) and ultra-high total pore volume (up to 4.6 cm$^3$ g$^{-1}$) were achieved.

### 5.2 Results and Discussion

#### 5.2.1 Synthesis of MOFs carbons

In this study, all the MOFs were synthesized by the solvothermal method according to literature, steps described in section 2.2.5.\textsuperscript{14,20,21}

MOF-5 (DEF) sample yield was 6.22 g, the dry product being in the form of orange crystal granules and size larger than MOF-5 (DMF).

MOF-5 (DMF) sample yield was 6.60 g, the dry product being in the form of white crystal granules.

Zn-MOF-74 sample yield was 4.95 g, the dry product being in the form of bright yellow powder with no obvious shape as observed by naked eyes.
After 1000 °C carbonisation, MOF-5 (DEF) yielded 230 mg (7.7%) MOF carbon, MOF-5 (DMF) yielded 276 mg (9.2%) MOF carbon and MOF-74 yielded 375 mg (12.5%) MOF carbon.

After 1100 °C carbonisation, MOF-5 (DEF) yielded 256 mg (8.5%) MOF carbon, MOF-5 (DMF) yielded 262 mg (8.7%) MOF carbon and 1.5 g MOF-74 yielded 183 mg (12.2%) MOF carbon.

Figure 5. 2. a) MOF-5 (DEF and DMF as solvents) and MOF-74 precursor prepared and mixed, b) Hydrothermal at 100 °C for 48 hours, c) MOF-5-DEF; MOF-5-DMF and MOF-74 structure formed, d)-f) MOF-5 (DEF), MOF-5 (DMF) and MOF-74 products; g) MOF carbon products produced by carbonisation at 1000 °C.

5.2.2 Chemical modification of MOF carbon substrates

MOF carbons were chemical modified using wet impregnation method as described in section 2.2.6. For simplicity, amine impregnated samples are labelled in short form. For example, a 10 mg MOF-5 (DMF) 1000 °C with 200 µl diluted PEHA solution is labelled as M102P.
5.2.3 Physical properties

MOF carbons discussed in this chapter were synthesized by 1000 °C/1100 °C MOF precursors carbonisation process. Thermogravimetric analysis (TGA) tests were carried out under the same condition as carbonisation to study the weight change of samples with temperature. Figure 5.3 represents the MOF mass change in percentage versus carbonisation temperature.

![TGA plot for MOF-5 and MOF-74 samples from room temperature to 1000 °C. Heat flow is in dashed line with Y axis.](image)

The carbonisation process mainly goes through three weight-losing stages. The first mass-loss occurring below 150 °C is due to the evaporation of adsorbed/terminal water molecules within the pores. As the MOF-5 samples are highly sensitive to moisture, it has been taken care of against exposure to water-containing environment, and therefore the loss at this stage is not obvious. The second mass-loss occurring between 400 °C and 600 °C is attributed to the framework decomposition, which leads to a major release of carbon containing gaseous products (mostly CO₂, CO, C₆H₆ and a small amount of H₂ and CₓHᵧ hydrocarbon mixtures) and formation of zinc oxide). The third mass-loss seen in MOF-5 and MOF-
74, starting at >900 °C, was due to further release of CO₂ and CO with Zn through the reduction of ZnO by carbon via ZnO + C → Zn(g) + CO. The residue structure after carbonisation above 900 °C is stable and metal-free porous carbon.

The SEM micrographs presented in Figure 5.4-5.6 show the morphology of MOF carbons. By comparing the structures of MOF precursors in literature, it reveals that the MOF carbons retain similar crystalline shapes and structures to their MOF precursors. It is also noticed that the parent MOF crystallites shrink after carbonisation as evidenced from the microcracks and the sponge-like surface morphology.

The hierarchical pore formation in the MOF carbons is understandable from their pre-defined well-ordered pore structures of MOF precursors. Considerable C and O mass-loss should occur from the framework ligands through the reduction of ZnO that leads to the evolution of Zn, CO and CO₂, leaving a more defective or hollow carbon network. This process is a simple self-etching for the carbon structure, similar to the KOH activation commonly used to create micro-porous structure.

Figure 5.4. SEM micrographs of DEF-MOF-5@1100 °C 6 h sample.
Figure 5. 5. SEM micrographs of DMF-MOF-5@1100 °C 6 h sample.

Figure 5. 6. SEM micrographs of MOF-74@1100°C 6 h sample.

SEM images of MOF-74 carbon showing homogeneous elongated column-like nano-crystallites with width ~3-10 µm aggregated in clusters.
The hierarchical pores with large cavities and microcracks can facilitate amine loading into most of the pores. Figures 5.7-5.9 are SEM images of MOF-5 carbons with 3x and MOF-74 carbon with 2x TEPA loading.

Figure 5. 7. SEM micrographs of DEF-MOF-5@1100 °C 6 h with 3xTEPA sample.

Figure 5. 8. SEM micrographs of DMF-MOF-5@1100 °C 6 h with 3xTEPA sample.
For E113T sample, the surface pores are mostly filled with amine and the cracks are less visible. M113T sample has the same amine loading as E113T, TEPA is still excess after filling the pores, and therefore a coating at the surface can be observed. For 74112T loading, the amine is already in excess amount for this MOF carbon. Amine acts like a glue joining several crystals together. Excess amount of amine also forms sphere-like shape sitting among the MOF structures.

Typical MOF-5 and MOF-74 XRD spectra are shown in Figure 5. 10.14 The powder XRD diffraction patterns reveal crystalline structure of the samples. The peak at 13.8° in the spectrum is due to the reflections of (400) planes and the 6.8° peak is due to (200) planes. The high intensity peak at around 9.7° may be due to the solvent residue when the sample dried at relative low temperature below 150 °C.23 The XRD pattern of Zn-MOF-74 structure indicating the peak at around 6.8° and 12° are due to the (110) and (300) planes.
Figure 5. 10. XRD patterns of a) MOF precursors. Figure derived from literature. b) carbonised MOFs, measured using Cu-K-alpha source.

During the carbonisation process of MOFs, framework decomposition leads to a major release of carbon containing gaseous products. The carbonisation yields materials with featureless XRD pattern. As from Figure 5. 10 b), there is no visible peak of MOF carbons from the XRD spectra, showing the samples are non-crystalline with disorderly oriented tiny graphenic type fragments in the structures.

The disorder of the samples was characterised using Raman Spectroscopy. Raman spectra of annealed samples obtained at 1000 °C and 1100 °C show disordered carbon D and G bands at ~1380 cm\(^{-1}\) and ~1560 cm\(^{-1}\) respectively, as shown in Figure 5. 11. Second order D-band between 2600 cm\(^{-1}\) and 2900 cm\(^{-1}\) are very broad and featureless. The highly intense disorder induced D-band and weak stacking induced 2D band in the Raman spectra represent highly disordered/defective nature of MOF carbons.
With chemical modification, Raman spectra still show representative Raman modes of carbon sample. The excess amine coating on surface is evident at smeared out D and G modes with a highly increased background. The increase in amine loading resulted in decreased peak (D and G modes) to background ratio. For TEPA@MOF carbons samples, the peaks become less obvious with amine loading.

FTIR spectra of MOF carbons before and after TEPA/PEHA are shown in Figure 5.13. The different amine loading amount demonstrate different peak intensities. The vibrational mode at 3400 cm$^{-1}$ is due to hydroxyl stretching vibrations in $\text{--COOH}$
and/or adsorbed water. 1630 cm\(^{-1}\) is owing to aromatic C=C/C=O stretching, \(\sim 1384\) cm\(^{-1}\) corresponds to O−H bending from hydroxyl/phenol groups and \(\sim 1270\) cm\(^{-1}\) due to C−O−C stretching. For bulk PEHA, the IR absorption modes at 1580 cm\(^{-1}\) corresponds to N−H stretching and bending vibrations, while those at 2935 cm\(^{-1}\), 2830 cm\(^{-1}\), and 1460 cm\(^{-1}\) could be due to C−H stretching and bending vibrations respectively.

Figure 5. 13. FTIR spectra of a) MOF carbons, b) PEHA and methanol, and c) d) amine impregnated MOF carbons.

Amine impregnated MOF carbons showed certain characteristic peaks of PEHA, such as the peaks at 2944 cm\(^{-1}\) (C−H), 2835 cm\(^{-1}\) (C−H), 1573 cm\(^{-1}\) (N−H) and 1471 cm\(^{-1}\) (C−H) indicating that PEHA had been impregnated onto support pores. The C−H modes of impregnated PEHA show blueshift to smaller wavelength
compared with that of free PEHA, while the N—H bands show red shift. All samples are amine loaded using wet impregnation method by which PEHA is diluted using methanol. Dried samples do not show any characteristics as methanol, indicating the samples are dried completely.

FTIR displays very weak IR absorption modes of chemical modified MOF carbons in Figure 5.13 c). This is because the well-confined phase of PEHA is highly dispersed within the pores of MOF-5 carbons rather than surface coating of bulk TEPA/PEHA in MOF-74 carbons (bottom right). In addition, the red shift (decrease in frequency) and blue shift of N—H and C—H modes, respectively, from bulk to impregnated TEPA confirmed the pore confinement and interactions with carbon-based supports. The amine interaction is also evident in the shifts of —OH and C=O stretching in substrates.

FTIR bands in the region (1650-1300 cm<sup>-1</sup>) are assigned to asymmetric and symmetric modes of carboxylates and the region (1300-600 cm<sup>-1</sup>) is assigned to the in-plane and out-of-plane deformation modes of aromatic ring. The changes in carboxylate asymmetric and symmetric vibrations in the region of 1650-1300 cm<sup>-1</sup> are due to decarboxylation. Therefore, MOF carbonised at high temperature (1000 °C and 1100 °C) do not have characteristic in the region. With higher amine loading, the characteristic peaks of amine become more visible in the amine impregnated samples.

The chemical composition of C, N, O and Zn was determined by XPS elemental surveys. The comparative C 1s, N 1s, O 1s, and Zn 2p core-level spectra of all samples are shown in Figure 5.14. There are no N and Zn detected in N 1s and Zn 2p core level XPS spectra in carbonised samples. The X-ray photoelectron spectroscopy (XPS) C 1s core level spectra fittings shown in Figure 5.15 indicate that the MOF carbon are graphenic in nature with a majority of sp<sup>2</sup> carbons. The peaks at around 285 eV are for graphitic sp<sup>2</sup> C structure. The peaks around 286 eV are suggested to be C—N and/or Zn—C interactions, therefore was extremely small in this sample where no obvious N and Zn peak are detected. The peaks around 289 eV are attributed mainly to the C—O/C=O bonds.
Figure 5. 14. XPS spectra of MOF carbons. Core level spectra of a) C 1s, b) N 1s, c) Zn 2p, d) O 1s and e) survey.
Figure 5. 15. XPS C 1s peak fitting spectra of MOF carbons.

The fitting of C 1s spectrum of MOF carbons show a combination of graphitic sp² and defective sp³ carbons at ~285 eV, with considerable C—O and —COOH functional groups.
Table 5. 1. XPS surface elemental analysis of MOF carbons. The spectra were recorded at multiple spots on each sample and an average value was taken. The atomic percentages for C and O are estimated from the C 1s and O 1s peaks in the survey spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>C (at%)</th>
<th>O (at%)</th>
<th>O/C ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-5 (DEF) 1000 °C</td>
<td>95.5</td>
<td>4.5</td>
<td>0.05</td>
</tr>
<tr>
<td>MOF-5 (DEF) 1100 °C</td>
<td>96.4</td>
<td>3.6</td>
<td>0.04</td>
</tr>
<tr>
<td>MOF-5 (DMF) 1000 °C</td>
<td>97.0</td>
<td>3.0</td>
<td>0.03</td>
</tr>
<tr>
<td>MOF-5 (DMF) 1100 °C</td>
<td>97.3</td>
<td>2.7</td>
<td>0.03</td>
</tr>
<tr>
<td>MOF-74 1000 °C</td>
<td>96.3</td>
<td>3.7</td>
<td>0.04</td>
</tr>
<tr>
<td>MOF-74 1100 °C</td>
<td>96.0</td>
<td>4.0</td>
<td>0.04</td>
</tr>
</tbody>
</table>

The carbonisation process involves reduction of ZnO by carbon and yields a pure porous carbon structure without Zn element in the final product. The XPS analysis show that no Zn is detected in all Zn 2p core level XPS spectra in the carbonised samples. Zn-MOF-74 is decomposed accompanying with Zn cation conversion into ZnO upon calcination, and the as-formed ZnO is gradually reduced by the carbon to form metallic Zn with the increase of the calcination temperature. At last, the metallic Zn is removed via evaporation when the temperature reached its boiling point at around 908 °C, resulting in the formation of metal-free porous carbon. The high oxygen content in the MOF-74 structure promotes the formation of large number of gaseous products such as CO$_2$ and H$_2$O during the carbonisation process, which is beneficial for creating favourable pores with large pore sizes.$^{19}$

For amine impregnated samples, the surface elemental analysis is not consistent with the loading amount and the variations do not have a clear trend. By comparing with SEM micrographs in Figure 5.7-5.9, it is found that the amine loading may leads to surface coating of MOF carbons. The excess amine polymer may sit at the surface or voids of the carbon substrate. And for heavily loaded MOF-74 carbons, the
polymers could surround the crystals. The unevenly distributed loadings have led to inconsistent elemental surveys from point to point.

Table 5. 2. XPS surface elemental analysis of amine impregnated MOF carbons. The spectra were recorded at multiple spots on each sample and an average value was taken. The atomic percentages for C and O are estimated from the C 1s and O 1s peaks in the Survey spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>O (at%)</th>
<th>C (at%)</th>
<th>N (at%)</th>
<th>O/C ratio</th>
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</thead>
<tbody>
<tr>
<td>E103P</td>
<td>9.1</td>
<td>75.2</td>
<td>15.7</td>
<td>0.12</td>
</tr>
<tr>
<td>E103T</td>
<td>10.0</td>
<td>76.2</td>
<td>13.8</td>
<td>0.13</td>
</tr>
<tr>
<td>E113P</td>
<td>7.4</td>
<td>76.2</td>
<td>16.4</td>
<td>0.10</td>
</tr>
<tr>
<td>E113T</td>
<td>10.5</td>
<td>75.3</td>
<td>14.2</td>
<td>0.14</td>
</tr>
<tr>
<td>M103P</td>
<td>16.5</td>
<td>70.0</td>
<td>13.5</td>
<td>0.24</td>
</tr>
<tr>
<td>M103T</td>
<td>15.5</td>
<td>70.2</td>
<td>14.3</td>
<td>0.22</td>
</tr>
<tr>
<td>M113P</td>
<td>9.0</td>
<td>72.1</td>
<td>18.9</td>
<td>0.12</td>
</tr>
<tr>
<td>M113T</td>
<td>11.2</td>
<td>67.3</td>
<td>21.5</td>
<td>0.17</td>
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<tr>
<td>74103P</td>
<td>10.1</td>
<td>81.2</td>
<td>8.7</td>
<td>0.12</td>
</tr>
<tr>
<td>74103T</td>
<td>15.0</td>
<td>69.1</td>
<td>15.9</td>
<td>0.22</td>
</tr>
<tr>
<td>74113P</td>
<td>8.1</td>
<td>82.6</td>
<td>9.3</td>
<td>0.10</td>
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<tr>
<td>74113T</td>
<td>16.4</td>
<td>69.6</td>
<td>14.0</td>
<td>0.24</td>
</tr>
</tbody>
</table>

The framework structure, metal-centres and initial porosity properties of the MOF precursor play crucial roles in developing desirable porosity in MOF carbons. In theory, MOF carbons gain surface area and pore volume from MOF precursors and leave more void space due to the extended pores within the crystals after carbonisation. The low-density, spherical pore structure and cubic crystallites of the MOF-5 precursor always yield high porosity in the MOF carbons.
Figure 5. 16. a) c) e) N₂ adsorption-desorption isotherms, b) d) f) pore size distribution and cumulative pore volume plots of MOF precursors and MOF carbons obtained with QSDFT and BJH methods.

The BET surface area and pore volume for the MOF carbons were obtained from the N₂ adsorption-desorption isotherms, as shown in Figure 5. 16. Measured N₂ isotherms at 77 K of MOF carbons belong to type I (microporous) and type II
(micro+meso+macroporous) isotherms classified according to the International Union of Pure and Applied Chemistry (IUPAC).\textsuperscript{24} The adsorption isotherms of MOF precursors and MOF carbons change from type II adsorption to type I adsorption before and after carbonisation process. Type I concave curve is mainly for microporous solids while type II curve is for micro-meso-macroporous solids. QSDFT method is valid for micropore region and limited to pore size \( \leq 50 \) nm, and BJH method is more suitable for meso- (\( >3 \) nm) and macro-pores (\( >50 \) nm). Therefore, both fitting models were used to analyse the pore size distribution and cumulative pore volumes of MOF carbons.

Pore size distribution diagram reveals that after high temperature annealing, MOF carbons generate more meso- and macro-pores due to loss of metal ion centres Zn, C and O from the framework ligands. Zn centres are reduced during the carbonisation process which leads to the evolution of Zn, CO and CO\(_2\), leaving a more defective or hollow carbon network.\textsuperscript{14}

The resultant MOF carbons has a hierarchical pore structure with high proportion of micro- and meso-pores. MOF framework structure acts as a self-template, microporosity from the MOFs precursors is mostly retained in the derived MOF carbons and the meso-and macro-pores are generated by reduction of ZnO with carbon and by evolution of Zn, CO and CO\(_2\).\textsuperscript{14} Therefore, MOF carbons show considerable enhancement in the total pore volumes and BET SSA compared with the MOF precursors. This process is a simple self-activation for the carbon, similar to the commonly used physical or chemical activation of the carbonaceous precursors with either CO\(_2\) or KOH to achieve porous activated carbons.\textsuperscript{25–27}

The framework structure, metal-centres and initial porosity properties of the MOF precursors are important to develop an ideal MOF carbon with desired porosity. Low density, spherical pore structure and cubic crystallites of MOF-5 precursor are more desirable for synthesizing MOF carbon as compared with MOF-74 in this case. The calculated BET surface area and pore volume values for the MOF carbons are obtained from the N\(_2\) adsorption-desorption isotherms and are summarised in Table 5.3.
Table 5. The BET surface area, total pore volume (micro+meso+macro pore volume), QSDFT micropore surface area and pore volume and BJH meso and macropore volume of MOF carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET SSA (m² g⁻¹)</th>
<th>V_total (cm³ g⁻¹)</th>
<th>QSDFT micro-SA (m² g⁻¹)</th>
<th>V_micro (cm³ g⁻¹)</th>
<th>V_meso+macro (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MOF-5 (DEF) 1000 °C</td>
<td>2237</td>
<td>4.69</td>
<td>2064</td>
<td>2.84</td>
<td>3.98</td>
</tr>
<tr>
<td>MOF-5 (DEF) 1100 °C</td>
<td>1857</td>
<td>1.83</td>
<td>1694</td>
<td>1.24</td>
<td>1.07</td>
</tr>
<tr>
<td>MOF-5 (DMF) 1000 °C</td>
<td>2186</td>
<td>2.33</td>
<td>2002</td>
<td>1.60</td>
<td>1.49</td>
</tr>
<tr>
<td>MOF-5 (DMF) 1100 °C</td>
<td>1896</td>
<td>1.86</td>
<td>1762</td>
<td>1.27</td>
<td>1.08</td>
</tr>
<tr>
<td>MOF-74 1000 °C</td>
<td>1486</td>
<td>0.98</td>
<td>1432</td>
<td>0.90</td>
<td>0.35</td>
</tr>
<tr>
<td>MOF-74 1100 °C</td>
<td>1566</td>
<td>0.82</td>
<td>1477</td>
<td>0.75</td>
<td>0.12</td>
</tr>
</tbody>
</table>

Notes: BET-SSA is a surface area obtained through BET method on the desorption isotherm in the P/P₀ pressure region between 0.01 and 0.2.

Micro-SA is a micropore surface area for the pores of up to ≤2 nm obtained through QSDFT fit to the desorption isotherm. V_micro is a micropore volume for the pores up to ≤2 nm obtained through QSDFT fit to the desorption isotherm. V_meso+macro is a meso to macro pore volume for pores >3 nm, obtained through classical BJH method on the desorption isotherm. Note that the total pore volume at P/P₀ ≈ 0.99 is in fairly good agreement with the total pore volume obtained through BJH method (meso+macro) + QSDFT method (micro).

N₂ adsorption-desorption isotherms indicate a considerable enhancement in the porosity of the samples after carbonisation. For instance, the SSA of 1100 °C carbonised MOF-74 has reached 1566 m² g⁻¹ from 1000 m² g⁻¹ of its precursor and pore volume increased to 0.82 from 0.40 cm³ g⁻¹. MOF-5 synthesized using DMF usually obtains an SSA of 1300-1800 m² g⁻¹ while DEF as solvent usually gives a SSA of 3000 m² g⁻¹.¹⁴,²³ But the resultant MOF carbons do not have large difference.
in this case. All MOF carbons show a considerable enhancement in their total pore volumes as compared with their MOF precursors, which is from 0.4 cm$^3$ g$^{-1}$.

The MOF carbons show predominantly hierarchical meso-scale porosities between 3 and 50 nm. The mesopores between 3 and 200 nm derived from the BJH method accounts 3.98 cm$^3$ g$^{-1}$. The micropores (up to 3 nm by QSDFT method) account for 2.84 cm$^3$ g$^{-1}$. And the total pore volume can reach 4.70 cm$^3$ g$^{-1}$. According to the TEPA density ($\approx$ 1 g cm$^{-3}$), the pores can accommodate up to 4.7 g of amine for each gram of MOF-5 (DEF) carbon.

![Digital image of amine impregnated MOF-5 (DMF)@1100 °C carbon, from left to right are 1x, 2x, 3x and 4x loading.](image)

The total pore volume of MOF-5 (DMF) 1100 °C carbon sample is 2.33 cm$^3$ g$^{-1}$. In theory it could accommodate over 2 g of amine for each gram of MOF-5 (DMF) carbon. However, excess amine polymer sticks to the glass sample vial with 2 g g$^{-1}$ TEPA loading and samples become stickier with increasing loading amount. This is also evident from the direct comparison of the N$_2$ isotherms, derived porosity and pore size distribution, as shown in Figure 5.18 to Figure 5.20. The reduction in pore volume with amine loading is larger than theoretical estimation based on amine liquid density, which may be due to pore blocking effect.
Figure 5. 18. Top four: N$_2$ isotherms of amine impregnated MOF-5 (DEF) carbons. Bottom four: Pore size distribution of amine impregnated MOF-5 (DEF) carbons.
Figure 5. 19. Top four: N\textsubscript{2} isotherms of amine impregnated MOF-5 (DMF) carbons. Bottom four: Pore size distribution of amine impregnated MOF-5 (DMF) carbons.
Figure 5. Top four: $N_2$ isotherms of amine impregnated MOF-74 carbons. Bottom four: Pore size distribution of amine impregnated MOF-74 carbons.
Figure 5.18-5.20. shows $N_2$ isotherms of carbonised MOF-5 (DEF) (both 1000 °C and 1100 °C) with different amount of amine (both TEPA and PEHA) impregnation. The highest adsorption point indicates the total pore volume of the sample, the higher the adsorption amount, the higher the total pore volume of sample. MOF carbons with higher amount of amine impregnation result in lower pore volume. This indicates the polyamides have occupied certain amount of the pores as well as coating on the surface of MOF carbons. All samples within the same group (plotted in the same figure) are consistent with the trend. It is worth noting that samples TEPA@MOF-5 (DMF) 1000 °C and TEPA/PEHA@MOF-5 (DMF) 1100 °C in 3x, 4x and 5x are not in the same trend. However, the total $N_2$ adsorption amount for these samples is extremely low, all below 10 cm$^3$ g$^{-1}$. This is within the machine's systematic error and is negligible.

After amine loading, the specific surface area and pore size distribution were altered. The total pore volume of mesopores and BET SSA decrease as the amount of loaded amine increased. Besides, the number of micro pores decrease significantly with higher loading but are still visible. Pores with size <10 nm also decrease, and the most distributed position tended to shift to the smaller size, which is the evidence of successfully impregnated MOF carbons. These observations suggest that the amines are loaded onto the surface of the structure instead of occupying the inside.

The pore size distribution of amine impregnated MOF carbons shows that with higher amount of amine loading, the number of pores from all ranges is reduced. CO$_2$ gas molecules have a kinetic diameter of 3.3 Å. Pore size slightly larger than 3.3 Å will have intrinsic capability of capturing CO$_2$ gas molecules. The pore size of the nanocomposite is centred in the range of 5-10 nm, which is larger than the kinematics diameter of CO$_2$ molecules. This is in good agreement with the amine content in the free pore space with low amine loading and thickened surface coating with high amine loading, respective to the relative pore volume of the specific sample.

Comparing with pore size distribution diagram and $N_2$ adsorption isotherms of MOF-5 carbons (Figure 5.18-5.19), it is predicted that the amine loading of 5 mmol g$^{-1}$ is approaching or has reached the maximum capacity of the substrates. Therefore, the
maximum CO\textsubscript{2} uptake amount obtained among the chemical modified samples could represent the best performance of the MOF carbon/amine absorbents.

### 5.2.4 TEPA/PEHA modified MOF carbons for CO\textsubscript{2} capture

The CO\textsubscript{2} capture capacities were determined using two methods, one by gravimetric method for single-component CO\textsubscript{2} uptake. The other is volumetric method by CO\textsubscript{2} adsorption-desorption isotherms.

The gravimetric CO\textsubscript{2} uptake tests were performed with TGA under a constant gas flow at 100 ml min\textsuperscript{-1} around 1 bar. The desorption process was obtained under dry N\textsubscript{2} flow (100 ml min\textsuperscript{-1}) at ≈100 °C. The sorption tests were conducted at different temperatures of 25 °C, 50 °C, and 75 °C.

![Graph showing CO\textsubscript{2} uptake](image)

Figure 5. 21. CO\textsubscript{2} uptake of amine impregnated MOF carbons measured with TG under pure CO\textsubscript{2} gas flow.

CO\textsubscript{2} adsorption on amine-modified materials is dominated by chemisorption as a result of direct interaction between the adsorbate and amine groups. CO\textsubscript{2} adsorption is governed by chemisorption in such sorbents. The CO\textsubscript{2} uptake kinetics are very fast and selective over other gases. It has been well established that the primary and secondary amino groups in polyamines form carbamates upon CO\textsubscript{2} interaction, which subsequently transform into bicarbonate if water is present during adsorption.
Chemisorption tends to occur at low temperature, which M112P achieved a 15.6 wt% uptake at 25 °C in pure CO$_2$ gas flow, correspond to 3.54 mmol g$^{-1}$. The adsorption of the same sample at 50 °C was 4.8 wt% and 3.2 wt% at 75 °C. M113P sample tested under 75 °C do not show visible CO$_2$ uptake occurred. This may be due to excess amine loading causes blocking of the pores, lead to limited access to adsorption sites.

All samples were screened with volumetric CO$_2$ adsorption-desorption isotherms using 100% dry CO$_2$ and measured up to 1 bar at different temperatures between 25 °C and 75 °C (temperature maintained by using an electric heating water bath) on a Quantachrome Autosorb-iQ2 outgas station. The samples are degassed at 80 °C overnight prior to the actual CO$_2$ adsorption isotherm measurement. The CO$_2$ gas uptake amount is calculated with respect to the net weight of each sample after outgassing.

Figure 5.22 displays the CO$_2$ adsorption isotherm for CO$_2$ at 0 °C. The isotherms can be classified as Type III isotherms. Type III isotherms demonstrate no point B (the beginning of the middle almost linear section) and hence no identifiable monolayer formation. The adsorbent-adsorbate interactions are relatively weak, and the adsorbed molecules are clustered around the most favourable sites on the surface of a nonporous or microporous solid. This is due to amine group interacts with polar surface groups since quadrupole moment of CO$_2$ is larger than N$_2$. The amount adsorbed remains finite at the saturation pressure of $P/P_0 = 1$, displaying effect of sorption temperature on CO$_2$ sorption capacity.

A summary of total pore volume and BET SSA of amine impregnated samples are listed in Table 5.4. Total pore volume and surface area of amine impregnated samples decrease with increasing amine content. However, the decreasing amount is not proportional according to the obtained data. CO$_2$ uptake amount of the samples is also not proportional to the amine impregnation loading amount.

CO$_2$ adsorption/desorption measurements of amine impregnated MOF carbons were characterised using BET CO$_2$ isotherms at various temperatures of 0 °C and 75 °C up to 1 bar. As pre- and post-combustion CO$_2$ capture temperature is between
40 °C and 75 °C, high-pressure pure component CO₂ and N₂ adsorption performance were measured. 0 °C adsorption tests are carried out on selected samples for reference. Before the adsorption tests, the sample are outgassed at 80 °C overnight to remove the adsorbed CO₂.

Figure 5. 22. CO₂ adsorption isotherms of MOF carbons with certain amine loading at 0 °C up to 1 bar.
Figure 5. 23. CO$_2$ adsorption isotherms of MOF carbons with different amine loading at 75 °C up to 1 bar.
Figure 5. 24. CO₂ adsorption isotherms of MOF carbons with different amine loading at 75 °C up to 1 bar.

Figure 5.22-5.24. presents the comparison of CO₂ adsorption on the MOF carbons with different amine loading measured by gas uptake isotherms at 75 °C. The results show that the amount of amine loading has effect on the CO₂ adsorption capacity of the adsorbents, which has an increase of 2 mmol g⁻¹ of MOF-5 (DEF)@1000 °C PEHA loaded samples when increasing from 2x to 5x. Other samples also have certain improvements or have similar adsorption amounts.

For an amine-based adsorbent, the CO₂ adsorption capacity is mainly dependent on the accessibility of amine groups on the polymer that interacts with CO₂. The greater loading provides more sites for CO₂ adsorption. However, excess loading will block the intrinsic pores and cause polyamine chains to agglomerate. Therefore, finding an optimum loading ratio is key to produce the best performing adsorbents. In this
case, ratio 5 loading is the optimum amine loading amount. Besides, MOF carbon with highest SSA and pore volume (1000 °C DEF-MOF-5 in this case) does not give the highest CO\textsubscript{2} uptake amount. This is due to that the intrinsic structure of the MOF carbons may affect the accessibility of the reaction sites.

The CO\textsubscript{2} isotherms of E112P/E113P (Figure 5.24) show that the adsorption capacity rises as the temperature increase, measured up to 75 °C. Increasing the temperature could accelerate the amine molecules motion in the adsorbents, simultaneously leading to enhanced adsorption capacity. As the uptake temperature environment is created using temperature-controlled water bath directly disposed to the ambient environment, for the sake of safety, the maximum temperature used for uptake tests is 75 °C.

From literature, the optimum temperature is 85 °C where adsorption and desorption reach an equilibrium. The equilibrium above 85 °C shifts to desorption and the capacity decreases.\textsuperscript{29} Another study has claimed that despite higher surface amine loading, the amine-saturated species exhibited a significantly lower CO\textsubscript{2} uptake capacity than unsaturated species, attributed to a steric hindrance to gas transport offered by the dense TEPA film on the surface of the saturated MOF. It is also claimed that amine saturated adsorbents with activation temperatures ranging from 110 °C to 250 °C showed lower CO\textsubscript{2} uptake level, with a less than 10 wt% CO\textsubscript{2} adsorption capacity at 25 °C.

This effect on CO\textsubscript{2} capacity with a low degree of functionalisation with TEPA can be attributed to an increase in extra available binding sites from the amines, which provide higher density of active site/mass. When the surface is saturated with an impermeable layer of amines, accessibility to the pores within the crystals is restricted.\textsuperscript{30}
Table 5.4: Porosity & volumetric CO$_2$ (100%, dry) isotherm uptake at saturation or near saturation point below 1 bar of TEPA and PEHA impregnated MOF carbon samples, measured at different temperatures (75 °C and 0 °C).

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET surface area (m$^2$ g$^{-1}$)</th>
<th>Total pore volume (cm$^3$ g$^{-1}$)</th>
<th>CO$_2$ uptake @75 °C (mmol g$^{-1}$)</th>
<th>CO$_2$ uptake @0 °C (mmol g$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E102P</td>
<td>212</td>
<td>1.43</td>
<td>0.86</td>
<td>/</td>
</tr>
<tr>
<td>E103P</td>
<td>67</td>
<td>0.66</td>
<td>2.01</td>
<td>/</td>
</tr>
<tr>
<td>E104P</td>
<td>23</td>
<td>0.21</td>
<td>2.35</td>
<td>/</td>
</tr>
<tr>
<td>E105P</td>
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<td>0.08</td>
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<td>/</td>
</tr>
<tr>
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<td>0.28</td>
<td>1.69</td>
</tr>
<tr>
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<td>0.44</td>
<td>0.62</td>
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</tr>
<tr>
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<td>0.78</td>
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</tr>
<tr>
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<td>12</td>
<td>0.08</td>
<td>0.73</td>
<td>0.70</td>
</tr>
<tr>
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<td>1.48</td>
<td>2.88</td>
</tr>
<tr>
<td>E113P</td>
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<td>0.44</td>
<td>3.14</td>
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</tr>
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<td>E114P</td>
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<td>3.13</td>
<td>1.73</td>
</tr>
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<td>E115P</td>
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<td>/</td>
</tr>
<tr>
<td>M114P</td>
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<td>/</td>
<td>0.44</td>
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<td>2.48</td>
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<td>M113T</td>
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<td>0.01</td>
<td>2.98</td>
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<tr>
<td>M114T</td>
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<tr>
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<td>/</td>
</tr>
<tr>
<td>74113T</td>
<td>15</td>
<td>0.02</td>
<td>1.18</td>
<td>/</td>
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</tbody>
</table>

Comparing the CO₂ adsorption capacity between 0 °C and 75 °C, unsaturated samples usually have higher capacity at 0 °C while saturated samples have higher capacity at 75 °C. This is due to that the CO₂ adsorption reaction is exothermic, the increasing temperature is unfavourable for CO₂ adsorption capacity. Therefore, the adsorption capacity is expected to be higher when the reaction kinetics is not strongly affected at lower temperature. However, the formation of bulk-like amines inside the pore at low temperature leads to CO₂ adsorption as a diffusion-limited process. The reaction rate, especially the initial reaction rate, increases when the temperature is high. The high diffusion rate results in a high capacity at 1 bar. The similar observation was also reported in the literature.³¹⁻³⁵

By cross comparison, DEF-1000 °C and DMF-1000 °C carbons have a better performance when impregnated with PEHA than TEPA. DEF-1100 °C and DMF-1100 °C carbons have similar performance with either PEHA or TEPA impregnation.
MOF-5 (DEF)@1000 °C and MOF-5 (DMF)@1000 °C have higher SSA and pore volume than MOF-5 (DEF)@1100 °C and MOF-5 (DMF)@1100 °C, which are ~2200 m² g⁻¹ and ~1850 m² g⁻¹ respectively. Therefore, it can be predicted that PEHA gives a better performance when the surface and pores have enough space for it to expand and give access to all the reaction sites. Similarly, when the surface area and pore volume of MOF-5 (DEF)@1100 °C and MOF-5 (DMF)@1100 °C are smaller, TEPA and PEHA show similar performance as PEHA does not have advantage of an extra reaction site. MOF-5 (DEF)@1000 °C and MOF-5 (DMF)@1000 °C are highly microporous structures, which are more suitable for CO₂ capture at 1 bar pressure because of large caging effect. Porous structure with high content of meso- or macro-pores are potentially more suitable for high pressure adsorption.

The adsorptive capacities of MOF carbons from peer literatures have an average uptake amount between 2 to 3 mmol g⁻¹. The 4.37 mmol g⁻¹ achieved in this series of experiments has stated that MOF carbons have great potential in CO₂ adsorption applications.

The adsorption curves of 75 °C adsorption tests indicate that the CO₂ uptake follows a two-stage process. The beginning stage is a quick weight gain due to the surface chemical reaction, and the second stage involves a comparatively slow diffusion until reaching saturation.

The chemical reaction between amines and CO₂ on the sample surface decides the CO₂ uptake rate at the beginning stage. This is because CO₂ interacts first through predominantly intermolecular forces on any solid surface, such as van der Waals. If there is no chemical interaction that would favour a chemical bond, the interaction follows simple condensation principles where layer-by-layer deposition is likely to take place. Adsorption of CO₂ on the pore walls is a favourable event and leads to CO₂ capture. This leads to a steep increase in uptake capacity until the pore is filled, for example, in a micropore. However, the slow diffusion of the CO₂ into the sorbents makes the rate slow down. The two-step adsorption process is not obvious in low temperature adsorption at low temperature, 0 °C in this case.
5.3 Conclusions

A group of highly hierarchical porous carbons with high surface areas up to 2237 m$^2$ g$^{-1}$ and high total pore volumes up to 4.69 cm$^3$ g$^{-1}$ have been synthesized by means of high temperature carbonisation of MOF-5 (DMF or DEF as solvent) and MOF-74. The MOF carbons have defective carbon structures with higher amount of micro- and meso-pores as compared with its MOF precursors. Carbonisation also solved the problem that these MOF precursors are highly moisture sensitive and will collapse when exposed to the air. The measured maximum CO$_2$ adsorption amount is 4.37 mmol g$^{-1}$ and has a potential double adsorption amount when in a humid environment. It can be concluded that the selection of MOF structure and the process conditions play a critical role in obtaining the desirable porosities in the carbon structures. It is important to have not only a sufficiently high surface area, but also high pore volume with a wide range of 3D hierarchical pores over the micro- to mesopore range in order to achieve near-space filling, strong confinement, and well dispersion of the impregnated amine. Further improvements may also be achieved by fine control of the pore size of the substrate.
Chapter 5 References


11. Sumida, K., Rogow, D. L., Mason, J. A., Mcdonald, T. M., Bloch, E. D., Herm,


Chapter 6 Summary of Findings and Conclusions

Carbon-based structures derived from GO and MOFs have been exploited for their applications on low temperature physisorption and chemisorption of CO₂ in this study. In general, the sorbent materials are chemically and physically stable porous materials with large porosity and high surface area. By modifying their structure, pore sizes, oxygen contents and surface chemistry, they have achieved high CO₂ uptake capacity and can be regenerated at relatively low temperature at 100 °C.

In this section, the exfGO, actGO and MOF carbons amine sorbents were compared for their physical properties and CO₂ capacity. A selection of best performing samples in terms of high surface area and total pore volume of each type of carbon materials is listed in Table 6.1.

Table 6.1. BET specific surface area and pore volume of selected GO, exfGO, actGO and MOF carbons.

<table>
<thead>
<tr>
<th>Sample</th>
<th>BET SSA (m² g⁻¹)</th>
<th>Total pore volume at P/P₀ of ≤0.994 (cm³ g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO-R6</td>
<td>99</td>
<td>0.11</td>
</tr>
<tr>
<td>exfGO-Z</td>
<td>797</td>
<td>5.88</td>
</tr>
<tr>
<td>exfGO@600C6h-Z</td>
<td>853</td>
<td>6.68</td>
</tr>
<tr>
<td>actGO-1</td>
<td>2540</td>
<td>1.50</td>
</tr>
<tr>
<td>MOF-5 (DEF) 1000 °C</td>
<td>2237</td>
<td>4.69</td>
</tr>
<tr>
<td>MOF-5 (DEF) 1100 °C</td>
<td>1857</td>
<td>1.83</td>
</tr>
<tr>
<td>MOF-5 (DMF) 1000 °C</td>
<td>2186</td>
<td>2.33</td>
</tr>
<tr>
<td>MOF-5 (DMF) 1100 °C</td>
<td>1896</td>
<td>1.86</td>
</tr>
<tr>
<td>MOF-74 1100 °C</td>
<td>1566</td>
<td>0.82</td>
</tr>
</tbody>
</table>

ExfGO and actGO substrates as described in Chapter 4 were synthesized from GO through thermal exfoliation and subsequent KOH activation. Oxidation level determines the nature of exfoliation and porosity development. The physical properties of these materials are directly associated with the oxidation degree of GO.
precursor. In chapter 3, GO structure was modified by varying the oxidising agent. The water adsorption capability of GO networks has also been explored. Suggested water adsorption mechanism in GO follows the steps of initial physisorption in the form of layers and clusters and followed by capillary condensation. GO-R6 showed high water uptake up to 1.3 times of its own weight. It is found that 6 wt. equivalent oxidising agent KMnO$_4$ to graphite can produce GO with the highest oxygen content (31.3 at%).

It is also found that the various oxygenated functional groups attached to the edges and interlayers at different stages of oxidation is of great importance for synthesizing a highly porous exfGO via thermal exfoliation. The exfGO had a dramatic increase in surface area and pore volume compared with GO to 797 m$^2$ g$^{-1}$ and 5.88 cm$^3$ g$^{-1}$ as well as decrease in oxygen content to $\sim$15 at%. Higher interlayer pressure build-up due to volatile oxygen functional groups and water can cause more vigorous exfoliation. It is reported that 40 MPa pressure can be generated between the layers at 300 °C for a well oxidised GO while a pressure as low as 2.5 MPa is enough to exfoliate a GO platelet. Further thermal annealing expenses the remaining oxygen and carbon skeleton to produce more pores and thus higher pore volume (6.68 cm$^3$ g$^{-1}$) and high surface area (853 m$^2$ g$^{-1}$).

KOH activation creates large amount of micropores by consuming carbon structure. Physical adsorption can be largely enhanced with micropores. However, as mesopores and macropores are sacrificed, the pore volume decreased to 1.50 cm$^3$ g$^{-1}$ while the surface area increased to 2540 m$^2$ g$^{-1}$. Limited amount of meso- and macro-pores affected the potential for chemical modification and thus chemisorption. It is found that the CO$_2$ adsorption capacity can be maximised by finding the balance between physisorption and chemisorption.

Another category of material studied in Chapter 5 is metal-organic framework. Direct carbonisation of MOFs precursors (MOF-5 and MOF-74) can lead to stable and defective carbon structures with higher amount of micro- and meso-pores. MOF-5 derived carbon structures at 1000 °C achieved high surface area of 2237 m$^2$ g$^{-1}$ and total pore volumes of 4.69 cm$^3$ g$^{-1}$. The selection of MOF structure and the process
conditions play critical roles in obtaining the desirable porosities in the carbon structures.

In order to enhance chemisorption of the solid sorbents, liquid amine impregnation method was applied to the solid substrates described above. The highest CO$_2$ uptake sorbents modified from each substrate materials are listed in Table 6.2. Chemical adsorption is exothermic and is companied by release of energy. With increase in temperature, chemical adsorption becomes unfavourable. However, reaction kinetics increases with temperature and polyamines becomes more flexible and thus give more access to amine reaction sites. For actGO+1xPEHA sample, higher temperature (75 °C) resulted a lower gas adsorption (2.75 mmol g$^{-1}$). This indicates physisorption dominated in the process.

Table 6.2 CO$_2$ uptake capacity of selected solid sorbents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CO$_2$ uptake (mmol g$^{-1}$)</th>
<th>Uptake temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>actGO+1xPEHA</td>
<td>4.60</td>
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</tr>
<tr>
<td></td>
<td>2.75</td>
<td>75</td>
</tr>
<tr>
<td>exfGO-E+6.5xTEPA</td>
<td>5.82</td>
<td>75</td>
</tr>
<tr>
<td>exfGO-E 600°C6h+6.5xTEPA</td>
<td>5.82</td>
<td>60</td>
</tr>
<tr>
<td></td>
<td>6.16</td>
<td>75</td>
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<tr>
<td>exfGO-E+5.6xPEHA</td>
<td>5.22</td>
<td>60</td>
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<tr>
<td></td>
<td>5.56</td>
<td>75</td>
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<tr>
<td>MOF-5 (DEF)1000°C+5xPEHA</td>
<td>2.82</td>
<td>75</td>
</tr>
<tr>
<td>MOF-5 (DEF)1100°C+4xTEPA</td>
<td>4.37</td>
<td>75</td>
</tr>
<tr>
<td>MOF-5 (DMF)1000°C+2xPEHA</td>
<td>2.49</td>
<td>75</td>
</tr>
<tr>
<td>MOF-5 (DMF)1100°C+3xTEPA</td>
<td>2.98</td>
<td>75</td>
</tr>
<tr>
<td>MOF-74 1100°C+4xTEPA</td>
<td>1.18</td>
<td>75</td>
</tr>
</tbody>
</table>

Exceptional functional performances from meso- and macro-pore rich GO-based networks with ultrahigh total pore volumes were achieved. The solid-amine system derived from GO, amine@exfGO, displayed efficient CO$_2$ capture and exceptional
CO₂ cyclic uptake stability. The networks have pores ranging from micro, meso to macro sizes where physisorption and chemisorption can be achieved at the same time. A CO₂ uptake capacity of 6.16 mmol g⁻¹ can be achieved by exfGO-E 600°C6h+6.5xTEPA at 75 °C. Besides, the stability of the adsorption system is largely improved compared with liquid amine scrubbing system. After over 40 cycles and 100 hours’ continuous operation, a sample with the same amine loading still showed high working capacity of 4.5 mmol g⁻¹. Typical loss of amine after 40 cycles was less than 2 mmol g⁻¹. The stability is among the top of other solid-amine system in literature reports. The long-term and high-temperature stability can be further enhanced with the incorporation of the more stable long chain and high molecular weight polyamines. Further improvements may also be achieved by fine control of the pore size of the substrate.

Amine@MOF carbons sorbents showed promising CO₂ uptake results and the measured maximum CO₂ adsorption amount is 4.37 mmol g⁻¹. However, it is less effective than amine@exfGO sorbent system. By comparing the pore volume and surface area of exfGOs and MOF carbons, exfGOs have lower surface area of less than 1000 m² g⁻¹ and higher pore volume over 5 mmol g⁻¹. The amount of micropores in MOF carbons is higher than that of exfGOs while meso- and macro-pores dominate in exfGOs. The topological polar surface area of TEPA and PEHA molecules used as amine sources are 88.1 Å² (0.88 nm²) and 100 Å² (1 nm²) respectively. The molecules are prone to occupy meso- and macropores. Though MOF carbons derived from MOF-5 and MOF-74 do not show as high capacity as exfGOs in this thesis, they are still promising carbon sources as the pores can be modified through the synthesis step.

In conclusion, various materials with porous structures have offered great potential for the design and development of complex materials as molecular sorbents. The products have high thermal/chemical stability, modifiable specific surface area and pore structure as well as high functionalities. Other advantages include low cost and easy scale-up of producing porous substrates, which lead to potential industrial level usage. It is important to have not only a sufficiently high surface area, but also high
pore volume with a wide range of 3D hierarchical pores over the micro- to mesopore range in order to achieve near-space filling, strong confinement, and well dispersion of the impregnated amine.

However, the existing challenges in practical usage include effective control of desirable binding sites, porosities and functionalities, the balance of functional properties with structural integrity, and further modifying molecular selectivity in gas mixtures for purification and sensing. These need to be further explored in the future studies of this field of research.
Chapter 7 Future research plan

From the basis of the promising results obtained through the study of carbon-based solid CO$_2$ sorbents, several other potential developments of the gas sorbent materials could be exploited with further investigation:

1. A potential application of CO$_2$ sorbent materials is towards direct air capture (DAC). The concentration of CO$_2$ in atmosphere is in ppm level which requires extremely high selectivity and strong binding between the molecules if exposed to the ambient environment for a long period of time. While exploiting the possibility of sorbents for DAC, it is found that water uptake of the sorbent from air dominants and an accurate CO$_2$ uptake amount cannot be determined with varying relative humidity. Therefore, the humidity factor needs to be carefully considered for further investigation in this application. Besides, the sorbents could be potentially used as CO$_2$ capture dehumidifier.

2. Two amine-rich polymers TEPA and PEHA have been used respectively for chemical modification in the study. The next step of research could be introducing blended amines to the solid substrate system. The blends of two amines are formulated such that the amines have complimentary characteristics. The formulation is both in terms of the selection of amines and the amount of each (i.e., blending proportions).

3. For the quantifying measurements of gas uptake capacity, single gas adsorption has been tested using BET adsorption-desorption isotherms in the study. Mixed gas separation of CO$_2$ and N$_2$ gas has been tested using TGA with two inlet streams mixture by controlling flow rate. However, a more accurate CO$_2$/N$_2$ selectivity can be determined by breakthrough experiments by using pre-mixed gases. Meanwhile, other gas mixture, such as CO$_2$/CH$_4$ separation can also be tested to allow extended applications to the gas industry.

4. Simulation study is also important when exploiting new materials, molecular dynamics inside a pore structure could be simulated to obtain a best model and
experiment goal to synthesis a particular gas sorption material. Simulations could also show the maximum gas uptake capacities and selectivity at an ideal condition.

5. A recent study by Cho et al. has exploited an in-situ X-ray diffraction on the extension of gas adsorption crystallography from MOFs with a single type of pore to those with multiple types of pores. Isotherms of individual pores are generated by combining gas adsorption measurements with in-situ XRD. The study uncovered the hidden adsorption stages under the overall gas adsorption isotherms, and to analyse gas adsorption in each individual pore in a continuous manner along the entire isotherm. This leads to the disclosure of previously inaccessible information concerning the subtle difference in pore metrics between the pores, the adsorbate framework interactions and the impact of pore geometry on the multilayer adsorption of different adsorbates. The approach is applicable to a large variety of MOFs as well as other types of porous materials, such as zeolite and mesoporous silica, with hierarchically arranged pores. The capability to elucidate gas adsorption at the individual pore level will be of great interest for the rational design of porous materials. Further study on the gas adsorption mechanism of each individual pores can be thoroughly conducted using this method.
Appendix

Table S1. MOF-5 BET surface areas and total pore volumes from literatures.

<table>
<thead>
<tr>
<th>BET surface area (m² g⁻¹)</th>
<th>Total pore volume (cm³ g⁻¹)</th>
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</tr>
<tr>
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Chapter 7 & Appendix References


Publication list


Paper in preparation

Synthesis and properties of graphene oxide (GO) with various degrees of oxidation. Amine impregnated nanoporous carbons derived from MOF-5 and MOF-74 for CO$_2$ capture.