Nanoengineering Graphene Oxide for Water Treatment Applications

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Nanoengineering Graphene Oxide for Water Treatment Applications

A DISSERTATION PRESENTED

BY

CARLO ALBERTO AMADEI

TO

THE JOHN A. PAULSON SCHOOL OF ENGINEERING AND APPLIED SCIENCES

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS

FOR THE DEGREE OF

DOCTOR OF PHILOSOPHY

IN THE SUBJECT OF

ENGINEERING SCIENCES

HARVARD UNIVERSITY

CAMBRIDGE, MASSACHUSETTS

APRIL 2019
Nanoengineering Graphene Oxide for Water Treatment Applications

ABSTRACT

The water crisis is one of the greatest challenges of our time. Water is essential to agricultural production, food security, ecosystems; its scarcity jeopardizes the development of nations and basic human existence. The current water crisis is exacerbated by anthropogenic phenomena, such as climate change and increased water demand, that also undermine access to clean water. Groundwater plays a pivotal role in the water supply. Almost half of the world’s population relies on this resource to satisfy basic needs. However, groundwater is extracted at faster rates than it is recharged by the natural cycle. New technological advances are needed to supply water in a more sustainable manner. One of these technologies is wastewater reclamation, in which wastewater is treated to a level that can be reused, thus avoiding the withdrawal of new freshwater from the natural cycles. Innovation in wastewater reclamation relies on the use of new materials with more effective filtration capabilities. In particular, nanomaterials that exhibit special physical and chemical properties make them interesting products and a valid alternative to the currently used polymeric membranes. In recent years, researchers have focused on the use of graphene oxide (GO) in water treatment after molecular dynamic simulations and filtration experiments demonstrated promising features including permeability and the ability to sieve out ions and molecules. These remarkable results sparked a new line of research that has opened up new avenues of inquiry and scientific questions. This dissertation attempts to address these scientific questions by elucidating the properties of GO and its performance as a molecular sieve. Three main results are contained in this work. (i) Standardization of GO offering high-throughput characterization techniques, which facilitates discussions within the research community and comparisons of results. (ii) Confirmation, using novel Lattice-Boltzmann simulations, of the friction-like water transport inside GO nanochannels. The simulations, supported by experimental permeation results, also identify the main GO properties affecting the water transport. (iii) Evidence of the fine-tuning of GO properties, by creating GO nanoscrolls and fully carbon membranes. The latter material also shows the potential of GO to be used in nanofiltration applications. This work ends with a concluding discussion aimed at establishing a new line of research based on the monitoring and control of possible GO toxicity based on its interactions with the human body.
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To a more habitable planet
Acknowledgments

Honestly the Ph.D. can be isolating, but luckily I had support from many people and friends that gave me strength to pull through. First and foremost, I would like to thank Professor Vecitis for accepting me into his group, and giving me all the support needed during this time. Chad crafted the work presented here with his ingenious way of thinking. Over the last five years, Chad has become a friend and a great advisor both within and outside research—it is a true pity that SEAS let him go. I also want to thank Professor Sunderland for “adopting” me into her lab, allowing me to use her research space and giving me research advice on the nanotoxicity part of this thesis. The scientific work presented here would not have materialized without the help of the following people: Professor Grossman with his insight on graphene oxide, Sauro Succi and Andrea Montessori with their experience in computational fluid dynamic methods, Paula Arribas and Luis Cruzado with their extended knowledge in the membrane field, and the research staff at CNS with their continuous support for the characterization of nanomaterials. During the last part of this thesis regarding toxicity, I also had the wonderful support of Professor Demokritou and Dr. Bitounis. Throughout my time here, I have had the opportunity to work next to great friends—Greg, Andrea, Marielle, and Jenny thank you for being awesome labmates and mentors.

Apart from research, what we should cherish are human connections. I was so lucky to meet the “tensome” group. We basically met at the very beginning of the Ph.D. and during my time here in Cambridge, we fostered a friendship that I hope will last for many years; we took care of each other, we celebrated each other’s successes, and we listened to each other venting and ranting. We went through hard times and we knew that we always had somebody ready to support and help us. I feel so privileged to know you guys! During my time at Harvard I also have had the wonderful opportunity to be part of two organizations that offer the distractions needed to carry out a Ph.D. First, the Harvard Italian Student Society made me feel like I was in Italy when I was homesick, and second, the Harvard Mountaineering Club made me feel alive. Finally, I would like to thank my parents for giving me the best thing they could have given me—the power of self-determination. I want to also thank my sister for being the closest person I have and a person I can always count on.
Introduction

1.1 Water Crisis

The growing global water crisis represents one of the greatest challenges that face humanity. This phenomenon, which affects different regions of the world to various degrees, has not only undermined the progress and the economic development of nations, but has also jeopardized basic human needs. The interaction between humans and water resources manifests itself in two dimensions: i) clean access to water and ii) safe access to sanitation services; (Fig. 1.1) the absence of either dimension can lead to a water crisis. In particular, the lack of access to clean water leads to economic losses such as lowered agricultural production, environmental effects (e.g., increased pollution of surface water and higher risks of fires), and social costs that negatively affect public health. On the other hand, the lack of sanitation services increases exposure to waterborne diseases such as diarrheal infections and compromises the quality of the watershed. To understand the extent of the magnitude of the water crisis across the world, it is beneficial to provide the following two numbers: 2.1 billion and 4.5 billion. These numbers refer to the number of people across the world who do not have access to safe drinking water and sanitation services, respectively.

Currently, two anthropogenic phenomena further stress the relationship between humans and water and thereby worsen the water crisis. First, climate change exacerbates the risks associated with variations in the distribution and availability of water resources. It is responsible for the severity and frequency of extreme events. For example, the increased variability in precipitation patterns
Figure 1.1: Water-humans interaction. Access to clean water and safe sanitation services are the pillars of sustainable development. Climate change and change in water demand are deeply influencing the water-humans interaction.

leads to changes in the hydrological cycle, which affects the rate at which the aquifers recharge and the availability of fresh water. As a consequence, in recent years, we have witnessed severe droughts in California, Brazil, China, Iran, South Africa, just to mention some.\footnote{233} Second, we are observing a change in the demand for water. Water usage is six times greater than it was a century ago, and by 2050, the global water requirement is projected to increase by 55\%, mainly due to growing demands from manufacturing, thermal electricity generation and domestic use\footnote{231}. Since the increase in water use is also influenced by increases in population and income, which are projected to flatten only by the end of this century\footnote{73}, global water withdrawal will increase by a staggering 150% by 2095.\footnote{51}

Groundwater plays a pivotal role in the global water supply. The world’s most extracted material, groundwater is withdrawn at a rate of $\approx 1000$ km$^3$/year. It accounts for approximately 26\% of total global water withdrawal\footnote{232} and more than 2 billion people rely exclusively on groundwater to satisfy their basic needs.\footnote{150} Agriculture also relies heavily on groundwater and accounts for 43\% of the total withdrawal. High rates of withdrawal lead to unsustainable use of groundwater with an estimated 20\% of the aquifers being over-exploited, leading to water-stressed regions.\footnote{231} Today, 4.3 billion people live in water-stressed areas for at least 1 month out of the year. (Note that an area is defined to be water-stressed when the amount of available freshwater per person per year is between 1000 and 1700 m$^3$.\footnote{158})

Needless to say, it is paramount to look at innovative technologies that can safely supply water with-
out undermining hydrological cycles and ecosystems, thus reducing the stress on freshwater bodies. In this sense, wastewater reclamation can be a valid alternative to the withdrawal of groundwater or even worse fossil water.

1.2 **Wastewater Reclamation**

Wastewater (WW) treatment decreases environmental impact and protects humans from risks associated with municipal and industrial water discharge. WW treatment plants are designed to remove contaminants from water via three treatments (Fig. 1.2). i) Primary treatments consist of physical methods that either rely on gravitational force to sediment heavy solids and particulates or scrape away grease and lighter solids that float. ii) Secondary treatments remove dissolved and suspended organic matter via biological treatment, in which bacteria and protozoa consume biodegradable, soluble organic contaminants. iii) Tertiary treatments mainly focus on the removal of nitrogen and phosphorus via biological oxidation or chemical precipitation. Finally, before discharging the treated WW to the receiving body of water (sea, river, lake, etc.), a disinfection process via chlorination, ultraviolet irradiation, or ozonation reduces the number of microorganisms in the water to below an acceptable threshold.

WW can be further treated during a polishing stage that removes dissolved solids and ions, thus reclaiming the water for agriculture, industrial, or drinking purposes. This stage is usually

![Figure 1.2: Wastewater treatment.](image)

In the primary, secondary, and tertiary treatments membranes can be used as a valid alternative to currently used technologies. Membranes are the only solution for the polishing stage required for wastewater reclamation.
1.3 Membranes

Membranes are recommended because it recovers water within the anthropogenic cycle and avoids the use of new freshwater from the natural cycle. In this sense, WW reclamation is an example of a circular economy, that short-circuits the transport of water through the natural water cycle thus decreasing our environmental impact. Furthermore, reclaimed WW is characterized by a relatively constant production during the year, due to its source being dependent not on natural hydrological cycles, but on the production of municipal sewage.

From an energy perspective, WW reclamation tends to be advantageous compared to other technologies such as desalination or groundwater extraction. WW reclamation uses a total of $2 - 3 \text{kWh/m}^3$, of which $1 \text{kWh/m}^3$ is the energy used by primary and secondary treatments, which are mandated by legislation. As a result, as low as $1 \text{kWh/m}^3$ is needed for the polishing stage to reclaim water, which is significantly lower than the energy used by desalination plants ($4 - 5 \text{kWh/m}^3$) or the extraction and transportation of groundwater to water-stressed areas (i.e., up to $4 \text{kWh/m}^3$ for Southern California). Although WW reclamation seems to be the ideal solution in terms of energy cost and environmental impact, there are a few obstacles to its implementation, including insufficient public acceptance and lack of an uniform legislation. In terms of technical performance, the main challenges are related to the functionality of the membranes used during the polishing stage.

1.3 Membranes

Membrane filtration is a physical process in which a semipermeable material separates substances when a driving force is applied. In the case of water treatment applications, the feed is made up of water and dissolved contaminants (e.g., salts). When the water is filtered through the membrane and the contaminants are rejected, the permeate is collected on the other side of the membrane. Membrane filters can be operated in dead-end configurations, but more common are cross-flow
Chapter 1. Introduction

Figure 1.3: Membranes operation. Dead-end filtration requires the flow of water to be perpendicular to the membrane surface. In cross-flow operations, the feed flow travels tangentially across the surface of the membrane.

Several forces can be used to drive the feed across the membrane: pressure, concentration, and temperature, just to mention some. In water technology, pressure-driven membrane filtration is an increasingly-used process and membranes are classified into four categories based on pore size. i) Microfiltration (MF) membranes are used to remove large suspended solids ranging from 0.1 to 10 µm and larger micro-organisms like protozoa and bacteria. ii) Ultrafiltration (UF) membranes are used to remove viruses and organic solids ranging from 10 to 100 nm. iii) Nanofiltration (NF) membranes are used to remove smaller dissolved solids and multivalent ions and have a pore size between 1 and 20 nm. iv) Reverse osmosis (RO) membranes remove ions and are characterized by sub-nanometer pore sizes. Table 1.1 summarizes the characteristics of each type of membrane.

Membrane technology is a valid alternative to traditional processes in drinking and WW treatment plants. A clear example is given by the membrane bioreactor, which can be used instead of primary and secondary treatments in domestic WW plants. On the other hand, for water reclamation, membranes are the only viable solutions and the typology of membranes used depends on the WW feed quality and on the reclamation purposes (urban, agricultural, environmental, potable uses, etc.). High water quality requirements (e.g., direct potable reuse) typically consist of conventional
1.3. Membranes

Table 1.1: Membranes characteristics.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Pore size (nm)</th>
<th>Removal Application</th>
<th>Pressure (bar)</th>
<th>Material Material</th>
</tr>
</thead>
<tbody>
<tr>
<td>MF</td>
<td>10 – 10000</td>
<td>Bacteria, protozoa, algae</td>
<td>0.5 – 1</td>
<td>polyvinylidene difluoride, polyethersulfone</td>
</tr>
<tr>
<td>UF</td>
<td>10 – 100</td>
<td>Large particles, viruses, proteins</td>
<td>0.7 – 10</td>
<td>polyvinylidene difluoride, polysulfone, polyacrylonitrile, polypropylene</td>
</tr>
<tr>
<td>NF</td>
<td>1 – 20</td>
<td>Dissolved organics, multivalent ions</td>
<td>5 – 30</td>
<td>Thin film composite (polyamide as selective layer)</td>
</tr>
<tr>
<td>RO</td>
<td>&lt; 1,</td>
<td>Monovalent ions</td>
<td>30 – 50</td>
<td>Thin film composite (polyamide as selective layer)</td>
</tr>
</tbody>
</table>

Wastewater treatment followed by UF, NF, and/or RO and, finally, disinfection by UV light or ozone. NF and RO technology is dominated by polyamide polymeric membranes, which are susceptible to membrane fouling, the Achilles’ heel of membrane separations. Fouling is defined as the accumulation of particles on the membrane and, in case of biological fouling, we observe a series of events including cell attachment, cell growth, and the production of extracellular polymeric substances. Fouling can be divided into reversible and irreversible fouling based on the attachment strength of particles to the membrane surface. Reversible fouling can be mitigated by shear force, backwashing, and the introduction of periodic cleaning steps into the filter’s operational cycle. However, in terms of biological fouling, sodium hypochlorite solution is used as a cleaning agent, which can cause membrane damage. For this reason, scientific research is currently trying to address the problem by investigating how to incorporate materials resistant to chemicals such as cleaning agents into the membrane. In the last five years, one of the materials that have received a lot of attention from the research community is graphene oxide (GO).
1.4 **Graphene Oxide**

GO is a single layer of carbon atoms arranged in a hexagonal (sp\(^2\)) lattice decorated with oxy-functionalities (Fig. 1.4) which make this material a mixed blessing. On the one hand, researchers can modify the amount of oxy-functionalities through oxidation and reduction processes, thus tuning the GO chemistry for a particular application. On the other hand, the oxy-functionalities can react with the surrounding environment to make the GO a metastable material without defined stoichiometry. This phenomenon can make it difficult to reproduce and compare results within the research community, which is a critical step in the translation of GO applications from "lab-scale" to "industrial-scale".

GO displays unique properties (see Fig. 1.5) such as near-atomic thickness, functionalization possibilities due to the presence of reactive oxygen species, scalable synthesis processes, and the possibility of controlled deposition of nanofilms through several techniques. This has led researchers to propose the use of GO in fields such as separation process, electronics, energy storage, sensors, just to mention a few; the reader can refer to literature reviews to gain a more complete view of GO applications.
1.4. Graphene Oxide

Figure 1.5: Graphene oxide properties. Clockwise from top: scanning electron microscope image displays the micrometer-sized GO flakes, atomic force microscope scan highlights the GO monolayer nature, Raman spectrum confirms the $sp^2$ bonding, X-ray diffraction spectra reports the separation distance between GO flakes, X-ray photoelectron spectra quantifies the presence of oxy-functionalities, Fourier transform infrared spectrum corroborates the presence of oxy-functionality.
Regarding separation processes, the use of two-dimensional graphitic materials was first proposed by Tanugi and Grossman using classical molecular dynamics simulations in 2012. In their investigation, they showed that single layer graphene could effectively filter ions from water. Researchers at MIT then experimentally engineered Tanugi and Grossman’s proposed design by creating pores in graphene fabricated via chemical vapor deposition (CVD). Concurrently, Nobel prize winner Geim was investigating the possibility of using stacked GO flakes instead of monolayer graphene. Although the results of the article remain controversial, the paper sparked an incredible amount of interest in the use of GO for water treatment applications. The surge was mainly driven by the ease of fabricating GO. In particular, GO can be synthesized at scale and in a cost-effective manner, which is hard to obtain in the synthesis of pristine graphene via bottom-up approaches (e.g., CVD).

Any major breakthrough in science brings with it new avenues of inquiry. This thesis addresses some of the key questions raised by recent developments in the field of GO for water treatment applications.

1.5 Thesis Overview

The work presented in this dissertation focuses on the nanoengineering of GO for water treatment applications with emphasis on its chemo-morphological properties and their effects on implementation.

Chapter 2 analyzes the state of the art for GO membranes and elucidates challenges in the implementation of GO in large-scale water treatment applications. The challenges presented in this chapter will be tackled in the following chapters to offer an in-depth look at the GO landscape.

Chapter 3 contains a discussion of GO’s chemo-morphological properties, offering high-throughput characterization methods. In this chapter, I also suggest a GO standardization method to enable the
1.5. Thesis Overview

leap of this nanomaterial from lab to industry. Chapters 4 – 6 offer GO applications for water treatment applications. In particular, Chapter 4 focuses on the fabrication of GO nanoscrolls and the tuning of their dimensions via ultrasound irradiation. Chapter 5 is centered around the creation of GO membranes whose chemo-morphological properties can be finely controlled. The properties act as knobs that dictate the transport of water in GO nanochannels. Computational fluid dynamics simulations based on mesoscale approaches provide supporting analysis. Chapter 6 reports the first fully carbon membrane in which the elemental composition of all materials is > 75% carbon and the repeating units (i.e., monomers) of the polymer have been replaced with elemental carbon architectures. In future directions, we tried to assess GO toxicity in order to limit risks connected to human exposure.
Signal-to-Noise Ratio in Graphene Oxide research

Apart from minor modifications, this chapter originally appeared as:


2.1 INTRODUCTION

Today, there is a blossoming of studies on graphene oxide-based membranes (GOMs) for water treatment driven by the simplicity of stacking graphene oxide (GO) monolayers into a laminate structure, which allows the passage of water while retaining larger molecules via size exclusion (Fig. 2.1a). However, a review of the GOM literature reveals a large variability (orders of magnitude) in experimental and simulation water permeability outputs without any quantitative attempt to create a unifying theory, allowing these discrepancies to be ignored.

A number of recent investigations have focused on design and construction of GOM heteronanoarchitectures, even though the basic physical phenomena controlling GO assembly are not yet understood. A few studies have hinted at specific GOM water treatment applications, although there is not a clear consensus on whether GOM will be practical for ultra/nanofiltration (NF) or reverse osmosis (RO). The potential number of GO surface chemistry and flake dimension, combinations as well as GO metastability, does not assist in creating a clearer picture. All of these disparities decrease the signal-to-noise ratio (SNR) when examining GOM studies as a whole. In order to invert the trend and increase GOM SNR, we suggest a nomenclature for GOM classification and
identify a number of key challenges that should be addressed.

![Figure 2.1: GOM schematic.](image)

(a) GOM rejection mechanism by size exclusion. (b) 3D (left) and 2D (right) sketch of the water structure in a GOM nanochannel. Note the water hydrogen-bonding interaction with GOM surface oxy-functional groups. Reprinted with permission from ref \[162]\.

### 2.2 Results and Discussion

#### 2.2.1 Extreme Variability in Experimental Output

GOM pure water permeabilities, expressed in LMH-bar (\(i.e., \text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}\)), from a detailed analysis of the current literature is summarized in (Fig. 2.2a). Of note is the large variability in reported permeability spanning over 2 orders of magnitude. In order to enhance clarity, GOM are divided into five categories: (i) intercalated-GO (I-GO): GOM formed by the intercalation of high aspect-ratio nanostructures in the GO laminate; (ii) as-prepared pristine GO (P-GO): GOM characterized by a surface (or separation) layer of untreated GO; (iii) chemically modified-GO (CM-GO): GOM consisting of a surface (or separation) layer of chemically modified GO (typically reduced, rGO); (iv) layer-by-layer-GO (LbL-GO): GOM formed by a layer-by-layer method where GO is alternatively deposited with a different material; and (v) GO-composite (GOC): GOM obtained by blending of GO with another material (\(e.g., \text{polymer}\)). I-GO displays the greatest permeabilities (10 – 200 LMH-bar) due to the widening of the GOM nanochannels (\(i.e., \text{the spacing between GO layers}\))
by the introduction of high-aspect-ratio nanostructures such as nanotubes or nanorods of various
diameter. On the other hand, GOC exhibit the lowest permeabilities (0.5 – 10 LMH-bar) due to the embedding of GO in a RO matrix (e.g., polyamide) with a low intrinsic permeability.
Intermediates are CM-GO (0.5 – 70 LMH-bar) and P-GO (3 – 70 LMH-bar), with CM-GO having a wide range because the chemical GO modification may involve either surface oxy-group reduction decreasing the spacing of the GOM nanochannel spacing or functional group addition increasing the spacing. LbL-GO (1 – 3 LMH-bar) display lesser permeabilities as compared to those of P-GO (3 – 70 LMH-bar) because LbL has a more ordered laminar structure due to improved intralayer GO packing.

The proposed categories have a reduced permeability range (typically 20 – 30-fold) as compared to the data set as a whole (≈ 400-fold) and may assist the community in comparing results between GOM studies. The intrinsic permeability for P-GO, CM-GO, and LbL-GO is displayed in (Fig. 2.2b). The intrinsic permeability is obtained by multiplying the permeability by the thickness of the GO layer and then normalizing to the greatest value for clarity. Note, I-GO and GOC are not composed of a distinct GO layer; thus, the GO thickness could not be determined (see Table 2.1).

The large variability in the intrinsic permeability data is striking. For example, P-GO intrinsic permeabilities span over 4 orders of magnitude. The CM-GO and LbL-GO values also display a large variability (> 3 orders of magnitude), which is difficult to explain by varying the reduction technique or LbL process. We identified three possible causes for such a noisy GOM permeability spectrum.

• First, although all reports claim to work with GO, the material can vary significantly from one report to another (see details in the GO standardization discussion).

• Second, some variability can be attributed to improper membrane performance evaluation as many reported experiments were not run long enough for permeability to reach steady-
Figure 2.2: GOM pure water permeability. (a) GOM permeability expressed in LMH-bar for all five categories in descending order. The dashed line represents the linear decrease in the average permeability from I-GO to GOC. (b) Normalized intrinsic permeability for the three relevant categories.

state (always lower than the initial permeability), that is, several reports evaluate permeability with just a few milliliters (or a few minutes) of water permeation while it can take hours to achieve steady-state. From an environmental engineering perspective, this may also affect rejection (size exclusion) performance that could be confused with adsorption to the high specific surface area GO (> $10^2$ m$^2$ g$^{-1}$).\cite{S01055}

- Third, GOM may contain large macroscopic defects (basal plane holes; disordered stacking), leading to erroneous conclusions on 1D fast water transport (FWT; similar to carbon nanotubes, CNTs) in the 2D GOM nanochannels (see the fast water transport discussion for details). For instance, GO reduction via thermal annealing under ambient conditions at 150°C can create basal plane holes > 10 nm in diameter.\cite{102}
### Table 2.1: GOM Pure Water Permeability and GO Properties.

<table>
<thead>
<tr>
<th>Category</th>
<th>#</th>
<th>Permeability (LMH-bar)</th>
<th>Thickness (nm)</th>
<th>Oxidation</th>
<th>Note</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>I-GO</td>
<td>1</td>
<td>205</td>
<td>n/a</td>
<td>n/a</td>
<td>intercalation with carbon dots</td>
<td>235</td>
</tr>
<tr>
<td>I-GO</td>
<td>2</td>
<td>50</td>
<td>n/a</td>
<td>n/a</td>
<td>intercalation with CNT</td>
<td>74</td>
</tr>
<tr>
<td>I-GO</td>
<td>3</td>
<td>12.13</td>
<td>n/a</td>
<td>n/a</td>
<td>intercalation with CNT</td>
<td>84</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td>intercalation with CNT</td>
<td>36</td>
</tr>
<tr>
<td>P-GO</td>
<td>5</td>
<td>71</td>
<td>2000</td>
<td>n/a</td>
<td>modified Hummers' method</td>
<td>100</td>
</tr>
<tr>
<td>P-GO</td>
<td>6</td>
<td>70</td>
<td>1000</td>
<td>53.7% (C-O, C=O) 46.3% (C-C, C=C)</td>
<td>modified ' method</td>
<td>237</td>
</tr>
<tr>
<td>P-GO</td>
<td>7</td>
<td>53</td>
<td>2500</td>
<td>n/a</td>
<td>modified Hummers' method</td>
<td>235</td>
</tr>
<tr>
<td>P-GO</td>
<td>8</td>
<td>48</td>
<td>55</td>
<td>n/a</td>
<td>modified Hummers' method</td>
<td>74</td>
</tr>
<tr>
<td>P-GO</td>
<td>9</td>
<td>27.2</td>
<td>50</td>
<td>45.8% (C-O, C=O) 54.2% (C-C, C=C)</td>
<td>commercial</td>
<td>238</td>
</tr>
<tr>
<td>P-GO</td>
<td>10</td>
<td>25</td>
<td>1</td>
<td>n/a</td>
<td>modified Hummers' method and Offeman's method</td>
<td>75</td>
</tr>
<tr>
<td>P-GO</td>
<td>11</td>
<td>212.9</td>
<td>2000</td>
<td>n/a</td>
<td>modified Hummers' method</td>
<td>100</td>
</tr>
<tr>
<td>P-GO</td>
<td>12</td>
<td>7</td>
<td>1</td>
<td>n/a</td>
<td>modified Hummers' method and Offema's method</td>
<td>75</td>
</tr>
<tr>
<td>P-GO</td>
<td>13</td>
<td>3.75</td>
<td>50</td>
<td>53.7% (C-O, C=O) 31.4% (C-C, C=C)</td>
<td>modified Hummers' method</td>
<td>19</td>
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<tr>
<td>CM-GO</td>
<td>14</td>
<td>71</td>
<td>150</td>
<td>n/a</td>
<td>GO reduced with hydrazine</td>
<td>8</td>
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<tr>
<td>CM-GO</td>
<td>15</td>
<td>45</td>
<td>n/a</td>
<td>n/a</td>
<td>GO reduced with thermal annealing in air</td>
<td>192</td>
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<tr>
<td>CM-GO</td>
<td>16</td>
<td>12.8</td>
<td>22</td>
<td>n/a</td>
<td>GO reduced with base reflux</td>
<td>87</td>
</tr>
<tr>
<td>CM-GO</td>
<td>17</td>
<td>11</td>
<td>55</td>
<td>n/a</td>
<td>GO reduced with hydroiodic acid</td>
<td>74</td>
</tr>
<tr>
<td>CM-GO</td>
<td>18</td>
<td>10</td>
<td>170</td>
<td>n/a</td>
<td>GO reduced with hydrazine</td>
<td>87</td>
</tr>
<tr>
<td>CM-GO</td>
<td>19</td>
<td>7.5</td>
<td>50</td>
<td>20.1% (C-O, C=O) 59.9% (C-C, C=C)</td>
<td>GO functionalized/reduced with diamine</td>
<td>238</td>
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<tr>
<td>CM-GO</td>
<td>20</td>
<td>4.76</td>
<td>40</td>
<td>n/a</td>
<td>GO reduced with thermal annealing in solution</td>
<td>87</td>
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<tr>
<td>CM-GO</td>
<td>21</td>
<td>3.26</td>
<td>53</td>
<td>n/a</td>
<td>GO reduced with base reflux</td>
<td>87</td>
</tr>
<tr>
<td>CM-GO</td>
<td>22</td>
<td>0.5</td>
<td>50</td>
<td>76.5% (C-O, C=O) 24.5% (C-C, C=C)</td>
<td>GO reduced with hydroiodic acid</td>
<td>0</td>
</tr>
<tr>
<td>CM-GO</td>
<td>23</td>
<td>0.4</td>
<td>600</td>
<td>n/a</td>
<td>GO reduced with ascorbic acid</td>
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<tr>
<td>LbL-GO</td>
<td>24</td>
<td>27.6</td>
<td>87</td>
<td>60% (C-O, C=O) 50% (C-C, C=C)</td>
<td>GO cross-linked by benzenetricarbonyl trichloride</td>
<td>274</td>
</tr>
<tr>
<td>LbL-GO</td>
<td>25</td>
<td>8</td>
<td>8.7</td>
<td>60% (C-O, C=O) 40% (C-C, C=C)</td>
<td>GO cross-linked by benzenetricarbonyl trichloride</td>
<td>274</td>
</tr>
<tr>
<td>LbL-GO</td>
<td>26</td>
<td>5.8</td>
<td>82.5</td>
<td>O/C=25-28%</td>
<td>GO cross-linked by poly(allylaminehydrochloride)</td>
<td>28</td>
</tr>
<tr>
<td>LbL-GO</td>
<td>27</td>
<td>2.1</td>
<td>33</td>
<td>O/C=30-50%</td>
<td>GO cross-linked by poly(allylaminehydrochloride)</td>
<td>28</td>
</tr>
</tbody>
</table>

15
2.2. Results and Discussion

<table>
<thead>
<tr>
<th>Category</th>
<th>#</th>
<th>Permeability (LMH-bar)</th>
<th>Thickness (nm)</th>
<th>Oxidation</th>
<th>Note</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>LbL-GO</td>
<td>28</td>
<td>2</td>
<td>80</td>
<td>O/C=50%</td>
<td>GO cross-linked by poly(allylaminehydrochloride)</td>
<td>98</td>
</tr>
<tr>
<td>LbL-GO</td>
<td>29</td>
<td>1</td>
<td>4</td>
<td>na</td>
<td>Lbl structure</td>
<td>39</td>
</tr>
<tr>
<td>GOC-GO</td>
<td>30</td>
<td>10</td>
<td>n/a</td>
<td>na</td>
<td>GO mixed with polyaniline</td>
<td>6</td>
</tr>
<tr>
<td>GOC-GO</td>
<td>31</td>
<td>5</td>
<td>n/a</td>
<td>na</td>
<td>GO mixed with polysulfone</td>
<td>68</td>
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<tr>
<td>GOC-GO</td>
<td>32</td>
<td>4.7</td>
<td>n/a</td>
<td>na</td>
<td>GO mixed with polysulfone</td>
<td>68</td>
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<td>GOC-GO</td>
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<td>n/a</td>
<td>na</td>
<td>GO mixed with polyaniline</td>
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<td>GOC-GO</td>
<td>35</td>
<td>1</td>
<td>n/a</td>
<td>65% (C-C, C=C)</td>
<td>GO mixed with polyamide</td>
<td>29</td>
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<tr>
<td>GOC-GO</td>
<td>36</td>
<td>0.5</td>
<td>n/a</td>
<td>65% (C-C, C=C)</td>
<td>GO mixed with poly(ethersulfone)</td>
<td>269</td>
</tr>
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</table>

2.2.2 Need for Standardization and Lack of In Situ Characterization

For pristine graphene research, standardization is underway. The International Electrotechnical Commission (IEC) released the IEC 62565-3-1,[108] which aims to tabulate all relevant graphene properties and standardized protocols for characterization. The end goal is to enable the purchase of materials with very similar properties and drive the broad use of graphene in manufacturing and industry. Concurrently, Graphene Flagship is establishing a standardization committee with the aim of creating a database listing all of the various graphene forms, their properties, and methods to characterize those properties.[109] A similar standardization is necessary for GO in order to enable successful commercialization and industrial application of the material. However, from our experience, as well as from discussions with academics and GO producers, we are still far from a standardized GO product. For example, characterization of GO from various producers yielded widely ranging material chemistry, as noted in Table 2.1 where the GO oxidation is characterized in less than one-third of the studies and that reported has a wide range of oxygen content.

In general, 2D material properties can be intrinsically divided into morphology and chemistry, which in turn affects practical properties such as electrical, mechanical, thermal, magnetic, and optical
Chapter 2. Signal-to-Noise Ratio in Graphene Oxide research

functionality.

GO morphology can be easily characterized by drop-casting a dilute solution of GO ($\approx 10^{-3}$ wt%) onto a flat substrate (i.e., silicon chip) and performing scanning electron microscope (SEM) imaging (Fig. 2.3a left) and subsequent thorough image analysis (Fig. 2.3a right). From SEM image analysis, the GO flake size distribution and monolayer percentage (flake contrast) can be determined, which can be utilized for standardization. Although atomic force microscopy (AFM) can also be used to evaluate GO morphology, it has lower throughput compared to SEM (10s $\mu$m$^2$s$^{-1}$ compared to 1000s $\mu$m$^2$s$^{-1}$), and AFM thickness results can be affected by the AFM operation mode and the level of humidity.

![Image of GO morphology characterized by SEM and XRD](image)

**Figure 2.3: GO chemistry and morphology characterization.** (a) GO morphology analyzed by SEM. The histogram summarizes the gray scale intensity counts of the SEM image, which can be deconvoluted with three Gaussian distributions whose areas represent the substrate, GO monolayer, and GO multilayer fractions. (b) XRD spectra of multilayer GO where $d$ is the GO nanochannel spacing. (c) Integration of the XPS C1s spectra deconvolution to quantify GO carbon bonding. Reproduced from ref. relevant categories.

Because GO flakes tend to stack in a laminar fashion, X-ray diffraction (XRD) is recommended
to evaluate GOM nanochannel spacing (Fig. 2.3b). From spacing information, it may be possible to infer the GOM molecular weight cutoff \((i.e.,\) rejection performance), making XRD a paramount tool for GOM characterization. Although GOM spacing has been reported, there is a lack of in situ characterization techniques. In particular, the evaluation of GOM spacing while the membrane is under operation has not been reported as it would require performing XRD analysis while pressurized water is flowing through the GOM. To date, XRD data in the literature refers to either the "dry" or "wet" state, qualitatively reporting GOM swelling (up to 25%) when immersed in water. However, these characterizations will not resemble the status of GOM under operation and may neglect other physical phenomena such as pressure-induced GO flake rearrangement and/or the presence of adsorbed molecules (spacers).

A proper GOM morphology characterization (GO flake dimension spacing) may also provide information on GOM tortuosity. The high GO flake aspect ratio can yield a membrane tortuosity that negates the benefit of an ultrathin \((<100\ \text{nm})\) membrane. Although considered an important membrane property, GOM tortuosity has not yet been considered in depth. If not single-layer GO, then for every additional GO layer there will be an additional water nanochannel. In turn, the water permeate will roughly travel on average half of the GO flake length for every additional layer. Thus, neglecting the presence of defects, for a bilayer GOM with 10 \(\mu\text{m}\) flakes, the water will have to travel 5 \(\mu\text{m}\), which is significantly greater (1000-fold) than the 5 nm thickness.

GO chemistry can be quantitatively analyzed by X-ray photoelectron spectroscopy (XPS), providing information on the oxygen and/or specific functional group content, which directly affects practical properties \((e.g.,\) spacing and conductivity). Deconvolution of the XPS C1s spectrum (Fig. 2.3c) can be used to quantify the predominant carbon bond type, in accordance with the Lerf-Klinowski model: (i) single (C-C) and double (C=C) carbon-carbon bonds; (ii) epoxide (C-O-C) and hydroxide (C-OH) single carbon-oxygen bonds; and (iii) carboxylate (O=O-C) double
carbon-oxygen bonds. Further deconvolution aiming to distinguish between epoxide and hydroxide functional groups has to be taken with a grain of salt due to binding energy chemical shifts approaching tool resolution. Raman spectroscopy has also been employed to analyze GO chemistry and generally displays a D band ($A_{1g}$ symmetry) at $\approx 1350$ cm$^{-1}$ representative of defects/disorder in the basal plane and a G band ($E_{2g}$ symmetry) at $\approx 1590$ cm$^{-1}$ that corresponds to the in-plane $sp^2$ bond stretching. However, GO is a metastable material, and the laser irradiation during Raman spectroscopy can unintentionally modify the material, leading to unreliable results. Depending on the acquisition time, this phenomenon also holds for XPS characterization, though with a limited negative effect compared to Raman. Thus, when reporting characterization methods, it is important to specify the acquisition time and other parameters that could alter material properties.

GO metastability not only affects the outcomes of characterization techniques but it is also a relevant element to consider when designing a GOM. A clear example is GO photo-reduction/oxidation that is highly dependent on light conditions and the environmental medium. Thus, it is important to work with either a stable GO material and/or a controlled environment to ensure that GO redox activity, as well as other potential chemistry, is negligible such that properties/performance do not significantly alter with time.

2.2.3 Possibility of CNT Fast Water Transport in Graphene Oxide Membrane

Several studies have reported FWT in GOMs possibly due to the low wall friction experienced by water when traveling through regions of 2D pristine graphene capillaries. At first glance, this could be similar to FWT through 1D CNTs due to a linear water dipole orientation parallel to the CNT axis offering the lowest water-CNT interaction potential. However, in GOMs, water can move in two directions; thus, the dipole orientation phenomena will not be as significant as that in 1D CNTs as there will be a viscous water-water interaction in one direction perpendicular to the flow. Moreover, due to the H-bonding interaction between water and GO basal plane oxy-groups, “friction”
2.2. Results and Discussion

will occur when water travels through GO nanochannels; thus, a slip condition seems improbable. This phenomenon is supported by experiments reporting permeability reduction with an increasing GOM thickness indicating Darcy (no-slip) behavior. This experimental evidence clashes with frictionless GOM FWT, which should be independent from permeate path length.

However, there are experimental and simulation studies reporting GOM water permeabilities not in accordance with the no-slip condition. A possible explanation for observation of enhanced permeabilities may be related to the presence of holes and/or macroscopic defects in GOMs, reducing tortuosity and increasing water permeability. Due to the high anisotropy of the GO flake dimension, the effect of GOM defects on the water permeability requires large simulation domains, which are computationally costly with tools currently used to evaluate GOM performance (i.e., molecular dynamics (MD), Fig. 2.4a-c). Thus, mesoscale simulation tools may offer the opportunity to investigate larger domains and evaluate the effect of GOM defects and tortuosity on water permeability. For example, 2D mesoscale simulations (Fig. 2.4d-e) recently displayed the potential to model water transport in GOMs and other 2D materials. Although discussion of GOM water permeability is paramount, selectivity is just as important. For instance, in terms of industrial/municipal applications, a 300% increase in membrane permeability will decrease the operational energy requirements for a desalination plant by only 2%; thus, the gain is only in the decrease of capital cost that is a fraction of the overall cost.

2.2.4 Casting Challenge (Scale-up) and Substrate Paradigm

For GOMs to succeed in existing laboratories and be employed for industrial applications such as municipal water treatment, they will have to overcome the "casting" challenge. So far, three general approaches have been used to cast GO on a support: filtration, casting/coating, and LbL assembly. Filtration onto a porous membrane separates the GO flakes from the solvent, and the filtration force dictates the GOM laminar structure. Casting/coating approaches include spray-coating, drop-
Figure 2.4: Simulation of water flow transport within GOMs. (a-c) MD simulations of water flow within GOM nanochannels (the scale bar is 2 nm for (c)); reprinted (adapted) with permission from Ref. 242. (d,e) Mesoscale simulations of water flow inside of GOM nanochannels. The scale bar is 5 nm for (d).

casting, spin-coating, and doctor blade-casting, and although the latter seems to be a promising casting method for industrial applications, it requires GO pretreatment in order to obtain a gel with proper viscous properties and it is unknown how the process affects assembly. The LbL assembly approach is specifically designed to introduce cross-linkers into the GO laminate unless GO is utilized for all layers. The first two methods are highly scalable but suffer from minimal control of GO assembly and final structure. In contrast, the LbL method yields increased control of the GO
layer number, packing, and thickness but is characterized by slow throughput, in particular, if the more controlled Langmuir-Blodgett (LB) method is used. Thus, academic researchers will need to investigate alternatives to traditional casting techniques and/or develop a hybrid approach that can guarantee control of the GO assembly, industrial-scalability, and rapid throughput.

A possible hybrid approach is presented in Fig. 2.5 in which spray- and LB dip-coating techniques are combined to manufacture GO films in a scalable manner. Alternative hybrid approaches have combined spin-coating and filtration processes to achieve scalable assembly methods. During GO casting, the support material, which represents the first layer of the hierarchical membrane structure, may play an important role because it can affect the morphology of the GO laminate. Although investigations are driven by advantageous GO properties (e.g., thermal and chemical resistance) compared to polymeric membranes, so far, researchers have primarily employed polymer membranes as GO substrates. We are back to square one. Ceramic supports may solve the chemical/thermal resistance problem and increase GO stability due to the release of multivalent cations, but would greatly increase capital cost (> 100-fold) compared to polymeric supports.

An alternative may be the design and construction of a fully elemental carbon (including substrate) GOM (FC-GOM) composed of a polymer-free support element such as carbon black, activated carbon, and/or CNT. This scenario requires improvement of the macroscopic FC-GOM mechanical properties, for example, binder or carbonization, in order to maintain structural integrity under the applied pressure necessary for NF and RO applications. Although GO has inherent anti-fouling properties, a chemical cleaning (e.g., harsh acid/base/oxidant) will eventually be needed to recover permeability. Then, the effect of chemical cleaning on FC-GOM performance will be another performance measure to evaluate. An example question is, "What is the stable pH and oxidant concentration/strength range that FC-GOM can withstand without degradation?"
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Figure 2.5: Hybrid casting method. A GO/ethanol (EtOH) mixture is sprayed on the water surface. A pump ensures the flow of GO flakes, which float at the water/air interface. The GO film at the interface can be packed with the use of movable barriers similar to LB casting. The floating GO layer can then be transferred to a solid substrate via vertical dip-coating. It is possible to insert reduction techniques, such as UV or hydroiodic acid (HI), in the casting method in order to obtain CM-GO.

2.3 CONCLUSIONS

Here, we suggested a GOM categorization method and report four critical challenges that need to be addressed to advance the development of more reliable high-performance GOMs and increase the signal-to-noise ratio in the research field. At the same time, reviewers should be holding authors to accurately perform detailed GO and GO laminate characterization, as well as performance-related permeability/rejection experiments, to ensure that the GO material reported in investigations is in accordance with future standardization. These efforts would guide the GO community toward commercialization for industrial applications and make GO a valid alternative material for membrane technology.
Aristotelian view on Graphene Oxide

Apart from minor modifications, this chapter originally appeared as:

“Graphene oxide standardization and classification: Methods to support the leap from lab to industry”. Carlo A. Amadei, Paula Arribas, and Chad D. Vecitis, Carbon, 2018, 133, 39-409.

ABSTRACT

Although graphene oxide (GO) has been widely used in a variety of research fields, the potential for GO implementation remains controversial. Researchers commonly define GO as a 2D carbon nanomaterial with oxygen functionalities, but this definition is too loose and leads the community to compare results among significantly different nanomaterials. In order to overcome this challenge, here we suggest high-throughput post-processing GO characterization techniques to rapidly and thoroughly define GO chemo-morphological properties. Then, based on characterization analysis and a clustering algorithm, we classified GO into six categories. The classification method was validated with GO samples obtained from different producers. The commercial samples were individually implemented to fabricate various macroscopic devices (e.g., membranes) and we observed that GO classified in the same category offered similar macroscopic performance. In contrast, samples from different categories resulted in a noticeable variation in macroscopic results, corroborating the importance of using standardized materials. The presented characterization and classification method will assist the research community by enabling a fair comparison between studies. Moreover, it will assist GO producers to target customers in a more-effective manner by distributing GO with optimal properties for a specific application, supporting the leap of GO from lab to industry.
According to Aristotle, in order to explain the world and objects around us we need to recognize four causes: i) the matter determined by the material of the object; ii) the form determined by the shape of the object; iii) the agent determined by the transformation of the object; and iv) the end determined by the purpose of the object. Although this knowledge was professed more than 2000 years ago, there is analogism with modern science. In particular, in materials science and/or nanotechnology when we describe an object, we tend to refer to those four causes: i) the matter is the chemistry of the material; ii) the form is the morphology of the material; iii) the agent is the process through which a material is modified; and iv) the end is the functionality of the material. For new nanomaterials, it is fundamental to well-define their morphology and chemistry, since different chemo-morphological combinations will lead to diverse surface and quantum size phenomena. For this reason, nanomaterials such as carbon nanotubes (CNTs) are undergoing a standardization process, which tabulates all relevant CNTs properties and standard protocols for characterization. A similar standardization process will be necessary for graphene oxide (GO), which can be thought as a single layer carbon sheet (i.e., graphene) decorated with oxygen functionalities, involving both basal-plane and edge-site chemical modification of graphene during oxidation and exfoliation. The standardization process can be included in the current effort to introduce a rational naming system for the two-dimensional carbon form.

GO has recently gained interest among academic researchers and industries. From the academic sector, the number of citations per year of scientific work whose title includes “graphene oxide” has increased by almost one order of magnitude (from \( \approx 900 \) to \( \approx 7000 \), Fig. 3.1) in four years (2011 – 2015). From the industrial sector, the GO manufacturing capacity has increased by a factor of five over roughly three years, with a current yearly production capacity of \( \approx 1000 \) tons/year. Moreover, the number of annual patents filed whose title contains “graphene oxide” has increased...
by an order of magnitude in four years (2011 – 2015).

![Graph of GO trends](image)

**Figure 3.1: GO trends.** Number of publications (white) and number of patents filed (gray), with a title that contains "graphene oxide", between 2011 and 2015.

The drive behind this increased interest is two-fold. First, the GO price per gram is about six orders of magnitude lower than pristine graphene, which opens different markets such as industrial applications. The price of GO is also steadily declining due to the development of scalable fabrication systems with current reactor capacity $> 100$ tons/year, which leads companies to predict a GO price as low as a few cents per gram in the next five years. These factors also raise the interest of investors and producers who want to place themselves in the market before an explosion of growth dictated by successful demonstration of applications; similar to what recently happened with quantum dots, which found their market in the display industry.\(^{10}\)

Second, GO displays unique properties such as near-atomic thickness,\(^{167}\) the presence of oxy-groups allowing for rapid functionalization,\(^{55}\) scalable synthesis processes,\(^{176}\) and the possibility of controlled deposition of nanothin films on a variety of substrates using solution-based casting tech-
niques (e.g., vacuum filtration, spin coating, layer-by-layer, or doctor blade printing). More importantly, the versatility and the possibility of tuning the primary GO properties (flake size and quantity of oxy-functionalities) led researchers to propose the use of GO in several fields such as energy storage, separation processes, and drug delivery, just to mention a few (readers can refer to exhaustive literature reviews of GO applications). In each specific application, the GO properties have been selected *ad hoc* to serve at best the functionality of the device in which GO is implemented. For example, in transparent conducting films, large-dimension and slightly-oxidized GO flakes are selected in order to enhance electron transport. Although slightly-oxidized GO flakes are also preferred for supercapacitor applications, recent studies explored the possibility of exploiting surface GO oxy-functionalities to increase device pseudo-capacitance via red-ox reactions. GO morphology is paramount for the enhancement of mechanical properties; for instance, large size GO flakes are preferred to maximize fiber reinforcement. In membrane technology for water treatment, the number of oxy-functionalities and GO dimensions can be tailored accordingly to the contaminant of interest and desired permeability; thus, the rational modification of the GO nanoproperties will allow controlled tuning of the permeability-selectivity trade-off.

In order to enable successful commercialization and industrial application of GO, it is paramount that researchers and industries have a common understanding of GO nomenclature and properties, which can have a large impact on the application of interest, *vida supra*. However, from our experience, studies in the literature, and discussions with academics and GO producers, GO properties are extremely wide-ranging, source-dependent, and, in some of the cases, are not even mentioned. In particular, the synthesis process plays a major role in determining GO properties. GO can be synthesized from 3D graphite flakes via the Hummers’ method, which represents an evolution of two previous chemical exfoliation methods (Brodie and Staudenmaier). As it has been recently
shown, even small tuning of the synthesis process (e.g., time and/or temperature of the oxidation process) can lead to significantly different GO properties. One clear example illustrating how poor GO characterization can lead to confusion in the research field is the recent controversy on the water transport in GO laminates. On one hand, studies have reported fast water transport (FWT) in GO possibly due to the low wall friction experienced by water when traveling through regions of 2D pristine graphene capillaries, this is similar to FWT through 1D CNT due to a linear water-water dipole alignment parallel to the CNTs axis offering the lowest water-CNTs interaction. On the other hand, surface friction might occur when water travels through GO nanochannels depending on the amount and type of GO basal plane oxy-groups. The origin of this controversy most likely arises from the difference in nanoproperties of the compared GO materials. Thus, it is fundamental that GO properties are well characterized when proposing theories and/or in order to enable a fair comparison between research results.

This work here aims to initiate the GO standardization process offering: i) high-throughput and lab-accessible GO characterization protocols and ii) a GO classification according to properties based on a clustering algorithm. The classification is similar to what has been done for bulk materials, which are divided into sub-categories (e.g., high-density polymer versus low-density polymer). The standardized characterization protocols are then validated by six GO samples collected from different producers across two continents. Investigation of GO-based applications utilizing material from different producers is used to highlight the effect of the nanomaterial properties on the macroscopic performance of a device.
3.2 METHODS

3.2.1 MATERIALS

GO was acquired from six different producers across two continents. Depending on the producer, the GO was either received in powder form or in an aqueous solution. All the samples were then diluted in water to the same concentration (0.05 wt%) and then subjected to the specific pretreatment required by the producer; possible pretreatments include sonication with a Branson sonicator (\( V = 1.9 \, \text{L}, \text{maxpower} = 480 \, \text{W}, \) and \( f = 420 \, \text{kHz} \)) and pH adjustment with NaOH. The polyvinylidene difluoride (PVDF) membrane used as the support for the vacuum filtered GO thin film was purchased from Sterlitech (TriSep YMTM103001). The PVDF membrane was cleaned by ultrasonication in IPA for 5 min, then in DI for 5 min, and kept in IPA prior to use. Escherichia Coli B (E. coli) CAROLINA™ 124300 (Carolina Biological Supply Company) was utilized as a model bacterium to evaluate the bacterial deposition on the GO membranes. BD Bacto™ tryptic soy broth (TSB), tryptic soy agar (TSA), NaCl (reagent grade), and ethanol (EtOH; laboratory grade) were purchased from VWR International. Formaldehyde (35% in water) was purchased from Sigma-Aldrich. Deionized (DI) water (> 18 MΩ) was produced by a Nanopure Infinity ultrapure water system (Barnstead/Thermolyne) and was used to prepare solutions and rinse containers. Methylene blue hydrate (> 95%) was purchased from Sigma-Aldrich and selected to evaluate the adsorption capacity of the different types of GO samples examined.

3.2.2 STRUCTURE AND MORPHOLOGY CHARACTERIZATION

Scanning electron microscopy (SEM): A Zeiss ULTRA Field Emission Scanning Electron Microscope with an In-lens secondary electron detector was used to characterize the GO morphology. The working distance, acceleration voltage, and aperture were set to 3–4 mm, 5 kV, and 30 \( \mu \text{m} \), respectively. The statistical SEM image analysis in Fig. 3.4 was completed using ImageJ where \( \approx 250 \)
3.2. Methods

GO flakes from different SEM images were analyzed. The monolayer percentage was obtained by deconvoluting the normalized pixel intensity (i.e., \(0 - 1\)) histograms in MATLAB. Pixels with higher intensity (brighter) represent monolayer flakes, whereas darker pixels represent the area characterized by two or more GO layers. The substrate background was discarded by applying a mask with the Magic Wand Tool in Photoshop. The GO solution needs to be diluted (< 0.01 mg/mL) to avoid overlap of the deposited monolayer GO flakes, which would then be identified as a multilayer GO structures by the algorithm.

**X-ray photoelectron spectroscopy (XPS):** The GO samples were analyzed by a Thermo Scientific K-Alpha XPS (ESCA). The X-rays were generated by a 12 keV electron beam and had a spot size of 400 \(\mu\)m. The O/C ratio calculation and peak deconvolution were performed by using the Thermo Scientific Avantage software. Three data points for each sample were taken. The dwell time was set to 10 ms for the survey spectra and 50 ms for the high-resolution (C1s) spectra. For each data point, the number of scans was set to 5 and 10 for the survey scan and for the high-resolution scan, respectively. The XPS instrumental error for atomic composition is \(\pm 1\%\), and the accuracy of the C1s peak fitting is \(\pm 2\%\). Being aware of the possible GO chemical change caused by prolonged X-ray irradiation (> 100 min), the number of scans was minimized to obtain the same information in terms of oxidation percentage. In this way, the limited dwell time and a low scan number used here were not enough to chemically alter the GO.

**Ultraviolet-visible spectroscopy (UV-vis):** The UV-vis absorbance spectra were obtained with a S-3100 SCINCO spectrophotometer. The wavelength range was from 200 to 1100 nm. The wavelength resolution was 0.95 nm. In order to avoid saturation of the absorbance signal, the samples were diluted to a concentration of 0.005 wt%.

**Atomic Force Microscopy (AFM):** The thickness of the GO flake was measured with an Asylum Cypher AFM using an Olympus 200TS cantilever (resonance frequency \(\approx 130\) kHz). The images
were acquired in amplitude modulation mode. The images in attractive (non-contact) and repulsive (contact) regime were obtained with a ratio between a set point amplitude and a free amplitude of 80% and 30%, respectively. The images were then flattened and a few scan lines were removed to increase the image quality using AR software from Asylum Research.

**X-ray diffraction (XRD):** The GO crystallographic structure was analyzed with a Bruker D8 equipped with a two-dimensional VANTEC-500 detector. The spectra were obtained by the integration of the 2D images via EVA software. The integration time was 600 ms and two data points were obtained for each sample. The data were then smoothened with the MATLAB built-in smoothening function. The width of the GO nanochannels (2 h) for each sample was determined using eqn (3.1, Bragg’s Law):

\[
2h = \frac{\lambda}{2\sin \theta}
\]

with \( \lambda = 1.54 \, \text{Å} \) (i.e., wavelength of the Cu k\( \alpha \)).

**Attenuated total reflection infrared spectroscopy (ATR-IR):** Infrared spectra were recorded using the ATR accessory for a Nicolet 670 Fourier transform infrared spectrometer. The spectral resolution was 0.5 – 1 cm\(^{-1}\) over a range of 1000 – 4000 cm\(^{-1}\) and subsequently averaged over 16 scans, representing a single analysis interval of 12s. A germanium crystal (no. 022-5450500, Pike Technologies) was employed as the ATR element and the GO samples were screw-pressed by the cap of the ATR cell, thereby bringing the samples into flush contact with the ATR crystal.

**Zeta potential (ZP) and Z-average (Z-Avg):** Both ZP and Z-Avg were evaluated using a Malvern Zetasizer ZS. The ZP was calculated from the electrophoretic mobility, whereas Z-Avg was obtained with dynamic light scattering. This technique is based on the evaluation of particle Brownian motion, which is converted to a size distribution using the Stokes-Einstein relationship. In the Zetasizer software, the solution was set to water and the material to carbon black. Three experiments for each sample were carried out.
3.2. Methods

**Raman spectroscopy:** Raman spectra were acquired using a WITec Confocal Raman Microscope. The laser wavelength was 532 nm and the signal was acquired using a 0.5 s integration time of 10 spectra.

**Static contact angle (SCA):** The SCA measurements were completed with a *Rame-Hart 190* contact angle goniometer under ambient conditions. SCA were measured using 5 µL droplets and the data refer to the average of 5 measurements obtained with the *Drop AnalysisDroSnake* plugin in *ImageJ*.

3.2.3  **GRAPHENE OXIDE CLASSIFICATION METHOD**

The literature nanoscopic properties of GO were acquired by researching scientific articles utilizing the keywords graphene oxide, O/C ratio, length, dimension, and distribution. More than 300 peer-reviewed works were used to produce the histograms. Each GO nanostructure included in this paper represents a GO characterization with both an O/C ratio and GO dimensions. Note that the length specified by the researcher was utilized (if a square flake was assumed) or it was estimated from the reported area assuming square flakes. A classification algorithm can be used here due to the independence of the chemistry and morphology variables (*i.e.*, O/C ratio and length). The K-mean clustering algorithm aims to minimize the loss function \( L \) in eqn (3.2), defined as the sum of the distance of each observation \( x \) from the centroid of the cluster \( k \).

\[
L = \sum_{k=1}^{K} \sum_{x \in k} (x - \mu_k)
\]  

(3.2)

where \( \mu_k \) is the number of data points in the class \( k \). A more comprehensive resource for further details on K-mean clustering can be found here. In this study, the number of observations is equal to 60 (20% of the total dataset), which corresponds to works that reported both GO morphology and chemistry. The number of clusters \( (K) \) is equal to 6. The number of clusters is chosen through
the optimization "elbow" method (see Fig. 9.5 in the Appendix A) where 6 is the minimum number of clusters to achieve a percentage of explained variance > 90%. This method allows removing any arbitrary decision on the number and definition of clusters which might be affected by bias. In contrast, the "elbow" method is derived from the statistical behavior of the data points. Note that for this classification only data points characterized by mean flake size < 3 µm were considered, representing more than two-thirds of the data found in the literature. The length for the remaining studies spans over two orders of magnitude and the information on the O/C ratio is often omitted, thus running a classification algorithm on this remaining data would not be feasible and thus has not been included here.

3.2.4 Graphene Oxide Membrane Fabrication and Evaluation

Graphene Oxide membrane fabrication: After the GO pretreatment suggested by the producers was performed, the six GO samples were diluted to the same concentration (ρ ≈ 0.05 wt%). Then 1 mL of each of the six GO samples was added to 20 mL of deionized water. The GO solutions were then vacuum filtered and dried onto separate PVDF membranes.

Bacteria attachment experiments E. coli was cultured in TSB by seeding from a TSA plate at 37 °C and harvested at mid-exponential phase. After centrifugation (2 min at 10,000 rpm) and resuspension twice in 155 mM NaCl, the bacterial stock solution was diluted to an optical density of 0.15 at 600 nm (OD_{600} = 0.15) in saline (10^8 CFU mL⁻¹ by fluorescence microscopy enumeration). Finally, 500 mL of bacterial saline working solution was prepared with a concentration of 6 x 10^7 CFU mL⁻¹ and 1/60 the volume of TSB was added to provide essential nutrients and avoid bacterial inactivation during the experiment. Graphene oxide membranes (GOM) were placed in a glass beaker with 500 mL of the saline bacterial working solution. The bacterial-GOM suspension was maintained at room temperature and stirred for 20 h at 80 – 100 rpm. Once the bacterial experiment was concluded, GOM were examined by SEM to determine surface bacterial density and morphol-
3.2. Methods

SEM of bacterial samples was completed after they were fixed with formaldehyde vapor for at least 12 h, dehydrated with 40 – 100% EtOH/DI solutions, dried at room temperature, and coated with 2 nm of Pt/Pd (80/20) (*EMS 300T* Dual Head Sputter Coater).

**Adsorption experiments:** The adsorption of methylene blue (MB) was quantified using a *S-3100 SCINCO* UV-visible spectrophotometer. GO aqueous solutions with a total volume of 14 mL were prepared by adding 0.5 mg MB solution (volume 1 mL) and 1 mg GO solution (1:2 ratio) into plastic centrifuge tubes and then vortex-mixed. The volume of the GO solution was dependent on the product due to the different initial densities. The final concentration of the different components in the solution were 35.7 mg/L for MB and 71.4 mg/L for GO. The sample tubes with the GO suspension were shaken for 24 h in an *Estella E24* incubator shaker at 25 °C to reach the equilibrium. Then the adsorbent was separated from the solution by centrifugation at 10,000 rpm for 15 min. The absorbance of the supernatant was recorded at a wavelength of 608 nm (**ε** = 36035 M⁻¹ cm⁻¹). Finally, the adsorption capacity of the different GO samples was quantified as the log removal value (LRV) in eqn (3.3):

$$LVR = \log_{10} \frac{C_0}{C_e}$$

where *C₀* and *Cₑ* were initial and equilibrium concentrations of MB (mg/L), respectively.

**GOM permeability:** The wet flow curves of the GOM were measured by the capillary flow porometry (CFP) method using a gas-liquid displacement Porometer (*POROLUX™ 100*). CFP is based on the displacement of a wetting liquid inside a porous network by means of an inert gas flow. In this study, *POREFIL®* (Porometer, surface tension of 16 dyn/cm) was used as the wetting liquid agent, compressed air was used as the inert gas, and the pressure scan method within a pressure range of 0 – 5.5 bar at room temperature was applied. Three different samples for each GOM were evaluated to obtain the final reported wet flow curve.
Chapter 3. Aristotelian view on Graphene Oxide

3.3 RESULTS AND DISCUSSION

3.3.1 GRAPHENE OXIDE CHEMISTRY

First, attention is focused on GO chemistry. A photo of the GO samples from different producers at a concentration of 0.01 wt% in water is presented in Fig. 3.2a. The samples have been ordered from darkest (1) to lightest (6), which also represents an increase in the extent of GO oxidation (O/C ratio values in Fig. 3.2b). For example, when a carbon atom is oxidized, the sp² conjugation of the carbon atom may be altered to sp³, thus modifying the sp² mediated light absorption. Moreover, by retrofitting the O/C ratio in the photo, it was possible to build a color chart qualitatively indicating the extent of sample oxidation (Fig. 3.2a, right).

To corroborate the extent of GO oxidation, XPS analysis of vacuum filtered GO thin films (see Methods) was completed. The deconvolution of the C1s XPS spectra (Fig. 2b) is based on one of the most accepted GO structural model (i.e., Lerf’s model[133]) and it is characterized by three peaks: i) single (C-C) and double (C=C) carbon bonds centered at \( \approx 285 \) eV; (ii) epoxide (C-O-C) and hydroxide (C-OH) functional groups centered at \( \approx 287 \) eV; and (iii) carboxylate (O=C-OH) functional groups centered at \( \approx 289 \) eV. However, the relative percentage of the three peaks greatly varies depending on the sample. For example, Sample 2 is the only sample that does not display a carboxylate peak and the least oxidized sample (1) has a C-C/C=C contribution of 72%, while the most oxidized sample (6) is characterized by a C-C/C=C contribution of 35%. Concurrent with the decrease of sp² conjugation in Sample 6, an increase in C1s epoxide and hydroxide functionalities to almost 60% is also observed. Overall, the O/C ratio varies from 0.19 – 0.55 and confirms the large chemical variability of the six samples. It is worth noting that a lower oxidation extent can also be induced by a higher number of GO layers in a single flake that could hinder internal basal-plane oxidation. Other elements apart from O and C, such as N and S, were also observed in small percentages (see Table 9.1 in the Appendix A for details) and are probably residuals of the synthesis
3.3. Results and Discussion

Figure 3.2: GO chemistry I. (a) Photo of the six GO samples in solution (left). A color gradient relative to the O/C ratio (right). (b) C1s spectra obtained by XPS analysis of GO samples. The data also display the percentage contribution of individual peaks obtained by deconvolution and the O/C ratio.

As seen in Fig. 3.2, XPS quantitatively characterizes the chemistry of GO thin films with limited and automated post-processing of the data (e.g., C1s peak deconvolution), leading to high-throughput measurements. The chemistry of GO thin films was also analyzed with spectroscopic.
techniques such as, UV-vis, ATR-IR, and Raman spectroscopy Fig. 3.3a. From the UV-vis spectra for Samples 2 – 6 in Fig. 3.3a, it is possible to observe an absorbance peak around 220 nm representing the $\pi - \pi^*$ transition of the aromatic C=C bonds remaining from the original graphitic structure. In contrast, Sample 1 is characterized by a red-shifted peak ($\approx 230$ nm) due to its lower oxidation state, confirming a lower oxygen content compared to the other samples. Furthermore, Sample 1 also presents multiple shoulder peaks (blue rectangle in the inset zoom) related to multilayer GO structures, where the carbon planes can approach one another closely enough to allow $\pi - \pi^*$ stacking, which also leads to a broader absorption peak in the region around 600 nm. Although the XPS analysis indicated that Samples 2 – 6 are characterized by a wide-range of oxidation states ($0.43 < O/C < 0.55$), the UV-vis fails to convey this information.

In Fig. 3.3b, the IR spectra confirms the oxidation of GO with alkoxy, epoxide, and carboxylate peaks centered at 1065, 1230, and 1730 cm$^{-1}$, respectively. The other major peak centered at 1625 cm$^{-1}$ is due to the presence of sp$^2$ domains. The IR also displays a broad absorbance spectrum in the
3.3. Results and Discussion

region 3200 – 3600 cm\(^{-1}\) related to OH stretching vibrations of adsorbed water for all the samples except for Sample 2 (i.e., the sample with no XPS carboxylate peaks). Although IR spectroscopy is able to quantify the concentration of gases via the Lambert-Beer law, the quantification of the thin film materials’ functionalities is challenging. The IR spectrum can be strongly influenced by the calibration curve, the morphology of the sample, and, in the case of ATR, also by the area of contact between the material and the germanium crystal. Thus, it is difficult to quantitatively compare the chemistry of different samples and the user can only report qualitative functionality information based on the presence or absence of peaks or relative change over time of a single sample. In summary, UV-vis and IR spectroscopy are useful techniques for confirming the GO oxidation state and identify functionalities, but are not able to quantify GO chemistry and oxy-functionalities since spectra from different samples are indistinguishable.

Raman spectra have also been used by researchers to characterize GO;\(^{253}\) in our case, the six Raman spectra samples are presented in Fig. 3.3c, and display a D-band at \(\approx 1350\) cm\(^{-1}\), representative of defects/disorder in the basal plane, and a G-band at \(\approx 1590\) cm\(^{-1}\) representative of the in-plane sp\(^2\) bond stretching.\(^{11}\) A primary quantifiable Raman measurement is the D/G intensity ratio (I\(_D\)/I\(_G\)), which is a measurement of the defect density. However, all GO samples with different XPS oxidation states display I\(_D\)/I\(_G\) \(\approx 1\), apart from Sample 2 which has a slightly lower defect density I\(_D\)/I\(_G\) \(\approx 0.94\); thus, Raman is not a suitable technique for quantifying the GO chemistry. Moreover, Raman spectroscopy tends to be a destructive technique\(^{127}\) for a metastable material such as GO; even a short laser irradiation time (< 2 s) would be sufficient to alter GO chemo-morphological structure and is likely responsible for the lack of Raman variation with oxidation state. In addition, during GO reduction, CO and CO\(_2\) are liberated producing defects; thus, one cannot reliably characterize partially reduced GO samples with Raman because the reduction converts one type of defect (oxy-groups) to another type (vacancies) produced during reductive deoxygenation.
Zeta Potential (ZP) can also be used to indirectly analyze the chemistry of materials in aqueous solutions. The ZP of moderately stable GO dispersions (ZP $\leq -30$ mV) in water at pH$ \approx 7$ is summarized in Table 3.1. The negative charge is connected to the ionization of the carboxylate functional groups, again indicating successful GO oxidation and making aqueous GO dispersion stable from aggregation. For Sample 1, it was not possible to obtain reproducible ZP values, since the material was not stable to aggregation and sedimentation in water. As observed by XPS, Sample 1 is characterized by the lowest extent of oxidation, which does not provide sufficient electrostatic repulsion to stabilize the colloidal solution, resulting in aggregation and subsequent settling of the GO dispersion (see Fig. 9.2 in the Appendix A).

Static contact angle (SCA) provides information on the properties of a thin film, such as the GO chemistry, assuming that the morphology of GO film does not significantly vary (i.e., all thin films here are made with the same casting procedure). The SCA decreases from $\approx 60^\circ$ to $\approx 25^\circ$ with increasing oxidation state (from Sample 1 to Sample 6). This result is related to a higher affinity of water to more highly oxidized surfaces, due to the increase in hydrophilicity, in accordance with previous reports analyzing the wettability of GO in different oxidation states. In particular, the presence of hydrophilic functional groups (e.g., hydroxyl) decreases the hydrophobic nature of pristine graphene and increases its surface energy. As stated for the UV-vis and IR techniques in Fig. 3, although ZP and SCA can deliver useful qualitative information on the GO oxidation state, this information cannot be directly translated into quantifiable properties across samples.

Table 3.1: Zeta potential (ZP), static contact angle (SCA), and Z-Avg for the six GO samples.

<table>
<thead>
<tr>
<th>Sample</th>
<th>ZP (mV)</th>
<th>SCA (°)</th>
<th>Z-Avg (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>n/a</td>
<td>60.5 ± 2.1</td>
<td>n/a</td>
</tr>
<tr>
<td>2</td>
<td>$-38.1 \pm 1.4$</td>
<td>49.3 ± 1.7</td>
<td>596 ± 14</td>
</tr>
<tr>
<td>3</td>
<td>$-32.4 \pm 1.1$</td>
<td>39.3 ± 3.3</td>
<td>1981 ± 224</td>
</tr>
<tr>
<td>4</td>
<td>$-33.2 \pm 0.3$</td>
<td>29.7 ± 1.7</td>
<td>507 ± 134</td>
</tr>
<tr>
<td>5</td>
<td>$-38.1 \pm 1.4$</td>
<td>25.7 ± 1.7</td>
<td>1503 ± 32</td>
</tr>
<tr>
<td>6</td>
<td>$-29.7 \pm 1.7$</td>
<td>25.3 ± 2.3</td>
<td>1604 ± 21</td>
</tr>
</tbody>
</table>
3.3. Results and Discussion

3.3.2 Graphene Oxide Morphology

After analyzing the GO chemistry, the attention is turned to techniques for characterizing GO flake morphology. SEM images and statistical data obtained by image processing are presented in Fig. 3.4. A representative SEM image for each of the samples is displayed in Fig. 3.4a, whereas the statistical data in Fig. 3.4b-c is based on multiple images (see Methods). SEM image data analysis was used to quantify the flake size distribution (see 3.4b and Fig. 9.1 in the Appendix A for details). In Fig. 3.4b, the flake areas have log-normal distributions (dashed red lines) characterized by a few larger flakes and more numerous smaller flakes. Noteworthy is the great extent of the variability of the average GO flake area between samples, which spans over an order of magnitude (e.g., from 0.2 to \(9.3 \, \mu m^2\)). In particular, Samples 3, 5, and 6 are characterized by larger GO flakes than those in Samples 1, 2 and 4. This difference is also captured by Z-Avg hydrodynamic diameter measurements, which are \(>1500 \, nm\) and \(<600 \, nm\) for Samples (3, 5, 6) and (2, 4), respectively (Table 3.1). In the case of GO, Z-Avg measurements cannot be compared to the actual flake size measured by other techniques since they are assumed to be monodispersed samples with spherical or near-spherical shape (GO is 2D) that uniformly scatter light (GO is partially transparent). For Sample 1, it was not possible to obtain a hydrodynamic value, since it is characterized by a polydispersivity index of 1 indicating that the sample likely contains aggregates that can sediment leading to a skewed size distribution (Fig. 9.2). In SEM images, GO flakes in the same image are characterized by different greyscale intensities: monolayer flakes appear brighter compared to multilayer aggregates. Using this intensity difference, we are able to quantify the percentage of monolayer for each sample (see Fig. 9.3 for details). GO Samples 2 – 6 have a monolayer percentage > 78% confirming effective exfoliation and the 2D nature of GO. For Sample 1, SEM analysis confirms UV-vis and Z-Avg results, which indicated the presence of multilayer structures and large aggregates as only 15% of the flakes are monolayer and the intensity distribution displays multiple peaks.
related to flakes with various numbers of GO layers (e.g., multilayer).

Although SEM can quantify the percentage of monolayer structures and geometry of the GO flakes, the flake thickness is another important morphological parameter for a 2D material. XRD of a GO thin film is able to measure the separation distance \(2h\) between GO flakes due to GO’s tendency to stack in a laminar fashion. XRD can give an approximation of the combined GO thickness including intercalants, such as water molecules, which will remain unless specific and rigorous drying protocols are used. The GO separation distance varies \(\approx 15\%\) from Sample 1 to Sample 6 (from 7.9 to 9.1 Å) increasing with increasing GO oxidation and basal plane oxy-functionality (Fig. 3.5a). Thereby, GO samples with higher extent of oxidation result in a less compacted thin film structure, whereas GO samples with lower extent of oxidation result in a more compacted thin film structure. Moreover, under ambient conditions GO samples with higher extent of oxidation will absorb more water molecules than the ones with lesser extent of oxidation. Considering that the graphene layer itself has a known vdW thickness of 0.34 nm and addition of oxygen groups can increase that thickness to 6 – 7 Å, any GO with a thickness larger than that is influenced by water adsorption. GO thickness can also be measured via AFM, however, AFM measurements can vary depending on the mode of operation and environmental conditions. As an example, GO morphology for Sample 5 obtained by operating the AFM in non-contact mode\(^{201}\) (attractive regime, phase values above 90°) is displayed in Fig. 3.5b. The GO monolayer thickness is \(\approx 2\) nm, which is considerably higher than the 1.5 nm thickness evaluated in contact mode\(^{201}\) (Fig. 3.5c; repulsive regime, phase values below 90°). Both values are in accordance with previously reported GO thickness.\(^{215}\) AFM results may also be affected by the AFM tip geometry and ambient conditions (e.g., presence of humidity),\(^{203}\) which will increase the thickness of the water layer trapped between the substrate and the GO flakes.\(^{203}\)

For this reason, AFM images comparing GO flakes from different producers are not presented here. However, AFM is useful for corroborating the monolayer nature of the GO observed by SEM.
Figure 3.4: GO morphology I. (a) SEM images of GO samples. (b) GO flake size distribution fitted to a log-normal distribution (red dashed lines); yellow square represents zoom in for the smaller GO flakes (Samples 1, 2, and 4). (c) Histograms of SEM image greyscale intensities that are deconvoluted to obtain mono-/multi-layer percentages.
3.3.3 **Graphene Oxide Characterization Tools**

All the tools used in this study to characterize the chemistry and morphology of GO are classified in Table 3.2. The information provided by the different techniques is divided between quantitative and qualitative; the latter should only be used in the GO prescreening phase and/or to obtain results in relative (and not absolute) terms that could validate quantitative measurements. To summarize, XPS is the primary tool to quantitatively analyze GO chemistry due to the ability to provide information regarding the oxidation state and the specific GO oxy-functionalities with minimal and automated data post-processing. Disregarding the time needed to pump down the XPS (pump and instrument dependent), an XPS measurement generally takes 1 – 2 min per sample. On the other hand, SEM is the primary tool to quantitatively characterize the GO morphology providing information on the monolayer nature and on the dimensions of the GO flakes. For SEM, the image acquisition generally takes 1 – 2 min per sample. Thus, the time required to quantitatively characterized the chemo-morphological GO properties is quite attractive. Other microscopy techniques, such as TEM...
3.3. Results and Discussion

or STEM, have not been included in this study as they would convey similar data obtained already by SEM on the GO morphology. However, TEM and STEM can give information regarding the atomic structure of GO and the interaction between GO and other nanostructures, such as metal nanoparticles. In regard to XRD, researchers can infer information on both chemistry and morphology from the separation distance $2h$, with a characterization time on the order of minutes per sample depending on the number of spectra acquired; moreover, XRD does not require particular experimental conditions. The alternative techniques presented here such as ATR-FTIR, UV-vis, and Raman spectroscopy can deliver complimentary qualitative information on GO morphology and chemistry, which can be used for prescreening or as orthogonal measurements.

3.3.4 Graphene Oxide Standardization

Careful research of the GO literature (> 300 peer-reviewed articles) was carried out in order to collect information on the chemistry and morphology of GO used in previous studies. The O/C atomic ratio distribution for GO, reduced GO (RGO), and multilayer (i.e., nanoplatets) GO (MLGO) found in the literature are presented in Fig. 3.6a.

The distribution greatly varies as the O/C atomic ratio for GO and RGO are characterized by very different average values, 0.46 ± 0.13 and 0.16 ± 0.10, respectively. MLGO has an O/C similar to RGO due to its poor exfoliation. The variation in the dimension of the GO flake is even greater than the O/C atomic ratio and spans over five orders of magnitude as illustrated in Fig. 3.6b. This variation is caused by the significant difference in the dimension of the starting materials (i.e., graphite flakes) and/or processes such as sonication and centrifugation used during GO synthesis and post-processing. The large variation in the nanoscopic GO properties hinders a true comparison among scientific works and can generate confusion in the research community. For this reason, an initial attempt to statistically classify GO based on its chemo-morphological properties is presented in Fig. 3.6c. The majority of the GO literature was researched in order to locate scientific
### Table 3.2: Summary of the techniques used to characterize the GO chemistry and morphology.

In bold are highlighted the quantitative techniques.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Morphology</th>
<th>Chemistry</th>
<th>Notes</th>
</tr>
</thead>
<tbody>
<tr>
<td>XPS</td>
<td>-</td>
<td><strong>Quantitative</strong></td>
<td>O/C atomic and oxy-functional group ratios via C1s peak deconvolution</td>
</tr>
<tr>
<td>Color Chart</td>
<td>-</td>
<td>Qualitative</td>
<td>Related to oxidation state</td>
</tr>
<tr>
<td>UV-vis</td>
<td>Qualitative</td>
<td>Qualitative</td>
<td>Presence/extent of sp² conjugation and multilayer nature/structure</td>
</tr>
<tr>
<td>ATR-IR</td>
<td>-</td>
<td>Qualitative</td>
<td>Presence of specific oxy-functional groups and sp² conjugation</td>
</tr>
<tr>
<td>Raman</td>
<td>-</td>
<td>Qualitative</td>
<td>Defect and sp² conjugation, but destructive to sample</td>
</tr>
<tr>
<td>SCA</td>
<td>-</td>
<td>Qualitative</td>
<td>Wettability as indirect measure of oxidation and surface roughness</td>
</tr>
<tr>
<td>ZP</td>
<td>-</td>
<td>Qualitative</td>
<td>Surface charge as indirect measure of oxidation (deprotonated oxy-groups)</td>
</tr>
<tr>
<td>SEM</td>
<td><strong>Quantitative</strong></td>
<td>-</td>
<td>Flake size distribution and monolayer percentage via image analysis</td>
</tr>
<tr>
<td>XRD</td>
<td><strong>Quantitative</strong></td>
<td>Qualitative</td>
<td>Flake-to-flake separation influenced by the presence of oxy-groups</td>
</tr>
<tr>
<td>AFM</td>
<td>Semi-Quantitative</td>
<td>-</td>
<td>GO thickness highly sensitive to experimental and operation conditions</td>
</tr>
<tr>
<td>Z-Avg</td>
<td>Semi-Quantitative</td>
<td>-</td>
<td>Hydrodynamic flake size distribution, skewed by spherical/opaque assumptions</td>
</tr>
</tbody>
</table>
3.3. Results and Discussion

Figure 3.6: GO characterization in the literature. (a-b) O/C atomic ratio and mean flake size distribution histograms. Each count represents a scientific work. (c) K-mean classification of the GO characterization based on O/C atomic ratio and mean flake size. Every white "x" represents the centroid (mean) of each class, white circles represent GO samples used in this study, and black dots represent the chemo-morphological data obtained from literature review. (d) The table lists the nanoscopic properties for the centroid of each category; the mean flake size of the samples used in this study was calculated from areas in Fig. 3.4b assuming a square GO flake.

<table>
<thead>
<tr>
<th>Category</th>
<th>O/C atomic ratio</th>
<th>Flake length (μm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SR-GO</td>
<td>0.12 ± 0.07</td>
<td>0.16 ± 0.17</td>
</tr>
<tr>
<td>S-GO</td>
<td>0.43 ± 0.05</td>
<td>0.10 ± 0.13</td>
</tr>
<tr>
<td>SHO-GO</td>
<td>0.58 ± 0.04</td>
<td>0.18 ± 0.14</td>
</tr>
<tr>
<td>MR-GO</td>
<td>0.11 ± 0.07</td>
<td>1.13 ± 0.39</td>
</tr>
<tr>
<td>M-GO</td>
<td>0.49 ± 0.07</td>
<td>0.97 ± 0.20</td>
</tr>
<tr>
<td>L-GO</td>
<td>0.50 ± 0.10</td>
<td>2.48 ± 0.47</td>
</tr>
</tbody>
</table>

works that characterized both GO chemistry and morphology and the data was classified using the K-mean clustering algorithm. The basic idea behind K-mean clustering is to determine the minimum number of classes into which the data will be partitioned, and then perform computations to group data so that observations within a cluster are similar and observations in different clusters are dissimilar. Each cluster is characterized by a centroid, which is typically the mean of the data. The algorithm assigns each observation to one cluster randomly and then repeats the following two steps until the clusters do not change: i) for each cluster computes the centroid; ii) given the centroids, reassigns all the observation based on their closeness to centroids. Via this iterative process, a local minimum is found by minimizing a cost function (details in Methods). K-mean clustering classified
the chemo-morphological data (black dots) into six categories: small and less oxidized GO (SLO-GO in pink), small GO (S-GO, in purple), small and highly oxidized GO (SHO-GO, in brown), medium and less oxidized GO (MLO-GO, in blue), medium GO (M-GO, in orange), and large GO (L-GO, in green). By assuming a Gaussian distribution of data points, the centroid (white exes in Fig. 3.6c) of each cluster is characterized by an O/C atomic ratio and a mean flake size as presented in the table in Fig. 3.6d. According to this characterization, Sample 1 is classified as SLO-GO, Sample 2 as M-GO, Sample 4 as SHO-GO, and Samples 3, 5 and 6 as L-GO. The fact that three samples fell in the same category could be an indication of a predominant GO synthesis method in industry, which yield nanomaterials with the same property. Note that the classification presented here can be refined with the introduction of data from future peer-reviewed publications. However, this classification could be used by producers to properly advertise their material and by researchers in presenting their work to allow for a more reliable comparison of results between different studies, and ultimately facilitating the rational development of GO-based applications. Furthermore, the 2D material chemo-morphological properties might have a significant impact on the industrial device performance. For this reason, we investigated a number of GO-based applications with GO material from different producers. In particular, we focused on applications that are relevant to the use of GO in membrane separation processes, which has recently attracted the attention of many research groups. The fabrication process (e.g., quantity of GO used in membranes and casting technique) was the same for all the membranes, and the tests were conducted by the same researcher reducing output variability related to experimental procedure. Thus, it is assumed that the variability in the results is primarily related to different GO properties.

The first application evaluated was bacterial adhesion onto GO membranes (GOM), which was motivated by recent reports indicating intrinsic antifouling properties of GOM in water treatment applications (e.g., nanofiltration, forward osmosis, etc.). The bacterial adhesion results are sum-
3.3. Results and Discussion

Figure 3.7: Performance comparison of GO toward macroscopic applications. (a) Representative SEM images of *E. coli* bacteria adhesion onto GOM (Samples 6 and 4, top and bottom image, respectively). (b) MB adsorption of GO samples before (top) and after (bottom) centrifugation. (c) Permeability data of GOM at 5 bar (top) and schematic of their GO flake arrangement (bottom).

Marized in Fig. 3.7a and Table 3.3, GOM were immersed in a solution containing bacteria (*E. coli*) for 20h (see Methods) and the extent of bacterial deposition on the membrane surface was evaluated via SEM analysis. The variation in bacterial deposition behavior (bacterial adhesion ≈ 50% and > 75%) is highlighted by comparison of SEM for Sample 6 (L-GO, Fig. 3.7a top) and Sample 4 (SHO-GO, Fig. 3.7a bottom). Representative images for the other samples can be found in Fig. 9.4. By comparing images in Fig. 3.7a, it is observed that larger GO flakes (Sample 6) result in increased deposition of *E. coli* as recently reported. This trend was also observed for the other samples (see Table 3.3) in which GOM composed of L-GO lead to higher (1.5 – 2-fold higher) bacterial adhesion. The variation is likely connected to the higher number of intrinsic defects of smaller flakes that hinders bacterial adhesion. For example, it has been reported that the presence of higher defect surface density in small flakes as compared to large flakes will induce oxidative stress and reduce bacterial adhesion.

The second application was the use of GO for the adsorption of methylene blue (MB), which is often used as a representative molecule for cationic dye wastewater. The adsorption of organic
molecules is a fundamental parameter to evaluate when calculating the rejection properties of a filter or membrane. The introduction of MB in most GO solutions causes an instantaneous aggregation of GO flakes (Fig. 3.7b top) due to GO surface charge neutralization. The GO MB aggregation phenomenon occurs in all samples, apart from Sample 1. The MB solution was in contact with the GO for 24 h, then the solution was centrifuged and the supernatant was extracted (Fig. 3.7b bottom) to quantify the MB removal via UV-vis (see methods section for further details). The GO MB adsorption capacities are compared via the log removal value (LRV) and summarized in Table 3.3. All GO samples have an average MB log removal capacity between 1.44 and 1.55 except for Sample 1 (SLO-GO), which has a log removal capacity of ≈ 1. Although Samples 4 and 1 are similarly characterized by small flakes, Sample 4 (SHO-GO) displays a 27% higher removal capacity compared to Sample 1 (SLO-GO); thus, the adsorption capacity cannot be connected to morphology. MB adsorption is more related to the GO surface charge due to the presence of oxy-functional groups, i.e., the lesser number of oxy-functional groups for Sample 1 (O/C atomic ratio < 0.2 as compared to 0.43 – 0.55 for Samples 2 – 6) results in a lesser MB adsorption capacity.

Although membrane permeability is a primary parameter in the design of membrane systems, recent studies report GOM permeabilities ranging over orders of magnitude. The GOM permeability for the six different samples obtained by capillary flow porometry is displayed in Fig. 3.7c top and

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### Table 3.3: Performance GO-based applications samples in terms of bacterial adhesion, adsorption properties, and permeability.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Category</th>
<th>Bacterial Adhesion (bacteria/area)*</th>
<th>Adsorption (MB removal, LRV)</th>
<th>Permeability (10³ LMH-bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>SLO-GO</td>
<td>46 ± 10</td>
<td>1.11 ± 0.17</td>
<td>38.3 ± 16.8</td>
</tr>
<tr>
<td>2</td>
<td>M-GO</td>
<td>53 ± 22</td>
<td>1.48 ± 0.17</td>
<td>0.5 ± 0.5</td>
</tr>
<tr>
<td>3</td>
<td>L-GO</td>
<td>77 ± 215</td>
<td>1.55 ± 0.17</td>
<td>128.4 ± 73.8</td>
</tr>
<tr>
<td>4</td>
<td>SHO-GO</td>
<td>51 ± 10</td>
<td>1.44 ± 0.17</td>
<td>186.3 ± 59.8</td>
</tr>
<tr>
<td>5</td>
<td>L-GO</td>
<td>100 ± 28</td>
<td>1.46 ± 0.16</td>
<td>116.9 ± 69.6</td>
</tr>
<tr>
<td>6</td>
<td>L-GO</td>
<td>75 ± 12</td>
<td>1.45 ± 0.15</td>
<td>171.6 ± 71.6</td>
</tr>
</tbody>
</table>

* Data have been normalized to 100 to increase readability. 100 bacteria/unit corresponds to 75 bacteria per 7000 µm².
Table 3.3 A large variation in the permeability (up to a factor of five) is observed, which is related to the variation in GO chemistry and morphology between samples. As recently proposed, GOM permeability is affected by two primary factors: i) flake size, which is proportional to membrane pore tortuosity, thus inversely proportional to permeability; and ii) extent of oxidation, which is directly proportional to the width of GO nanochannels or interlayer separation distance (XRD data in Fig. 3.5a), thus permeability. In summary, both GO chemistry and morphology will affect the GOM membrane permeability and a scheme illustrating the individual effects of these two factors is displayed in Fig. 3.7c bottom. Samples 3 and 5 have similar oxidation and flake size, leading to similar permeability results. Sample 4 displays the highest permeability value, predominantly due to both its high O/C ratio value (high nanochannels width) and small flake size (low tortuosity). Although Samples 4 and 6 exhibit similar permeability results, the cause is significantly different; for Sample 4 the permeability is partially originated by a small flake size (reduced tortuosity), whereas for Sample 6 the permeability is mostly driven by the increased O/C ratio (increased width of GO interlayer nanochannels), which compensates the larger flake size. Sample 1 displays a significant lower permeability due to the poor oxidation of the GO flakes leading to narrow GO nanochannels. Incorporation of GO into polymer membranes has been reported to enhance permeability by increasing overall membrane hydrophilicity. Similarly, here the most hydrophilic GOM samples (SCA < 40°) have a higher permeability. In contrast, Sample 2 was nearly impermeable under 5 bar of applied pressure due to the absence of carboxylate functional groups (Fig. 3.2b), which creates a compacted laminate structure and reduces wettability as corroborated by the absence of an O-H water vibration band in Fig. 3.3b.
Chapter 3. Aristotelian view on Graphene Oxide

3.4 CONCLUSIONS

By defining the most relevant characterization techniques, a vast-range of GO materials were classified into distinct categories according to their chemo-morphological properties. The classification process is based on GO chemistry and morphology determined by SEM image analysis and XPS spectra analysis. A K-mean clustering algorithm classified the chemo-morphological data into six categories SLO-GO, S-GO, SHO-GO, MLO-GO, M-GO, and L-GO. Although the classification relied on thorough literature research (> 300 papers) for calibration, this work does not represent an ultimate classification process and could be extended and refined with other characterization techniques and more training data (e.g., future research investigations). The main goal of this work is to create momentum and raise awareness about the need of a GO standardization process and that the existing variation in device performance obtained from different research groups may be attributed to the highly variable properties of the GO starting material. This was highlighted in the last part of this work, in which GO-based applications yielded quite different results based on the diversity of what should have been, as advertised, the "same" GO material. This initial GO classification aims to facilitate the recognition of adequate material by setting standards for industrial GO producers. Concurrently, researchers will be able to make fair comparisons and increase the reproducibility of their and interlab results, leading to a higher signal to noise ratio in the development of GO materials for practical applications.
Abstract

Here we report the synthesis of graphene oxide nanoscrolls (GONS) with tunable dimensions via a high frequency ultrasound solution processing technique. GONS can be visualized as a graphene oxide (GO) sheet rolled into a spiral-wound structure and represent an alternative to traditional carbon nano-morphologies. The scrolling process is initiated by the ultrasound treatment which provides the scrolling activation energy for the formation of GONS. The GO and GONS dimensions are observed to be a function of ultrasound frequency, power density, and irradiation time. Ultrasonication increases GO and GONS C-C bonding likely due to in situ thermal reduction at the cavitating bubble-water interface. The GO area and GONS length are governed by two mechanisms; rapid oxygen defect site cleavage and slow cavitation mediated scission. Structural characterization indicates that GONS with tube and cone geometries can be formed with both narrow and wide dimensions in an industrial-scale time window. This work paves the way for GONS implementation for a variety of applications such as adsorptive and capacitive processes.
4.1 INTRODUCTION

The thermomechanical and electrical properties of low dimensional carbon nanomaterials make them candidates for the next-generation conductive light-weight high-strength architectures. However, the cost and difficulty associated with scalable synthesis of macroscopic architectures from low dimensional carbon materials leaves room for improvement.

Recent work on graphene oxide (GO) indicates there is potential for nanomanufacturing via cost-effective solution techniques that retain GO properties such as thermal conductivity, mechanical stiffness, elasticity, and optical transparency. Moreover, the GO oxygen functional groups act as both a spacer and a functionalized site for molecular adsorption, which enables GO conversion into nanomorphologies that could be used for applications such as filtration membranes, supercapacitors, electrochemical sensors, and hydrogen storage devices. One potential nanomorphology is a GO nano-scroll (GONS), i.e., a GO sheet rolled into a spiral-wound structure (Fig. 4.1a). GONS are similar in morphology to a carbon nanotube (CNT), but with a significantly more accessible inter-wall area.

Previous work on the formation of spiral-wound graphene-based structures has focused on graphene nanoscrolls (GNS). Studies have demonstrated that there is an energy barrier (100s to 1000s J mol$^{-1}$) to initiate GNS formation after which the scrolling process self-propagates due to $\pi - \pi$ interactions forming a nanoscroll with an internal diameter of $\approx 2$ nm. The two primary methods to overcome the scrolling energy barrier are: i) template initiators such as carbon nanotubes, nanodroplets, and nanoparticles, and ii) external stimuli such as ultrasonication, microwave sparks, mechanical manipulation, thermal processing, electric fields, and solvents. GNS have diameters of $\approx 20 - 600$ nm, lengths of $\approx 0.7 - 10$ $\mu$m, and the dimensions are a function of experimental processing conditions and graphene flake surface chemistry.
4.1. Introduction

In contrast to GNS, studies on GONS have been relatively limited. For example, previously synthesized GONS cannot be characterized by metrics such as dimension since the structures are typically composed of crumpled and/or folded GO\(^{60,138}\) instead of a properly scrolled morphology. GONS have been synthesized by mechanical manipulation\(^{54,138}\) and/or chemical initiators.\(^{131,194}\) In contrast, GONS formation via ultrasonic irradiation has not been investigated in depth. Ultrasonic pressure waves results in transient bubble cavitation, \textit{i.e.}, the sequential nucleation, growth, and collapse of microscopic bubbles.\(^{179}\) The ultrasonic energy imparted to bubbles and, in turn the GO flakes, provides the scrolling activation energy to form GONS. However, such extreme energy release (bubble vapor \(T \approx 4000\) K; bubble interface \(T \approx 800\) K) will also chemically modify and cleave the GO flakes impacting the surface chemistry and morphology of the resulting GO nanostructures.\(^{77}\)

Here, we complete a systematic study on the effect of ultrasonic frequency, power density, and irradiation time on GONS production, morphology, dimensions and surface chemistry. GO was synthesized via the oxidation of graphite flakes following a modified Hummers’ method.\(^{103,188}\) The GO was subjected to two frequencies of ultrasonic irradiation; 20 kHz low frequency (LF) irradiation generated by a commercial tip-sonicator and 390 kHz high frequency (HF) irradiation generated by a homemade reactor, at both low and high power densities (Fig. 4.1b). The time-dependent structure and morphology of the GO and GONS was analyzed by scanning (SEM) and transmission (TEM) electron microscopy, and the GO and GONS surface chemistry and interlayer interactions were analyzed by Raman spectroscopy and X-ray photoelectron spectroscopy (XPS).
Chapter 4. Graphene Oxide Nanoscrolls

![Figure 4.1: Structure and fabrication methods of GO and GONS. (a) Illustration of the GO flake chemistry showing the arrangement of the oxygen functional groups, and the cross-sectional morphology of GONS. (b) Summary of the GONS fabrication process starting from graphite flakes and demonstrating the difference between the low frequency (LF) and high frequency (HF) processing.](image)

### 4.2 METHODS

#### 4.2.1 GRAPHENE OXIDE SYNTHESIS

The GO solution was prepared using a modified Hummers’ method[^103] with additional pre-processing of the graphite powder.[^124] Additional details can be found in Appendix B.

#### 4.2.2 GRAPHENE OXIDE TREATMENT

For the LF treatment, 8 mL of GO solution was dispersed in 392 mL of ethanol(EtOH) (final GO concentration 0.002 wt%) in a 600 mL glass beaker, and was subjected to 20 kHz LF tip-sonication treatment (Sonifier S-450D; from *Branson Ultrasonics Corp.* with high gain horn) at 10% and 90% of the maximum amplitude (130 μm for the used tip geometry), which results in a calorimetric power density (see below) of \( \approx 10 \) W (9.7 ± 1.3 W) at 10% and 100 W (99.9 ± 13.2 W) at 90% respectively. To explore the impact of the GO solution volume on the observed GO and GONS...
morphologies, the LF treatment was also carried out at a reduced volume of 2 mL of GO solution dispersed in 98 mL of EtOH (in a 150 mL glass beaker) at 10% of the maximum amplitude (≈ 10 W of power according to calorimetry). For the HF treatment, 25 mL of GO solution was dispersed in 1.175 L of EtOH (final GO concentration 0.002 wt%) and processed via 390 kHz HF treatment in a reactor comprised of a 1.5 L jacketed glass reactor composed (Chemglass Inc.) and a cylindrical PbZr₆Ti₁₋₆O₃ (PZT) piezoelectric crystal (5 cm diameter, 0.35 cm thickness, PZT-840, APC International, Ltd.). The piezo was attached to a steel plate (12.7 cm diameter, 0.05 cm thick) using a conducting silver epoxy (CHO-bond 584, Parker Chomerics) with electrical leads connected using a non-lead solder. The electrical signal used to drive the PZT crystal is produced by an arbitrary waveform generator (Agilent; 33522A) and was amplified by a linear RF power amplifier (ENI; 2100L; 100 W max; 10 kHz−12 MHz). Since there are no commercially available setups capable of ultrasonic treatment at frequencies ≥ 100 kHz, the HF setup used here was custom built for this experiment. On the other hand, there are large-scale commercial systems on the market that capable of ultrasonic treatment at 20−40 kHz, e.g. from Industrial Sonomechanics, LLC, and Branson Ultrasonics Corp. The HF power was controlled by setting the arbitrary waveform generator peak-to-peak voltage amplitude, where 0.8 V peak-to-peak was used for HF(1 W) 1.2 ± 0.2 W, 1.8 V peak-to-peak for HF(10 W) 10.2 ± 2.3 W, and 2.5 V peak-to-peak for HF(20 W) 19.7 ± 3.8 W with power determined via calorimetry. The ultrasonically-irradiated GO solution was then drop-cast on either a Si wafer (SEM/Raman/XPS) or a TEM grid for further characterization. The calorimetric powers \( Q \) were calculated \( Q = mC_p\Delta T \) where \( C_p \) is the specific heat capacity of ethanol, \( m \) is equal to 0.32 kg and 0.95 kg for HF and LF, respectively, and \( \Delta T \) is the change in temperature recorded during irradiation time.
4.2.3 Structure and Morphology Characterization

Scanning electron microscopy (SEM): The surface morphology of the GO flakes was characterized using a Zeiss ULTRA Field Emission Scanning Electron Microscope with an In-lens secondary electron detector. In order to image the GONS, a working distance of 3 – 4 mm, an acceleration voltage of 3 – 4 kV, and an aperture of 20 µm was utilized. These operating conditions allow visualization of the GONS overlapped structure and recognition of the fine details on the order of tens of nanometers. The statistical SEM image analysis of the GO and GONS was completed using ImageJ (see Fig. 10.7 in the Appendix B), where > 300 GO flakes and > 15 GONS were analyzed for each processing time.

Transmission electron microscopy (TEM): The GO structures were analyzed using a JEOL-2100 LaB6 TEM (see Fig. 10.3 in the Appendix B). The accelerating voltage was 80 or 200 keV depending on the image. The second largest condenser aperture was used. The GO and GONS were drop-cast on a 200 mesh Cu TEM grid covered by a continuous carbon film (Ted Pella, Inc.).

Raman spectroscopy: Raman spectra were acquired using a WITec Confocal Raman Microscope/SNOM/AFM. The laser wavelength was 532 nm and the spectra are characterized using a 0.3 s integration time of at least 20 spectra. Raman intensity maps (500 acquisition points for a 25 × 25 µm image) were constructed by scanning during acquisition. The spectra were deconvoluted using a single Lorentzian and a Breit-Wigner-Fano for the D-and G-band, respectively.

Atomic force microscopy (AFM): The thickness of the GO and GONS was measured with an Asylum Cypher AFM using an Olympus 200TS cantilever (resonance frequency ≈ 150 kHz). The images were acquired in amplitude modulation mode with a free amplitude of 20 nm and a set point of 15 nm. The images were then flattened using AR software from Asylum Research.

X-ray photoelectron spectroscopy (XPS): The GO were analyzed by Thermo Scientific K-Alpha XPS (ESCA). The X-rays were generated by a 12 kV electron beam and had a spot size of
400 µm. The C/O ratio and peaks deconvolution were performed by using the *Thermo Scientific Avantage* software.

4.3.1 Morphology and Surface Chemistry of Graphene Oxide flakes

An SEM image of GO flakes prior to ultrasound exposure is displayed in Fig. 4.2a. The GO flakes have an area of 52.8 ± 3.9 µm². The AFM thickness of the GO flakes (Fig. 4.2b) is ≈ 1.5 nm in accordance with previous studies. XPS was completed on drop-cast GO flakes (Fig. 4.2c) and the C/O ratio was 1.42. Deconvolution of the C1s spectrum results in three peaks corresponding to: (i) 30% single (C-C) and double (C=C) carbon bonds; (ii) 65% epoxide (C-O-C) and hydroxide (C-OH) functional groups; and (iii) 5% carboxylate (O=C-OH) functional groups.

4.3.2 Morphology and Surface Chemistry of Graphene Oxide Nanoscrolls

GONS produced by HF ultrasonic irradiation exhibit concentric geometries with a distinguishable number of outer-walls as displayed in Fig. 4.3a, e.g., six walls for the top-left GONS. This indicates that the GONS produced here are of high quality, similar to a recent report, as they are not assemblies of crumpled and/or folded GO layers. The resulting GONS were characterized by two distinct geometries: a constant outer diameter tube-like GONS (T-GONS); and a variable outer diameter cone-like GONS (C-GONS). The formation of T-GONS is a result of a constant scrolling speed and/or direction whereas surface inhomogeneities/defects may cause a variable speed/direction resulting in C-GONS formation. SEM images illustrating the scrolling process that leads to the formation of both T-GONS and C-GONS structures (Fig. 10.1 and Fig. 10.2) and TEM images that illustrate the hollow nature of the produced GONS (Fig. 10.3) can be found in the Appendix B.

Narrow and wide T- and C-GONS structures are observed and characteristic diameters were
quantified by SEM image analysis (Fig. 4.3a). Narrow T-GONS structures are characterized by $d_{\text{tube}} = 215 \pm 75$ nm, while narrow C-GONS structures exhibit a minimum diameter $d_{\text{cone, min}} = 215 \pm 75$ nm and maximum diameter of $d_{\text{cone, max}} = 1.65 \pm 0.39$ μm. Wide GONS structures have $d_{\text{tube}} = 1.80 \pm 0.27$ μm for T-GONS and $d_{\text{cone, min}} = 0.95 \pm 0.32$ μm and $d_{\text{cone, max}} = 1.84 \pm 0.33$ μm for C-GONS. Note for narrow GONS $d_{\text{tube}} \sim d_{\text{cone, min}}$, and for wide GONS $d_{\text{tube}} \sim d_{\text{cone, max}}$. Size distribution histograms are displayed in Fig. 10.4 of the Appendix B. The observed GONS diameters are related to the area of the parent GO flake and the inter-layer separation of the GONS walls. The GONS have an observed inter-layer separation on the order of $10 - 100$ nm, as can be seen in Fig. 4.3a, which is much larger than the inter-layer separation of GNS and CNT ($\approx 0.34$ nm).
Thus, the GONS inter-wall regions will be more accessible to atoms and molecules than GNS/CNT, providing utility for applications requiring readily accessible surface areas such as adsorptive and capacitive processes. Another important factor that may contribute to variations in $d_{\text{min}}$ is related to the extent of GO flake oxidation and surface chemistry, which in turn will affect the elastic modulus of GO and weaken inter-layer $\pi - \pi$ interactions. The GO and GONS structures were characterized via Raman spectroscopy and both display a D-band ($A_{1g}$ symmetry) at $\approx 1350 \text{ cm}^{-1}$ representative of defects/disorder in the basal plane and a G-band ($E_{2g}$ symmetry) at $\approx 1590 \text{ cm}^{-1}$ that corresponds to the in-plane $sp^2$ bond stretching. The G-band full width half maximum (FWHM) of the GONS is larger than the FWHM of the G-band of pristine graphene and bulk graphite, i.e. $\approx 20 \text{ cm}^{-1}$ as displayed in Fig. 4.3b. To quantitatively analyze the relative defect density of the GO and GONS, the Raman spectra were fit ($R^2 > 0.99$) using single Lorentzian (D-band) and Breit-Wigner-Fano (G-band) distributions as displayed in Fig. 4.3b. The D- and G-band fits indicate that the FWHM of the D-band remains constant at $119 \pm 6 \text{ cm}^{-1}$ after GONS formation, whereas the FWHM of the G-band increases from $64 \pm 3$ to $78 \pm 4 \text{ cm}^{-1}$. The broader GONS G-band is due to scrolling effects on the basal plane breathing mode since the formation of a multi-layer morphology will increase elastic strain. The fitted G band peak position for the GONS is red-shifted by $\approx 10 \text{ cm}^{-1}$ as compared to the original GO flakes, which is indicative of reduced disorder in nanocrystalline graphitic materials, in agreement with the decrease in $A_D/A_G$ from GO to GONS. The $\approx 15 \text{ cm}^{-1}$ increase of the GONS G-band FWHM can be utilized to distinguish the GO and GONS using a spatially-dependent integration (50 nm resolution) of the G-band intensity (Fig. 4.3c-right) where the GONS are of
Figure 4.3: Morphology and defect density of GONS. (a) SEM displaying narrow and wide cone-like (C-GONS) and tube-like (T-GONS) that are characterized by their diameters ($d_{\text{tube}}$) and ($d_{\text{cone}}$). (b) Raman spectra of the D- and G-bands for GO and GONS. (c) SEM and spatial integration of G-band intensity of a partially-scrolled GO where scrolled regions are of greater intensity than the flat regions.

higher integrated intensity (compare to SEM; Fig. 4.3: left) that originates from the broader G-band of GONS caused by the phenomena explained above.
4.3. Results and Discussion

4.3.3 Effect of Ultrasonic Frequency on Dimensions

The effect of ultrasound frequency (20 kHz LF vs. 390 kHz HF) and power density on the GO flake area \( A_{\text{GO}} \) and GONS length \( L_{\text{GONS}} \) as a function of the ultrasonic irradiation time \( t \) was evaluated as displayed in Fig. 4.4. Calorimetry indicates that \( \approx 10^3 - 10^4 \) J mol\(^{-1} \) is introduced to the GO solutions during the 1 hr ultrasonic treatments (see Methods section for calorimetry calculation), which is similar to the previously reported theoretical energy barrier for scrolling graphene.\(^{22,23,131} \)

Since we can observe GONS formation at treatment times as short as 5 min where only \( 10^2 \) J mol\(^{-1} \) is introduced, the calorimetry suggests that the GONS scrolling process may occur at local ‘hot spots’ generated by bubble cavitation.\(^{22,23,131} \) Calorimetry also indicates that both LF and HF ultrasonic irradiation transfer \( \approx 10 \) W to the GO solution, thus observed differences in \( A_{\text{GO}} \) and \( L_{\text{GONS}} \) can be attributed to the difference in ultrasonic frequency.

For both ultrasonic frequencies, \( A_{\text{GO}} \) decreases over the 60 min irradiation time with the majority of the decrease occurring over the first 10 – 20 min of irradiation from \( A_{\text{GO}}(t=0) = 53 \pm 4 \) µm\(^2 \) to \( A_{\text{GO}}^{\text{HF}}(t=60) = 30 \pm 2 \) µm\(^2 \) and to \( A_{\text{GO}}^{\text{LF}}(t=60) = 7 \pm 0.7 \) µm\(^2 \). A similar decrease is observed for \( L_{\text{GONS}} \) as presented in Fig. 4.4b, where the majority of the length decrease occurs over the first 20 – 30 min from \( L_{\text{GONS}}^{\text{HF}}(t=5) = 11 \pm 1 \) µm to \( L_{\text{GONS}}^{\text{HF}}(t=60) = 7 \pm 0.8 \) µm and from \( L_{\text{GONS}}^{\text{LF}}(t=5) = 7 \pm 0.6 \) µm to \( L_{\text{GONS}}^{\text{LF}}(t=60) = 3 \pm 0.2 \) µm. For both cases, \( A_{\text{GO}} \) and \( L_{\text{GONS}} \) are relatively constant after the first 30 minutes of irradiation, a favorable time-window for industrial-scale processing.

Note that \( L_{\text{GONS}} \) achieves a minimum after \( A_{\text{GO}} \) achieves a minimum and that the final \( A_{\text{GO}} \) is roughly the same as the final \( L_{\text{GONS}}^2 \) suggesting that the energy to scroll GO is less than the energy to cleave.

Additional details pertaining to the GO and GONS dimensions can be found in the Appendix B. The \( A_{\text{GO}} \) and \( L_{\text{GONS}} \) results indicate that the LF ultrasonic irradiation is harsher than the HF treatment as expected. The cavitation energy released during transient adiabatic bubble collapse is proportional to \( R_{\text{max}}^3 \) where \( R_{\text{max}} \) is the maximum bubble radius (\( PdV \) energy release)\(^{22,23,129} \) and the 20 kHz LF
Figure 4.4: Effect of ultrasonic frequency and irradiation time on GO and GONS dimensions. (a) Plot of the GO area ($A_{GO}$) for the low frequency (LF) and high frequency (HF) treatment at 10 W of calorimetric power as a function of the irradiation time $t$. (b) Plot of the GONS length ($L_{GONS}$) as a function of $t$ for the two conditions. The fitting lines are based on eq (4.1) and eq (4.2).

The effect of ultrasound calorimetric power density (HF 1, 10, & 20 W; LF 10 & 100 W) on the time-dependent $A_{GO}$ and $L_{GONS}$ is displayed in Fig. 4.5. If the HF ultrasonic power is decreased to 1 W, then there is no significant change in $A_{GO}$ with $t$, whereas increasing the HF ultrasonic power to 20 W (2-fold) decreases $A_{GO}$ as compared to 10 W by 2-fold ($A_{GO}^{HF(20\,W)}(t = 60) = 15 \pm$.
1 µm²). If the LF ultrasonic power is increased from 10 to 100 W, then the \( A_{GO} \) was decreased 3-fold \( A_{GO}^{LF(100 \, W)}(t = 60) = 2 \pm 0.2 \, \mu m^2 \). Similar trends were observed for \( L_{GONS} \) with regards to power and frequency as displayed in Fig. 4.5b. For example, decreasing HF power to 1 W resulted in a negligible decrease of \( L_{GONS} \) with time suggesting there is not enough acoustic power for high-energy transient bubble cavitation and that stable cavitation may be enough to scroll GO. Increasing the HF ultrasonic power from 10 to 20 W results in a negligible change in \( L_{GONS}^{HF(20 \, W)}(t) \), in contrast to the 2-fold reduction in \( A_{GO}(t) \), again indicating the GONS are more difficult to cleave than GO. However, increasing the LF power to 100 W resulted in a 3-fold decrease, in \( L_{GONS}^{LF(100 \, W)}(t = 60) = 1 \pm 0.1 \, \mu m \), similar to the decrease in \( A_{GO} \).

Here, the kinetics of \( A_{GO} \) and \( L_{GONS} \) dimension decrease are quantitatively examined to gain insight into the physical mechanisms that mediate ultrasonic cleavage. The two predominant mechanisms are: I) GO flake and GONS cleavage at defect (oxygen) sites \( (E_A = 50 - 60 \, \text{mJ mol}^{-1}) \) that was previously modeled with exponential kinetics \( ^{123,196} \) and II) cavitation mediated scission that was previously modeled using power kinetics. \( ^{115,180} \) Mechanisms I and II can be modeled by kinetic eqn (4.1) & eqn (4.2), respectively:

\[
A_{GO}(t) = \begin{cases} 
A_1(e^{-k_{GO}t}), & t \leq t_{\text{crit}} \\
A_2(t)^{-s_1}, & t \geq t_{\text{crit}}
\end{cases}
\]  

\[
L_{GONS}(t) = \begin{cases} 
L_1(e^{-k_{GONS}t}), & t \leq t_{\text{crit}} \\
L_2(t)^{-s_2}, & t \geq t_{\text{crit}}
\end{cases}
\]

where \( A_1 \) and \( A_2 \) are constants related to the area of the GO flakes, \( L_1 \) and \( L_2 \) are constants related to the GONS length, \( k_{GO} \) and \( k_{GONS} \) are kinetic rate constants for mechanism I, and \( s_1 \) and \( s_2 \) are power exponents for mechanism II. Note the two mechanisms are operating simultaneously;
Table 4.1: Kinetic parameters for time-dependent GO and dimensional decrease. The critical time ($t_{crit}$) is approximated via the intersection of the exponential scaling and power scaling. See eqn (4.1) & eqn (4.2) for the functional forms.

<table>
<thead>
<tr>
<th>Process</th>
<th>Power [W]</th>
<th>$A_1$ [µm²]</th>
<th>$k_{GO}$ [min⁻¹]</th>
<th>$A_2$ [µm²]</th>
<th>$s_1$ [-]</th>
<th>$t_{crit}$ [min]</th>
<th>$L_1$ [µm]</th>
<th>$k_{GONS}$ [min⁻¹]</th>
<th>$L_2$ [µm]</th>
<th>$s_2$ [-]</th>
<th>$t_{crit}$ [min]</th>
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<tr>
<td>HF(1 W)</td>
<td>1.2 ± 0.3</td>
<td>52.8</td>
<td>0</td>
<td>52.8</td>
<td>0</td>
<td>&gt; 60</td>
<td>9.43</td>
<td>0</td>
<td>9.43</td>
<td>0</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>HF(10 W)</td>
<td>10.2 ± 2.3</td>
<td>52.8</td>
<td>0.028</td>
<td>29.6</td>
<td>0</td>
<td>20.7</td>
<td>12.6</td>
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<td>6.56</td>
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<tr>
<td>HF(20 W)</td>
<td>19.7 ± 3.9</td>
<td>52.8</td>
<td>0.066</td>
<td>14.7</td>
<td>0</td>
<td>19.4</td>
<td>12.3</td>
<td>0.031</td>
<td>7.22</td>
<td>0</td>
<td>17.2</td>
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<tr>
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<td>10.2 ± 2.3</td>
<td>52.8</td>
<td>0.199</td>
<td>17.3</td>
<td>0.213</td>
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<tr>
<td>LF(100 W)</td>
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<td>—</td>
<td>5.13</td>
<td>0.421</td>
<td>≤ 5</td>
</tr>
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</table>
4.3. Results and Discussion

Figure 4.5: Effect of ultrasonic power and frequency on GO area (a) and GONS length (b) as a function of time (t). Black circles, blue squares, and red triangles refer to 1 W (HF), 10 W (HF) and 100 W (LF) irradiation power, respectively. Shaded grey trends represent experimental data from Fig. 4.4. The fitting lines are based on eq (4.1) and eq (4.2).

However, mechanism I, is just much faster than the mechanism II. Once all of the defect sites are cleaved, the cavitation-based cleavage dominates the kinetics. The competing GO/GONS cleavage mechanism is modeled using a critical irradiation time ($t_{\text{crit}}$), which represents the transition time point from defect-based cleavage Mode I ($t \leq t_{\text{crit}}$) to the cavitation-based mechanical cleavage Mode II ($t \geq t_{\text{crit}}$). Due to the high temperature of the surface of the bubbles (e.g. 600 – 800 °C), in situ thermal reduction may also occur concurrently with the cleavage governed by Mode I and Mode
II. For example, after 5 min of ultrasonic irradiation (LF and HF) the C-C/C=C peaks increased (30 to 60 – 65%), the C-O peak decreased (45 to 20 – 25%) and the O=C-O peak slightly increased (5 to 15%) in the C1s spectrum (Fig. 10.6).

Since the HF process generates smaller less-energetic and more spherical bubbles than the LF process, mechanical scission likely does not occur to a significant extent e.g., \( s_1 \) and \( s_2 \) for HF are negligible. The LF produces larger bubbles that undergo more energetic and non-spherical collapse of bubbles during sonication leading to the formation of microjets that are known to cause scission in graphene and CNTs. The LF exponents \( s_1 \) and \( s_2 \) range from 0.21 \( \leq s_1 \leq 0.31 \) and 0.38 \( \leq s_2 \leq 0.42 \) (See Table 4.1). These values are in good agreement with the previously reported exponents of \( \approx 0.21 – 0.25 \) for scission of micrometer-long CNTs (\( s_1 \) scission of GO flakes), and exponents of \( \approx 0.41 – 0.5 \) for scission of short CNTs (\( s_2 \) scission of GONS). \( L_1, L_2, k_{GONS}, \) and \( s_2 \) for HF(10W) and HF(20 W) are nearly identical demonstrating that the HF treatment is not effective at producing short GONS, which may be desired during processing. These previously reported kinetic coefficients are valid irrespective of the solution volume used during the ultrasonic treatment, and are in good agreement with an LF(10W) treatment done using a smaller beaker and GO solution volume (see Fig. 10.8 in the Appendix B). Further work is required to elucidate the fundamental mechanism of Mode I and how \( t_{crit} \) can be controlled.

4.4 Conclusions

The synthesis of graphene oxide nanoscrolls with tunable dimensions was achieved via 20 kHz low frequency and 390 kHz high frequency solution processing techniques. Simultaneous fine-tuning of GO flake dimensions and surface chemistry was achieved in a industrial-scale time window. Electron microscopy indicates that the produced GONS exhibit well-defined tube or cone geometries with a finite number of walls. Raman spectroscopy indicates that defect concentration, decreases
from the parent GO ($A_D/A_G \approx 1.4$) to the resulting GONS ($A_D/A_G \approx 1.2$) suggesting GO with lower
defects have a lower scrolling activation energy. Two mechanisms are responsible for the ultrasonic
reduction of the GO area and GONS length as a function of the irradiation time: cleavage at defect
(oxygen) sites at short $t$ (exponential kinetics) and cavitation microjet mediated scission at long
$t$ (power kinetics). XPS indicates that both LF and HF ultrasonication decreases GO C-O bonds
and increases C-C bonds by at least 2-fold, likely due to in situ thermal reduction at the cavitating
bubble-water interface. Further work via experiments, theory, and simulation is required to model
the underlying physics that govern these two mechanisms, and the effect of parent GO dimensions
and surface chemistry. An understanding of the underlying ultrasonic that determine the character-
istics of the produced GO and GONS will allow tunable modification of the diameter and surface
chemistry for a range of applications.
Graphene Oxide Architectural Laminate

Apart from minor modifications, this chapter originally appeared as:


ABSTRACT

Active research in nanotechnology contemplates the use of nanomaterials for environmental engineering applications. However, a primary challenge is understanding the effects of nanomaterial properties on industrial device performance and translating unique nanoscale properties to the macroscale. One emerging example consists of graphene oxide (GO) membranes for separation processes. Thus, here we investigate how individual GO properties can impact GO membrane characteristics and water permeability. GO chemistry and morphology were controlled with easy-to-implement photoreduction and sonication techniques and were quantitatively correlated, offering a valuable tool for accelerating characterization. Chemical GO modification allows for fine control of GO oxidation state, allowing control of GO architectural laminate (GOAL) spacing and permeability. Water permeability was measured for eight GOALs characterized by different GOAL chemistry and morphology and indicates that GOAL nanochannel height dictates water transport. The experimental outputs were corroborated with mesoscale water transport simulations of relatively large domains (thousands of square nanometers) and indicate a no-slip Darcy-like behavior inside the GOAL nanochannels. The experimental and simulation evidence presented in this study
helps create a clearer picture of water transport in GOAL and can be used to rationally design more effective and efficient GO membranes.

5.1 INTRODUCTION

Membrane technology has climbed to a paramount role in engineering applications such as water treatment, gas separation, energy storage, and food packaging. Recent works demonstrate that graphene could represent a valid alternative to traditional polymeric membranes because of its mechanical strength, chemical stability, near frictionless water transport, and the potential to engineer well-defined surface pores and/or internal nanochannels. However, a clear challenge is to understand how graphene nanoproperties affect the macroscopic performance of a device, such as water filtration membranes.

With regard to nanoproperties, graphene-based membranes can be classified into two main groups: nanoporous graphene (NPG) and graphene oxide laminates (GOL). NPG is obtained by creating nanopores in a pristine graphene monolayer via ion bombardment and/or etching. GOL are synthesized by casting graphene oxide (GO) flakes on porous substrates. The flakes spontaneously arrange in an ordered fashion to form a laminate structure characterized by interconnected GO nanochannels. The study of water transport in elemental carbon nanomaterials began in the mid-2000s, when fast (slip) water transport within nanometer-wide one-dimensional carbon nanotubes was reported. In 2012, the study of water transport in carbon materials expanded to two-dimensional (2D) carbon nano-architectures (such as NPG and subsequently GOL). GOL water transport has been modeled using molecular dynamics (MD), and results indicated a fast flow caused by the low wall friction of water within GO nanochannels or the presence of defects in the GO flakes. Experimental studies also observed GOL fast water transport, although a clear consensus about the mechanism (low wall friction vs nanometer defects) has not yet been reached.
In this study, we provide insight into the influence of the properties of nanomaterials, e.g., GO surface chemistry, on the mechanism of water flow within GOL via a combination of pressure-driven pure water permeability experiments and mesoscale lattice-Boltzmann (LB) fluid dynamics simulations. Ultrathin graphene oxide architectural laminates (GOAL, Fig. 5.1a) membranes were synthesized by vacuum filtration (VF) and then subsequently photoreduced by ultraviolet (UV) irradiation (in ambient or vacuum) or hydroiodic acid (HI) to finely tune nanomaterial chemistry (Fig. 5.1b). GO morphology was also controlled by varying the GO flake size via sonication prior to VF. The effect of GO surface chemistry and flake size on GOAL nanochannel architecture, e.g., interlayer spacing (2h) and tortuosity (l), was characterized by scanning electron microscopy (SEM), X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). GOAL pure water permeability was determined in dead-end filtration mode, and mesoscale LB simulations were used to elucidate hydrodynamic phenomena.
5.2 Methods

5.2.1 Graphene Oxide Architectural Laminate Fabrication

GO was synthesized by a modified Hummers method, and the detailed protocol can be found in our previous work. Postsynthesis, the GO solution was dispersed in ethanol at a concentration of 0.15 mg/mL. 1 mL of the GO solution was then dispersed in 20 mL of ethanol and vacuum-filtered onto a polyvinylidene difluoride (PVDF) membrane (Sterlitech). In the case of sonicated GOAL
(GOAL-son), prior to VF, the GO solution was bath sonicated for 23 min in a Branson sonicator ($V = 1.9$ L, maximal power $= 80$ W, and $f = 20$ kHz). UV-GOAL was obtained by exposing the VF membrane to UV light ($\lambda = 254$ nm) in ambient air. Vacuum UV treatment was performed in a 

**5.2.2 Graphene Oxide Architectural Laminate Characterization**

**Scanning electron microscopy (SEM):** The morphology of the bare PVDF, GO flakes, and GOAL was characterized using a Zeiss ULTRA Field Emission Scanning Electron Microscope with an In-lens secondary electron detector. The working distance was $4 – 5$ mm, and the acceleration voltage was $4$ kV. The GO flake area was determined using ImageJ SEM analysis. In (Fig. 5.2), the Adobe Photoshop blend option was used at the border between bare PVDF and GOAL.

**X-Ray photoelectron spectroscopy (XPS):** GOAL chemistry was analyzed by a Thermo Scientific K-Alpha XPS instrument (ESCA) with X-rays generated by a $12$ kV electron beam with a spot size of $400$ $\mu$m. The O/C ratio and peak deconvolution were quantified by Thermo Scientific Avantage software, and then convert to mass ratio by using C and O molecular weights. The XPS instrumental error for atomic composition is $\pm 1\%$, and the accuracy of the C1s peak fitting is $\pm 2\%$.

**Atomic force microscopy (AFM):** GOAL and bare PVDF morphology was characterized with an Asylum Cypher atomic force microscope using an Olympus 200TS cantilever (resonant frequency of $\approx 150$ kHz). The images were acquired in amplitude modulation mode and the tip size was constantly monitored.

**X-ray diffraction (XRD):** The GOAL crystallographic structure was analyzed with a Bruker D8 instrument equipped with a 2D VANTEC-500 detector. The spectra were recorded by the integration of the 2D images via EVA software. Depending on the sample, the integration time was between
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600 and 1200 s. Note that the bare PVDF XRD spectrum is characterized by peaks that could overlap with that of GO. Thus, to increase the signal-to-noise ratio, the GOAL was cast and reduced on a porous alumina oxide ($d_{\text{pore}} = 200$ nm) from Whatman.

**Static contact angle (SCA):** The SCA measurements were completed with a Rame-Hart 190 contact angle goniometer under ambient conditions. SCA were measured using 5 $\mu$L droplets and the data refer to the average of 5 measurements obtained with the Drop Analysis DroSnake plugin in ImageJ.

**Raman spectroscopy:** Raman spectra were acquired using a WITec Confocal Raman Microscope. The laser wavelength was 532 nm and the signal was acquired using a 0.3 s integration time of at least 10 spectra.

5.2.3 **LATTICE-BOLTZMANN SIMULATIONS**

The numerical simulations are based on the LB method adapted using a novel Langevin-like frictional force to account for the GO-water H-bonding interactions. Because the LB method has largely been documented in the literature, in the following we briefly introduce the LB model and the heterogeneous Langevin frictions term to account for the frictional interaction of oxy-functional groups on water molecule transport as described in eqn (5.1):

$$ f_i(x + c_i \Delta t, t + \Delta t) = f_i(x, t) + \frac{1}{\tau} \left[ (f_i^{eq}(\rho, \rho u) - f_i(x, t)) \right] + \Delta f $$  \hspace{1cm} (5.1)

where $f_i$ is the probability distribution function at position $x$ and time $t$ with a lattice-constrained velocity $c_i$, where index $i$ runs over the nine directions of the lattice, $f_i^{eq}$ is a proper expansion of the Maxwell-Boltzmann distribution that can be expressed as a function of density $\rho$ and linear
momentum $\rho u$, and the frictional force, $\Delta f$, is described in eqn (5.2)

$$\Delta f \sim -\rho \gamma(y)u$$  (5.2)

where the function $\gamma$ is described in eqn (5.3)

$$\gamma(y) \sim \gamma_0[\exp\left(-\frac{y}{w}\right)]$$  (5.3)

where $w = 0.2$ is the representative size of the protruding oxy-functional groups and $\gamma_0$ is a characteristic water-hydroxyl collision frequency taken to be equal to 70 ps$^{-1}$.[123] This comes from the conversion between LB and physical units, namely, $\gamma_{\text{phys}} = \gamma_{LB}/dt$, where $dt = 3 \times 10^{-15}$ s. Thus, the value of $\gamma_0$ has been chosen to match the characteristic water-water collision frequency value, which can be determined via MD simulations by monitoring the velocity autocorrelation function.[123] Wall function $H_L(y)$ takes a value of 1 when $0 < y < \delta$ and 0 elsewhere. Likewise, $H_R(y) = 1$ for $2h < y < 2h$ and 0 elsewhere.

Assuming the GOL structure to be symmetric and periodic,[87] we consider only two nanochannels out of the full device, characterized by a width equal to the spacing of GO (2$h$) and a length equal to $l$. A similar geometry has been recently employed to investigate the permeation of water through graphene-based membranes by means of MD simulations.[164] These two channels are connected via two openings of half the width of the inlet/outlet pores (Fig. 11.1 in the Appendix C). The boundary conditions at the left-right and top-bottom surfaces are periodic, to simulate the proximity of two adjacent GO layers. If applied, at solid walls, the molecules experience the Langevin frictional force previously described. The grid resolution is 10000 x 20, corresponding to a flake length of $10^{-6}$ m. The physical idea behind the Langevin frictional force is to account for the complex water-GO surface molecular interactions at a coarse-grain level, whereby all atomistic details are channeled into
parameters $\gamma_0$ and $w$. Note that the frictional force is considered to be uniform along the nanochannels. However, further studies could investigate the influence of heterogeneous frictional force characterized by regions with lower and/or higher friction, which would represent heterogeneity in the distribution of the oxy-functionalities. Refer to ref. [162] for more details.

### 5.2.4 Permeability Measurements

The permeability tests were performed in a custom-made dead-end filtration system (Fig. 11.2 in the Appendix C). The filtration system includes a 3.1 L reservoir (e.g., pressure pot from Alloy Product Corp.) allowing large-volume experiments to be performed. The pressure was regulated with a pressure gauge (Ingersoll). The pure water permeability was evaluated by monitoring the permeate volume with a Sartorious laboratory balance every 30 min. The pure water permeability was then obtained by dividing the flow rate by the applied pressure and membrane area.

### 5.3 Results and Discussion

#### 5.3.1 Tuning of Graphene Oxide Dimensions

GOAL were cast on a PVDF microfiltration membrane via VF, and their morphology was determined by SEM (Fig. 5.2). In the right portion of Fig. 5.2a, the bare PVDF membrane is characterized by a flowerlike structure with a pore size of 310 ± 126 nm. After VF, the GOAL homogeneously coats the PVDF (Fig. 5.2a, left), but the flowerlike structure of the PVDF is still observed (inset in Fig. 5.2a), because of the ultrathin (47 ± 6 nm) GOAL (mass and SEM analysis), which is highlighted by a cross-sectional image (Fig. 5.2b). Morphology conservation is important for membranes because specific nano- and micro-morphology affects fouling. GOAL morphology and thickness are also corroborated by AFM images (Fig. 5.2c-d and Fig. 11.3 in the Appendix C). In particular, the images are taken at the boundary (highlighted with a black line) between the GO
and the bare PVDF. From the topography image (Fig. 5.2c), again it is possible to notice that the thin GO layer preserves the flowerlike structure of the PVDF membrane. Important information can also be derived from the AFM phase image (Fig. 5.2d), which is affected by the chemistry of the sample. Thus, heterogeneity between GOAL and PVDF chemistry can be easily recognized.

The GOAL and PVDF are then subjected to reductive treatment, such as UV irradiation (15 – 1440 min). Previous reports indicate that the effects of UV irradiation on GO will depend on the environment (e.g., water or air) and can dictate whether GO reduction occurs. In this work, we for the first time explore the UV reduction of GO in vacuum, which may reduce the extent of photochemical degradation and increase conductivity. The evolution of the GOAL XPS C1s spectrum with UV irradiation time is shown in Fig. 5.3a. After 1440 min, GOAL graphitization is indicated by an increase in the carbon–carbon (C-C and C=C, binding energy of 285 eV) bond peak percentage of total C bonds from 28 ± 2 to 71 ± 2%. Correspondingly, the relative carbon-oxygen single-bond peak intensity, such as hydroxide (C-OH, 287 eV), decreases from 69 ± 1 to 14 ± 1%, and the carbon-oxygen double-bond peak intensity (C=O, 289 eV) increases by 5%. The oxygen/carbon mass (i.e., O/C) ratio decreases from 72 ± 2 to 35 ± 2% from the untreated GOAL to the 1440 min UV-irradiated GOAL, respectively. The XPS characterization data are summarized in Table 5.1 and eqn (5.4) represents a possible chemical reaction during UV irradiation in which an epoxide is photolyzed to a C=C bond:

\[
C-O-C + hv \rightarrow C=C + O_2(g)
\]  

(5.4)

The GOAL XRD spectrum as a function of UV irradiation time is shown in Fig. 5.3b. All spectra display a peak corresponding to the GOAL interlayer spacing (2h) (Fig. 5.1b). The interlayer spacing is quantitatively correlated to the GOAL oxygen content indicating basal plane oxy-groups mediate GOAL interlayer spacing at the angstrom level. Specifically, UV reduction of oxy-functional groups
Figure 5.2: GOAL morphology via SEM and AFM. (a) Areal top-down and (b) cross-sectional images of GOAL membranes obtained via SEM. (c) Topography and (d) phase image acquired at the boundary between the GOAL and the bare PVDF via AFM. The boundary between the two regions is highlighted with a solid black line.

results in an XRD peak shift of 2.7 Å or a 25% decrease in 2θ, 7.9 Å for untreated GOAL to 6.2 Å for GOAL after UV treatment for 1440 min. Elemental carbon reduction has been observed to be dependent on the environment; thus, we compared the reduction via UV irradiation in vacuum
versus ambient air. The GOAL O/C mass ratio after UV irradiation for 60 min in vacuum is similar
to that after 360 min in air, indicating significantly faster reduction kinetics, and the final O/C mass
ratio after 1440 min is $35 \pm 2\%$ and $46 \pm 2\%$ for UV in vacuo and air, respectively (see Table 11.1 in
the Appendix C). GOAL UV irradiation in air results in slower reduction likely because of ambient
$O_2$ propagating reactions with GO surface radicals and slower removal of UV-produced gaseous
radicals (eqn (5.4), which is similar to phenomena during thermal reduction of GO). Correspondingly,
UV GOAL treatment in air results in broader XRD peaks indicating a more disordered
structure than that after UV treatment in vacuum. For example, the full widths at half-maximum
after UV treatment for 60 min are $\approx 1.2^\circ$ and $\approx 1.8^\circ$ for vacuum and ambient air, respectively
(Fig. 11.4b in the appendix C). Alternatively, the GOAL were also reduced by concentrated HI at
50 °C for 1 min. HI reduces the GOAL to a greater extent than UV, in accordance with previous re-
ports, resulting in an O/C mass ratio of $20 \pm 2\%$ and an interlayer spacing of 5.5 Å (Fig. 11.5
in the Appendix C). Again, HI reduction of GOAL oxy-functional groups led to a decrease in in-
terlayer spacing and indicated a possible relationship between the two variables. Although other
studies investigated the effect of GO reduction on oxygen content and spacing, a quantitative
relationship between these parameters has not been previously reported. GOAL interlayer spacing
($2h$) as a function of oxygen content ($O$) is displayed in Fig. 5.3c and well fit ($R^2 > 0.99$) by an
exponential rise to a maximal GO interlayer spacing:

$$2h = a - b(e^{-cO})$$  \hspace{1cm} (5.5)

where $a$, $b$, and $c$ are empirical coefficients with values of 29.6, 26, and 0.004, respectively. The
difference in coefficients $a$ and $b$ that defines the spacing for pristine graphene (i.e., $O = 0$) yields
$2h = 3.63$ Å, which is similar to the theoretical spacing (3.4 Å) supporting the theoretical reliability
of the trend in Fig. 5.3c. In the case of completely oxidized GO ($O = 100$; one $O$ atom for one

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Figure 5.3: GOAL interlayer spacing as a function of oxygen content. (a) XPS and (b) XRD time-dependent spectra for UV-irradiated GOAL membranes in vacuum. The XRD full width at half-maximum peak is equal to 0.7°, 1°, 1.2°, 1.3°, 2°, and 3.5° for irradiation times of 0, 15, 60, 360, 720, and 1440 min, respectively. (c) The GOAL interlayer spacing as a function of GO oxygen content can be fitted with an exponential rise to maximal GO interlayer spacing. In the equation, a-c are empirical coefficients with values of 29.6, 26, and 0.004, respectively.
C atom), eqn (5.5) yields $2h = 12.2$ Å, the upper limit for GO spacing. Note that a GO with an O/C mass ratio of $\geq 1$ has never been obtained to the best of our knowledge, and experiments that aimed to investigate the oxidation of GO achieved a maximum of $\approx 60\%$ carbon bonds oxidized.\textsuperscript{357} The small $c$ value indicates that large changes in $O$ will result in subangstrom variation in GOAL interlayer spacing. The relation in eqn (5.5) has potential to significantly decrease GOAL characterization time by performing a single characterization (e.g., XPS or XRD) to determine both oxygen content and interlayer spacing. Note that eqn (5.5) currently applies to our synthesized GOAL, but deviations from this may be expected due to alternative casting techniques and/or varying GO properties (e.g., flake size and/or oxy-functional group content and/or distribution). GOAL reduction results in a corresponding reduction of GO nanochannel spacing. However, it is also possible to rationally modify the length ($l$) of the nanochannels (Fig. 5.1 right) by ultrasonic irradiation of the GO solution before VF casting.\textsuperscript{10} For example, the GO flake area decreased by more than 1 order of magnitude, from $52.2 \pm 18.9$ to $1.3 \pm 0.4$ $\mu m^2$ (Fig. 11.6 in the Appendix C), after bath sonication for 23 min corresponding to a decrease in $l$ by a factor of $\approx 7$, assuming a square flake. Note that the modifications of $2h$ and $l$ are not interdependent as it is possible to modify one dimension without affecting the other (Fig. 11.7). In other words, sonication does not affect the spacing ($2h$) and chemical modification does not affect the morphology of the flakes ($l$).

5.3.2 \textbf{GRAPHENE OXIDE ARCHITECTURAL LAMINATE PERMEABILITY}

Once we had demonstrated the ability to tune primary GOAL dimensions ($2h$ and $l$) by exploiting GO metastability, the GOAL water permeability as a function of GO nanoscopic properties was investigated. Attention was focused on eight GOAL: (i and ii) untreated GOAL (0-GOAL and 0-GOAL-son), (iii and iv) 15 min UV-irradiated GOAL in vacuum (15-GOAL and 15-GOAL-son), (v and vi) 360 min UV-irradiated GOAL in vacuum (360-GOAL and 360-GOAL-son), and (vii
and viii) HI-treated GOAL (HI-GOAL and HI-GOAL-son). Note that -son refers to membranes obtained by casting a GO solution that was sonicated and, thus, characterized by a smaller GO flake size. Sonication does not introduce significant changes into the defect density as corroborated by Raman image analysis (see Appendix C). The pure water permeabilities were obtained via dead-end filtration (Fig. 11.2 in the Appendix C) and are summarized in Fig. 5.4.

Figure 5.4: GOAL pure water permeability. (a) Darcy behavior of the UV-treated GOAL membranes in vacuum. (b) Permeability of eight GOAL membranes. Each permeability was evaluated in at least duplicate.

The normalized flux for two membranes [0-GOAL (blue) and 360-GOAL (black)] at three pressures (2, 3, and 4 bar) is presented in Fig. 5.1a. The water flux is linearly dependent on the applied pressure indicating Darcy behavior. These data are also supported by the decrease in permeability with an increase in GOAL thickness (Table 11.2). In the Darcy hydrodynamic regime, water transport follows the no-slip condition. The permeability in LMH-bar (i.e., liters per square meter per hour per bar) for the eight GOAL membranes is displayed in Fig. 5.4b. In terms of absolute values, the permeability varies from 3 – 4 to 0.25 – 0.75 LMH-bar, in accordance with values reported for reduced ultrathin GO membranes on polymer substrates. Although higher values (tens of LMH-bar) of permeability have been reported for GO membranes, these values may be related to
the presence of defects or GO nanochannels larger than those observed here because of the reduction of the GO membranes in air. Increased permeability (> 100 LMH-bar) can also be achieved by intercalating GO with high-aspect ratio nanostructures such as rods. Discrepancies between permeability values reported in Fig. 5.1b and previous literature values could also emerge from the fact that previous studies did not evaluate the membrane performance under steady-state conditions (always lower than the initial permeability). For example, the time-dependent permeate volume (Fig. 11.8) shows that the GOAL flow rate decreases with time until reaching steady-state conditions at ≈ 700 min, similar to the case for polymer membranes, and the GOAL initially compresses after pressure is applied likely because of GO flake rearrangement. For example, 0-GOAL have an initial permeability 3 – 4-fold greater than the steady-state permeability.

A clear decrease in GOAL permeability is also observed upon GO chemical reduction (Fig. 5.1b). For example, a 6 – 7-fold reduction in permeability is observed for HI-GOAL (0.54 LMH-bar) compared to 0-GOAL (3.77 LMH-bar) even though there is only a 50% reduction in 2h. Increasing the UV irradiation time also leads to a decrease in GOAL permeability [2.11 and 1.29 LMH-bar for 15-GOAL (2h = 7.2 Å) and 360-GOAL (2h = 6.8Å), respectively]. In summary, permeability is predominantly related to a decrease in GO interlayer nanochannel spacing (2h), which in turn is related to the extent of GO chemical reduction, and there is little effect from reducing GO length (l) by sonication.

The permeability decrease with reduction indicates that the process does not create macroscopic defects (i.e., holes) in the GOAL structure, which would result in an increased permeability, and instead favors an increase in the extent of interlayer π – π GO interactions and a reduction in nanochannel spacing (2h). Enhanced π – π interaction is confirmed by Raman spectroscopy as the D/G peak intensity ratio (I_D/I_G) decreases with an increase in UV irradiation time, confirming the restoration of the graphitic domains via GOAL reduction (Fig. ??). I_D/I_G is 1.1 for untreated
GO and decreases to 0.95 and 0.90 for GO UV after irradiation in vacuum for 15 and 720 min, respectively. GOAL reduction also increases hydrophobicity, with the static contact angle (SCA) increasing from $55.6 \pm 1.2^\circ$ (0-GOAL) to $77.2 \pm 2.1^\circ$ (HI-GOAL). In particular, the increase in hydrophobicity is exponentially dependent on the extent of GO reduction (Fig. 5.5) according to eqn (5.6)

$$2h = g - d(e^{-fO})$$ (5.6)

A theoretical basis of this trend is confirmed by the fact that eqn (5.6) yields a SCA of $82.1^\circ$ for pristine graphene/graphite ($O = 0\%$), which is corroborated by several experimental and simulation reports. The increase in hydrophobicity may also affect the water transport and thus GOAL permeability. For comparison, sonication increased GOAL permeability by only $0.6 \pm 0.3$-
fold (gray bars, Fig. 5.4b), even though \( l \) decreased by \( \approx 7 \)-fold. The permeability increase is related to the decrease in membrane tortuosity caused by a decrease in the length (\( l \)) of the GO. Considering HI-GOAL, it is of note that a \( 2h \) decrease of 30% (from 7.9 to 5.5 Å) results in an \( \approx 90\% \) decrease in water permeability; in contrast, a decrease of \( \approx 700\% \) in \( l \) (\( \approx 7 \) to \( \approx 1 \) µm) resulted in an increase of only \( \approx 100\% \) in the water permeability, suggesting a 2D transport regime that does not follow Hagen-Poiseuille flow.

The change in permeability (\( \Delta k \)) was divided by the respective change in the dimension for the two scenarios (\( \Delta 2h \) and \( \Delta l \)) to produce \( \Delta k_l \) and \( \Delta k_{2h} \) normalized to the unmodified GOAL, where subscripts indicate the dimension in question. Note that the \( \Delta 2h \) values refer to a dry state whereas the \( \Delta k \) values refer to a hydrated state. It is known that upon immersion in water the GO spacing can increase 20 – 25%\(^\text{[224]}\). However, the GO spacing decreases after the pressure is applied (decrease in permeability in Fig. 11.7); thus, monitoring of \( 2h \) when the membrane is in operation is challenging.

In our recent perspective, we discuss the need of a characterization tool, which can measure the spacing of the GO membrane when in operation.\(^\text{[11]}\) To overcome this challenge, normalized coefficients (i.e., \( \Delta k_{2h} \)) based on relative and not absolute values, were used. This choice is also supported by the fact that both the reduced and non-reduced GOAL swelled to a similar magnitude (20 – 25% increase) upon being hydrated (Fig. 11.10). The \( \Delta k_{2h} \) values range from 2.80 to 6.35, whereas \( \Delta k_l \) values range from 0.02 to 0.1 (Table 11.3 and Table 11.4). The order of magnitude difference between the two ranges highlights that the characteristic dimension dominating permeability is \( 2h \), which is controlled by the GO chemistry, whereas in comparison, \( l \) has a limited effect on permeability.

To gain a deeper understanding of the GOAL water transport mechanism, an LB approach augmented with a novel Langevin-like frictional forcing term between water molecules and the GO nanochannel basal plane oxy-functional groups via H-bonding was employed (Fig. 5.6). The model
5.3. Results and Discussion

geometry and the characteristic water flow path within the GO nanochannel are displayed in Fig. 5.6a.

Of note is the large simulation domain (thousands of square nanometers), which would be computationally costly for simulation tools currently used to evaluate water transport within GO nanochannels (e.g., MD or first-principle calculations). The $D_k$ versus GO nanochannel height variation ($\Delta 2h$) is plotted in Fig. 5.6b. Simulations were performed for four different interlayer spacings of 7.2, 6.7, 6.3, and 6.1 Å and for a flake size equal to the size of the sonicated flake ($\approx 1 \mu m$). From the simulation, $\Delta k_{2h}$ decreases with a decrease in GO interlayer spacing from 5 ($2h = 7.2 \text{ Å}$) to 3 ($2h = 6.1 \text{ Å}$), in agreement with experimental range ($2.80 < \Delta k_{2h} < 6.35$). The simulations support the trend of a decreasing permeability with a decrease in GOAL interlayer spacing. Of note for both experimental and simulation outputs, the smallest variations in the spacing ($< 10\%$) lead to the largest normalized variations in permeability ($> 5$). This spacing variation could also be achieved by unintentional reduction of the GOAL (i.e., prolonged exposure to sunlight) and highlights how GO metastability\cite{119,256} may affect the macroscopic performance of GO-based applications. In summary,

we report on methods for independent fine control of GOAL nanodimensions (length and height of the GOAL nanochannels) and surface chemistry via easy-to-implement techniques such as photoreduction and bath sonication. In particular, the permeability tests highlight that GO interlayer

![Figure 5.6: LB simulations. (a) GOAL geometry setup employed in the simulations and a magnification of the velocity field inside. (b) Normalized permeability vs interlayer spacing change for experimental and simulation outputs. The interlayer spacing change is normalized to the largest spacing value (7.9 Å).](image)
Chapter 5. Graphene Oxide Architectural Laminate

spacing is the predominant dimension dictating GOAL water transport, although hydrophobicity effects may also need to be taken into account.

5.4 Conclusions

The environmental implications of this study center on GO metastability and are two-fold. First, the GO photochemical oxidation state is highly dependent on the surrounding medium and on the time of exposure. For the performance of GOAL in environmental applications to be consistent with time, it is paramount to use a stable GO material with limited redox activity. In other words, the GO should be reduced in a controlled manner before being implemented and utilized in a controlled environment. Second, GO metastability may be exploited to tailor the specific nanoproperties, which will affect the macroscopic GOAL properties. Thus, tuning of GO chemistry and morphology will allow GOAL to be a versatile material utilized for a range of environmental applications.

The results presented here offer fundamental knowledge about simple methods for controlling GO properties and thus the ability to rationally design and construct GOAL membranes. This deep understanding of the effect of GO nanoproperties on membrane performance represents a major challenge for the widespread use of GO in separation processes.
Fully Carbon Membranes

Apart from minor modifications, this chapter originally appeared as:


ABSTRACT

Research effort in membrane technology is divided into two fields depending on the material used: i) ceramic and ii) polymeric membranes. Motivated by the aim to harmonize the two research fields and to create solutions for advanced wastewater treatment, we investigated the possibility to originate a new class of membranes uniting the advantages of polymer and ceramic membranes. In particular, a Fully Carbon Membrane (FCM), constituted by hierarchical elemental carbon structures from the mechanical support to the selective layer, was manufactured. The FCM were characterized by a combination of surface science tools, capillary flow porometry studies, and thermogravimetric analyses, which reveal the ability of the FCM to resist to harsh cleaning by hypochlorite solutions and annealing cycles (typical of ceramic membranes). The FCM permeability and rejection performance were evaluated in a cross-flow setup and confirm the operation of the membrane in the nanofiltration regime (typical of polymeric membranes). In summary, the aspiration here is to initiate a new line of research in hybrid elemental carbon membrane materials that will support technologies for sustainable water resource use through wastewater reclamation.
6.1 INTRODUCTION

According to Hegel’s dialectic process (Entwicklung; development), the progress and the creation of knowledge originates from clashing of opposing sides and is constituted by a triad. First (An-sich; per-se), we discover the definition of a concept, then a second concept is introduced (Anderssein; be different), which abolishes or cancels the first. As a result of this opposition, during the last step of the process (An-und-für-sich; on-and-for-itself) a third new concept is introduced, which is higher and truer compared to the original. Fitzche described this triad in what is most commonly known as the thesis-antithesis-synthesis. The dialectic process can also be observed in the world surrounding us and in the progress of science.

For instance, social media is an interesting example of synthetic evolution. On the one hand, simple social interaction can be described as a sort of physical instinct movement with a specific individual purpose. On the other hand, mass media can be described as the electronic transmission of information invisible to human senses with primary marketing purposes. From the opposition between these two spheres, social media arises in which the interaction has lost the animal and physical-like interaction for a possibly greater and more expansive interaction (i.e., one-on-one versus one-on-many). An evident example in science is the advance in robotics with the creation of androids, generated from the synthesis of humans and machine. Another example found in science is the description of fluid motion. In general, we can describe the behavior of a system from a macro and continuum (Navier-Stokes) perspective; on the other hand, the same system could also be described by a particle-particle (molecular) interaction perspective given extreme computational power. Nowadays, there are available methods that synthesize these two perspectives by treating the system with novel intermediate mesoscale concepts such as Lattice-Boltzmann, which allows a mesoscale description of the system useful at length scale for which the continuum body assumption breaks down, but the dimension of the system is too large to be considered particle-particle
Synthetic advances via the Hegelian process can also be observed in the study of water engineering. For instance, desalination was first widely practiced utilizing thermal processes such as distillation. Today, membrane desalination technology has become predominant in practice separating water from ions through reverse osmosis (RO). The synthesis of thermal and membrane technology has, in turn, sparked a new line of research in membrane distillation, highlighting the importance of the synthetic approach. In the sub-topic of water treatment membranes materials, two opposing research fields can be distinguished: ceramic versus polymeric membranes. On the one hand, ceramic membranes excel in thermal and chemical stability and the simplicity of their cleaning process. On the other hand, polymeric membranes feature thinness, cost-effectiveness, and ease of property manipulation, which allows them to excel in industrial and municipal applications such as ultra-/nano-filtration (UF/NF).

A chemically and thermally resistant membrane resilient to harsh cleaning (typical of ceramic membranes) and able to operate in the nanofiltration regime (dominated by polymer membranes) has potential for advanced wastewater treatment (AWWT) applications. AWWT aims to convert wastewater into water that can be reused, depending on its quality, for other purposes such as urban, agricultural, environmental, and potable uses. Although AWWT varies depending on feed quality and on the standard effluent requirements, membranes processes are generally used to remove ions and organic molecules to meet the strict environmental standards. Nowadays, membrane processes in AWWT are dominated by polyamide polymeric membranes, which are subject to fouling and cleaning issues due to their poor chemical resistance. Membrane fouling leads to increased treatment plant operations and maintenance (O&M) cost due to several reasons such as cleaning chemical cost and increased plant downtime. For instance, a two-fold more expensive chlorine-resistant nanofiltration membrane will lead to savings in the overall plant O&M due to the reduction of chemicals.
use and downtime.\textsuperscript{10} Similarly, other studies estimated that at least 50\% of O&M is dominated by membrane cleaning and replacement.

Previous studies have investigated using a protective layer to enhance the selectivity or the chemical stability of the membranes. For example, GO embedded in RO membranes drastically improved the chlorine resistance due to the prevention of polyamide chlorination.\textsuperscript{29} However, the chemical resistance was limited to the selective layer, as the polymer-based substrate was subject to degradation when oxidizing agents permeate the membranes.\textsuperscript{11,24} Moreover, polymer-based membranes will also limit the membrane operating temperature as well as permeating fluid properties.

Motivated by the aim to develop cost-effective AWWT solutions, we hypothesized that a Fully Carbon Membrane (FCM) operating in the NF regime could be manufactured with the exclusive use of fully carbon nanomaterials with no polymers, \textit{i.e.}, the elemental composition of all materials is $> 75\%$ carbon and the monomer repeating units of a polymer have been replaced with elemental carbon architectures. To our knowledge, this is the first study to manufacture a filtration FCM in all its components: from the mechanical substrate to the selective layer.\textsuperscript{24}

In this study, a FCM was manufactured via a 3D printed custom-made vacuum filtration system with the use of carbon fiber (CF), carbon nanotubes (CNT), and GO. The potential of the FCM for AWWT is focused on two main performance measures: i) the capability of the membranes to reject ions in a cross-flow apparatus (typical in municipal applications) before and after harsh cleaning processes; and ii) the chemical and thermal resistance of the membranes challenged by permeation of oxidizing agents and annealing cycles. The FCMs were characterized via a combination of surface characterization tools (scanning electron microscopy and X-ray photoelectron spectroscopy), capillary flow porometry, thermogravimetric analysis, and ion rejection evaluation.
6.2 Methods

6.2.1 Chemicals and Materials

The Spectr carb 2050-1050 GDL CF paper was purchased from Engineering Fiber Technology. C-grade multiwalled nanotubes (CNTs) with > 95% purity were purchased from NanoTechLabs (Yadkinville, NC). Graphene oxide (GO) aqueous solutions (≈ 4 mg/mL) were purchased from Graphenea (Cambridge, MA). Sodium sulfate (NaSO₄, ≈ 99%), sodium chloride (NaCl, ≈ 97%), and sodium hydroxide (NaOH, ≈ 97%) were purchased from Sigma-Aldrich, sodium hypochlorite (NaClO, 8%) and isopropyl alcohol (IPA, 99%) were purchased from VWR chemicals, and 5 wt% Nafion solution was purchased from Fuel Cell Earth (Woburn, MA).

6.2.2 Fully Carbon Membrane Fabrication

A flowchart in Fig. [2.1] in the Appendix D summarizes the overall fabrication process. First, a CNT solution was prepared by mixing 30 mg of CNT with 60 mL of IPA and 0.2 mL of Nafion solution (5 wt%), then dispersed by probe-sonication (Sonifier S-450D with high gain horn; Branson Ultrasonics Corp.) at 50% of the maximum amplitude (100 W) for 3 min, and subsequently, bath sonicated for 4 min in a Branson sonicator (V = 1.9 L, maximal power = 80 W, and f = 20 kHz).

The obtained CNT solution was vacuum filtered onto a CF paper (1st layer, substrate of the FCM) using a custom 3D printed filtration system (see Fig. [2.2] in the Appendix D). Another solution containing GO and CNT was prepared in the same manner as the first CNT solution but also included 0.15 mL of GO solution (≈ 4 mg/mL) added prior to the bath sonication step. This GO-CNT solution was then vacuum filtrated onto the CF-CNT composite substrate, constituting a transition layer between the intermediate CNT support layer (2nd layer) and the final GO selective layer (3rd layer). Then, a 0.2 mL GO solution (≈ 4 mg/mL) was diluted with 80 mL of DI water and bath sonicated for 1 min. The final GO solution was then filtered onto the GO-CNT transition layer,
Chapter 6. Fully Carbon Membranes

constituting the selective layer of the FCM. Finally, the FCM was thermally reduced at 150 °C for 20 min in an inert atmosphere (i.e., N\(_2\)) with the use of a Thermolyne 21100 tube furnace, in order to increase membrane stability. Once the FCM was prepared, it was cut with a razor blade in a rectangular shape (8 x 4 cm\(^2\)) and placed into the filtration device for testing. FCM were initially tested for integrity by permeating through DI at 5 bar of applied pressure and only those passing the test (i.e., permeability < 30 LMH-bar (i.e., L m\(^{-2}\) h\(^{-1}\) bar\(^{-1}\)) indicating overall structural integrity) were used in subsequent experiments.

6.2.3 Fully Carbon Membrane Characterization

**Scanning electron microscopy (SEM):** The morphology and structure of the FCMs were characterized using a Zeiss ULTRA Field Emission Scanning Electron Microscope with an In-lens secondary electron detector. The working distance was 3 – 4 mm, and the acceleration voltage was 5 kV. The statistical SEM image analysis of the FCM layers was completed using ImageJ software.

**X-Ray photoelectron spectroscopy (XPS):** FCM surface chemistry was analyzed by a Thermo Scientific K-Alpha XPS instrument (ESCA) with X-rays generated by a 12 kV electron beam with a spot size of 400 \(\mu\)m. The O/C ratio and peak deconvolution were quantified by Thermo Scientific Avantage software, and then converted to mass ratio by using C and O atomic weights. The XPS instrumental error for atomic composition is ±1%, and the accuracy of the C1s peak fitting is ±2%.

**Thermogravimetric analysis (TGA):** The FCM thermal stability was evaluated with a Discovery TGA. The samples were cut into 5 x 5 mm\(^2\) pieces for a total weight of \(\approx\) 5 mg. The target temperature was set to 500 °C with a 10 °C/min heating rate under air flow (25 mL/min). The mass change over time was monitored and quantified with Trios software.
6.2. Methods

6.2.4 Permeability and Rejection Test

The FCMs were tested using a multi-cell cross-flow apparatus (see Fig. 12.3 in the Appendix D). The cross-flow apparatus allows the simultaneous evaluation of nine membranes at a pressure ranging from 4 to 10 bar. The effective filtration area for each membrane is 7 x 3 cm$^2$. The pure water permeability, expressed in LMH-bar, was evaluated by monitoring the permeate volume with a Sartorius laboratory balance every 30 or 60 min. The permeate was collected in vials and the conductivity rejection ($R$) was calculated with eqn (6.1):

$$R = \left(1 - \frac{C_p}{C_f}\right) \times 100$$ (6.1)

where $C_p$ and $C_f$ are the conductivity of the permeate and the feed, respectively. The conductivity rejection tests were carried out with a 1 mM NaCl and 1 mM NaSO$_4$ aqueous solution. The conductivity rejection was determined with a ThermoFisher Scientific conductivity probe. The individual ion rejection ($R_{ion}$) was calculated with equation similar to eqn (6.1):

$$R_{ion} = \left(1 - \frac{C_{ion,p}}{C_{ion,f}}\right) \times 100$$ (6.2)

where $C_{ion,p}$ and $C_{ion,f}$ are the specific ion concentration of the permeate and the feed, respectively. The anion (Cl$^{-}$ and SO$_4^{2-}$) concentrations were measured with a Dionex ICS-3000 Ion Chromatograph (Dionex Corporation, Sunnyvale, CA) consisting of a SP single pump, DC detector, AS40 autosampler, and a Chromeleon 6.8 software. Cl$^{-}$ and SO$_4^{2-}$ were separated from other anions using a Dionex IonPac AS25 analytical column (4.0 x 250 mm$^2$) and a Dionex IonPac AS25 guard column (4.0 x 50 mm$^2$) with anion self-regenerating suppressor (ERS 500) in recycle mode. Mobile phase (21 mM NaOH) was prepared using a 50% (w/w) sodium hydroxide aqueous solution and deionized water (18.2 MΩ-cm). The isocratic eluent flow rate was 1 mL/min for 6 min with an
injection volume of 50 µL and a column temperature of 30 °C. Quantification of individual ions was done using a five-point linear calibration curve over the range of 5 – 100 mg/L. All samples were diluted before injection and blanks were included in each run. Standard additions were used to confirm the retention time of each anion. Theoretical ion rejection can also be calculated using eqn (6.3):

$$R_{ion} = \left(1 - 2 \left(1 - \frac{d_{ion}}{d_{pore}}\right)^2 + \left(1 - \frac{d_{ion}}{d_{pore}}\right)^4\right) \times 100$$

(6.3)

where $d_{ion}$ and $d_{pore}$ are the diameter of the hydrated ions and of the membrane pores, respectively. The wet flow curves of the membranes were calculated by the capillary flow porometry (CFP) method using a gas-liquid displacement Porometer ($POROLUX^TM$ 100, Porometer). CFP is based on the displacement of a wetting liquid inside a porous network by means of an inert gas flow. In this study, POREFIL® (Porometer, surface tension $\gamma = 16$ dyne/cm) was used as the wetting liquid agent, compressed air was used as the inert gas, and the pressure scan method was applied within a pressure range of 0 – 5.5 bar at room temperature ($\approx 23 ^\circ C$). The membranes were first wetted by the POREFIL® and the gas permeation flow was measured by increasing the transmembrane pressure at a rate of 0.0125 bar/s to obtain the wet curve. The diameter of all the samples was 18.5 mm. At least three different samples for each membrane were evaluated to obtain the final reported wet flow curve.

### 6.2.5 Fully Carbon Membrane Stability

The chemical stability of the FCM was evaluated by comparing the membrane performance (rejection and permeability) before and after 9 hr of NaClO filtration at 1000 ppm and 5 bar of applied pressure. Moreover, the surface chemistry of the FCM exposed to chlorination was compared to that of the control ones (exposed to DI). In terms of thermal stability, the surface chemistry of membranes exposed to multiple annealing cycles (up to four) at 150 °C in air was compared to the
6.3. Results and discussion

chemistry of membranes exposed to a single annealing cycle to evaluate any thermal modifications of the surface. Moreover, TGA analysis were also performed here to observe the loss in mass of FCMs exposed to annealing cycles in air.

### 6.3 Results and Discussion

#### 6.3.1 Fully Carbon Membrane Characterization

A FCM is characterized by a hierarchical structure composed of three layers: a CF layer, a CNT layer, and a GO layer as displayed in Fig. 6.1. More details about these three layers can also be found in the SEM images displayed in Fig. 12.4. The quantitative morphology dimensions of these carbon nanostructures, summarized in Table 6.1, were determined via statistical analysis (see Fig. 12.5 for more detail) of the SEM images in Fig. 12.4 in the Appendix D.

The first layer is a commercially available carbon paper, which is a porous (41 ± 5 µm superficial pore size) composed of "graphitized" resin bonded CF. The fibers are circa 6.8 ± 0.5 µm in diameter. The CF paper layer has a low compressibility and is highly permeable (800 LMH-bar) and constitutes the mechanical substrate of the FCM. The second layer is composed of an intercalated multi-walled CNT network with a thickness of ≈ 10 µm. Individual CNT have an average length of 100 µm (manufacturer data) and an average diameter of 16.5 ± 1.3 nm (experimental data), which agrees with the reported value from the manufacturer (15 nm). The CNT layer creates a permeable network (25 LMH-bar) with an average superficial pore size of ≈ 200 nm onto which a GO solution can be vacuum filtered. The GO solution is composed of single-atom-thick GO sheets with an average flake size of 10 µm². The micrometer-sized GO flakes are stacked on top of each other creating a 200 – 300 nm selective layer comparable in thickness to the polyamide layer used in thin-film composite (TFC) membranes. Apart from the increased energy efficiency dictated by the 100s nm-thickness and thus lesser required driving pressure, the possibility of producing exceptionally
Figure 6.1: FCMs advantages and hierarchical structure. (a) Advantages of FCMs derived from the Hegelian approach. (b) Schematic of the hierarchical structure of a FCM composed of three layers (GO, CNT and CF). (c) SEM images of a FCM: top image is a cross-section of a FCM, middle image is a zoom-in of the cross-section (the extension of the CNT and GO layers are indicated with arrows) and bottom image is an aerial view of the FCM in which the three carbon architectures (CF, CNT, and GO) are visible.


6.3. Results and discussion

Table 6.1: Specifications of the FCM hierarchical structure.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material (SEM)</th>
<th>Dimension (SEM)</th>
<th>Elemental composition (XPS)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st CF (CF)</td>
<td>CF Diameter: 6.8 ± 0.5 µm</td>
<td></td>
<td>C: 95.1 ± 1.0 %</td>
</tr>
<tr>
<td></td>
<td>Thickness: 160 ± 10 µm</td>
<td></td>
<td>O: 4.5 ± 1.0 %</td>
</tr>
<tr>
<td></td>
<td>Pore Size: 41 ± 5 µm*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2nd CNT (CNT)-Nafion (includes intermediate CNT-GO)</td>
<td>CNT Diameter: 16.5 ± 1.3 nm</td>
<td></td>
<td>C: 78 ± 1.0 %</td>
</tr>
<tr>
<td></td>
<td>Thickness: ≈ 10 µm</td>
<td></td>
<td>F: 19.1 ± 1.0 %</td>
</tr>
<tr>
<td></td>
<td>Pore Size: 208 ± 60 nm*</td>
<td></td>
<td>O: 3.1 ± 1.0%</td>
</tr>
<tr>
<td></td>
<td>CNT length: 100 µm</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3rd GO (GO)</td>
<td>Thickness: 200 – 300 nm</td>
<td></td>
<td>C: 70 ± 1.0%, O: 30 ± 1.0 %</td>
</tr>
<tr>
<td></td>
<td>GO flake thickness: ≈ 1.5 nm</td>
<td></td>
<td>(before reduction)</td>
</tr>
<tr>
<td></td>
<td>Pore Size: dense layer</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>GO flake area: ≈ 10µm²</td>
<td></td>
<td>C: 82.1 ± 1.0%, O: 18.9 ± 1.0%</td>
</tr>
<tr>
<td></td>
<td>(after reduction)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Superficial pore size measured at the feed side of the membrane.

thin selective layers, which conserve the underlying morphology (see Fig. 12.4), is fundamental in regard to membranes whose performance is enhanced by the underlying microstructure. The elemental composition of the FCM is dominated by carbon (> 75% atomic C). The CF layer contains the least amount of oxygen due to the graphitization of the fibers during the fabrication process. The CNT layer contains 19% fluorine (F) due to the addition of Nafion to increase CNT dispersion in IPA. The oxygen content of the GO layer significantly decreases from 30 to 18% after the thermal annealing and subsequent chemical reduction of the oxy-functionalities.

6.3.2 Fully Carbon Membrane Permeability and Rejection

FCM permeability was evaluated in a cross-flow apparatus (see Methods) at pressures ranging from 4 to 10 bar. Application of pressures greater than 10 bar damaged the membranes by creating holes or fractures in the selective layer (see Fig. 12.6 in the Appendix D for an example of mechanically-damaged FCM), producing a significant increase in membranes permeability. Similar to polymeric membranes, the FCM experienced compaction and permeability reduction under applied pressure likely caused by the pressure-induced changes in the FCM selective layer microstructure. The cir-
cles in Fig. 6.2 display the reduction in normalized permeability (to the initial value) over time under 5 bar of applied pressure for two FCM (green and blue). The compression/compaction stage required more than 30 hours to achieve steady-state permeability, which was about 10-15% of the initial permeability. Chong et al. recently reported similar behavior for GO membranes with a reduction of nearly 80% of the initial flux due to the compression of GO laminate interlayer spacing. Although the magnitude of the FCM permeability reduction is in agreement with the previous study, more time (approximately more than one day versus 5 hours) was needed here to reach steady-state permeation. The longer time is likely connected to the presence of void cavities in the FCM structural hierarchy (CF&CNT) as compared to previous studies in which a GO layer was cast on top of a denser polymeric substrate. Alternatively, the longer compaction time may be connected to the filtration mode of operation as Chong et al. utilized a 6 bar dead-end filtration in comparison to the 5 bar cross-flow filtration used here.

![Figure 6.2](image.png)

**Figure 6.2: FCM filtration "representative" measurements. Permeability (circles) and conductivity rejection (triangles) performance over time at 5 bar of applied pressure.** Colors represent different membranes tested (Membrane I in blue and Membrane II in green). The change over time is influenced by the compaction of the FCM hierarchical structure.

The steady-state permeability of the FCM was 1.3 ± 0.6 LMH-bar, which is in accordance with
a previous study and is in the nanofiltration regime. The triangles in Fig. 6.2 represent the normalized conductivity rejection (R) of a solution containing monovalent (Na\(^+\), Cl\(^-\)) and polyvalent ions (SO\(_4^{2-}\)). As expected the conductivity rejection follows an inverse trend compared to the permeability with rejection increasing during GO selective layer compaction from \(< 10\%\) to \(\approx 85\%\).

The specific ion rejection (\(R_{\text{ion}}\)) was then evaluated via ion chromatography of the feed and permeate (see Methods). The membranes display a moderate selectivity (36 \(\pm\) 5\%) for monovalent anions such as Cl\(^-\). This is in agreement with other studies that highlighted the inefficacy of GO membranes to sieve monovalent ions. However, we observe a greater selectivity (86 \(\pm\) 4\%) for polyvalent ions such as sulfate. The diameter of the membrane pores (\(d_{\text{pore}}\)) can be estimated using eqn (6.3).

For example, using the rejection values obtained for Cl\(^-\) and SO\(_4^{2-}\) (\(\approx 36\%\) and \(\approx 86\%\)) and their corresponding hydrated diameters (0.66 and 0.76 nm), an average \(d_{\text{pore}}\) of 1.83 and 1.05 nm, respectively, was estimated for the membranes. The discrepancy in the pore size dimension here is related to charge repulsion effects connected to the divalency of the sulfate anion, which increases rejection leading to smaller "effective" pore sizes estimated by eqn (6.3). For GO membranes, the physical pore size or "diameter" is related to the interlayer distance (2\(d\)) between GO flakes, which can be estimated from X-ray diffraction experiments. Previous X-ray diffraction studies indicate a 2\(d\) value around 0.8 nm for a dry GO membrane. Under aqueous operation, the membrane will be hydrated and the GO laminate will undergo swelling characterized by a factor around 2, thus leading to a hydrated GO interlayer distance (2\(d\)) between 1.5 and 2 nm. This value range is in agreement with the \(d_{\text{pore}}\) value estimated using chlorine rejection (i.e., 1.83 nm) and is also consistent with the results obtained in previous reports.

### 6.3.3 Fully Carbon Membrane Chemical Stability

The FCM chemical stability was initially evaluated using the common oxidant sodium hypochlorite (NaClO). Anions (Cl\(^-\), SO\(_4^{2-}\)) rejection before and after filtering 1000 ppm NaClO through the FCM
for 9 hours at 5 bar is displayed in Fig. 6.3a. Chlorination did not have a significant effect on FCM anion rejection highlighting the FCM chemical resistance to oxidizing agents. The slight increase in observed FCM anion rejection suggests a decrease of the GO interlayer spacing as a result of NaClO addition, which increases the feed pH to 10 and reduces the ionic GO interlayer screening effect resulting in narrower GO channels/pore size. This increase in anion rejection is also supported by the results obtained from CFP measurements, as shown in Fig. 6.3b. The chlorination process decreases the membranes wet flow by a factor of 5 at approximately 4 bar. The decrease and the absolute value of flow rate here cannot be directly compared to the valued obtained with the saline solutions as the CFP analysis is carried out with a lower surface tension wetting liquid (POREFIL®, 16 dyne/cm) compared to that of water (72 dyne/cm). Moreover, the driving force behind the CFP is capillary, which is different as compared to the pressurized aqueous flow used in the cross-flow setup. In summary, the analyses completed here exemplify the FCM chemical stability and their resilience to oxidizing cleaning solutions since the extended application of concentrated NaClO did not have a significant effect on the FCM permeability and rejection. To further evaluate the FCM stability to oxidants, their surface chemistry was characterized via XPS as displayed in Fig. 6.3c. The untreated and chlorinated FCM are characterized by an XPS O/C ratio of 0.38 and 0.43, respectively, revealing minor surface oxidation post-chlorination. Even though the membranes were rinsed with copious DI water post-chlorination, the chlorinated FCM XPS is influenced by the presence of surface-associated ions, e.g. 2% Na in FCM atomic composition. The slightly increased O/C content of the chlorinated FCM can also be observed in the deconvolution of the C1s high resolution spectra, which is characterized by three peaks corresponding to: (i) single (C-C) and double (C=C) carbon bonds centered at 285 eV; (ii) epoxide (C-O-C) and hydroxide (C-OH) functional groups centered at 287 eV; and (iii) carboxylate (O=C-OH) functional groups centered at 289 eV. In particular, FCM chlorination results in a 4-5% increase in the epoxide concentration, followed
Figure 6.3: FCM chemical stability. (a) Normalized ions rejection before (light grey) and after (dark grey) chlorination. (b) CFP analysis of FCM after DI filtration (in green) and NaClO filtration (in blue). The figure includes photos of the FCMs used in the analysis. (c) C1s deconvolution spectra of the FCM before (top) and after (bottom) chlorination.
by the same magnitude decrease of the carbon sp$^2$ signal centered at 285 eV. Thermal annealing in an inert atmosphere would reduce the formed epoxides back to olefins returning the membranes to their original state. FCM chemical stability was also challenged with common organic solvents such as acetone. The immersion of polyamide TFC membranes in acetone quickly and permanently degrades the membrane with the selective and ultrafiltration layers crumpling and detaching from the substrate. In stark contrast, the FCM are resistant to organic solvent degradation. The FCM organic solvent stability can be also verified by examining SEM images presented in Fig. 12.7 which reveals similar morphology (i.e., no visible damage) for FCM immersed in acetone compared to that of FCM immersed in water. For example, after acetone immersion, the GO and CNT layers still homogeneously cover the underlying CF paper, preserving its morphology as single carbon fibers are still recognizable. Stability to organic solvents may open new avenues for membrane cleaning e.g. a CNT electrochemical filter poisoned with an insulating polymer coating could be regenerated using an organic solvent. Moreover, organic solvent resistance opens the FCM to a range of separation applications such as those in the petrochemical, food processing, and pharmaceutical industries, which commonly involve the use of aggressive aprotic solvents (e.g., acetone).

6.3.4 Fully Carbon Membrane Thermal Stability

FCM thermal stability was initially evaluated during the fabrication process where the FCMs were reduced at 150 °C in a N2 atmosphere. No physical damage was observed to either the selective layer or the underlying substrate after this thermal annealing. The results of previous studies highlight the thermal stability of CNT and CF paper up to 300 – 400 °C in air and once reduced, GO tends to be stable under similar thermal conditions. More intense GO thermal treatment (e.g., T> 350 °C) will lead to thermolysis of oxygen functionalities and possibly defect formation in the parent sp$^2$ graphene sheet. To corroborate the FCM thermal stability, the membranes were subjected to four sequential thermal annealing cycles of 15 min at 150 °C in an oxidizing environment.
(i.e., ambient air). Afterwards, the XPS C1s peak profiles of the FCM (see Fig. 6.4 and Table 12.1 in the Appendix D) were used to evaluate the effect of the annealing cycles on the FCM surface chemistry. The sp² peak (C=C; C=C) is constant at ≈ 65% before and after every annealing cycle highlighting the FCM thermal stability. A TGA (Fig. 12.8 in the Appendix D) indicates that the FCM is stable until 350 °C with less than 0.1% loss in mass; at this temperature, the Δm/ΔT begins to increase signaling the onset of FCM thermal decomposition. For comparison, a traditional polyamide TFC is observed to lose 70% of its mass by 500 °C, whereas the loss is < 1% for an FCM. The FCM thermal stability can be utilized for membrane regeneration similar to ceramic membranes, in which the regeneration temperature (> 200 °C) depends on the adsorbed/deposited species. The superior FCM thermal stability compared to traditional polymeric membranes will increase potential for a broader range of industrial applications such as the treatment of cooling/boiler water in thermoelectric generation plants or oil/water separations in petroleum processing plants.

6.3.5 Non-linear and Reversible Permeability Pressure-dependence

Here, the FCM pressure-dependent permeability post-compaction was investigated as displayed in Fig. 6.5. Of note is that when the applied pressure is increased from 4.5 to 7.5 bar (1.67-fold) the normalized permeability (in red) increases from 0.4 to 0.9 (2.25-fold) (see Fig. 6.1), which is at odds with Darcy’s Law that predicts a pressure-independent permeability. This behavior has been previously reported both experimentally and through molecular dynamic simulations for carbon nanostructures and it differs from polymeric membranes behavior, where the pressure-normalized flux (i.e., LMH-bar) is invariant of the applied pressure. The increase in permeability with increasing pressure is corroborated by a concomitant decrease in ion rejection of around 1.6-fold (in green). The decrease in the rejection at higher pressures may be related to the energy barrier required to dehydrate ions since similar barrier is also present in the disruption of the hydrogen bond network for water entering in the GO nanochannels from the bulk. However, the latter energy is significantly
lower than the necessary dehydration of ions (≈ 6 kJ/mol versus 102-103 kJ/mol); in other words, the low pressure increase (≈ 3 bar) provides enough energy to break the hydrogen bonding network, but is not sufficient for the dehydration of the ions. Thus, pressure-induced ion dehydration is likely not active here. Thus at first glance, the decrease in the rejection could also be attributed to pressure-induced membrane damage. However, once the pressure is reduced back to 4.5 bar the FCM permeability and rejection reversibly return to their original state and this phenomenon was reproduced with a number of FCM samples. The reversibility of FCM performance with pressure could be a noteworthy addition to the recent developments in the field of active membranes. In particular, there is a continuous effort to develop smart membranes that are active and/or reactive in

\[ \text{Figure 6.4: FCM thermal stability. C1s deconvolution spectra of the FCM subjected to four annealing cycles of 15 min at 150 °C in an oxidizing environment (i.e, ambient air).} \]
response to external stimuli. A recent study demonstrated that GO membrane performance can be altered by an externally applied unidirectional force. GO studies have also used other externally applied stimuli such as voltage, which ionizes water molecules inside the GO channel leading to a blockage of water transport. Similarly, studies have attempted to modify the structure of the GO nanochannel by altering the pH of the feed, inducing pH-dependent membrane performance phenomena. Thus, the ability of the GO nanostructure to adapt to multiple external stimuli makes it an ideal candidate for the fabrication of structurally-active membranes with reversible behavior.

![Figure 6.5: FCM reversible behavior](image)

**Figure 6.5: FCM reversible behavior.** Permeability (in red) and rejection (in green) performance of a FCM over time under different pressures applied. The dashed line indicates the times when the pressure was changed.

### 6.4 Conclusions

This investigation highlights the possibility of creating a new class of fully carbon membranes that possess the combined advantages of typically disparate polymeric and ceramic membranes, thus completing the Hegelian triad. The unique FCM characteristics are a result of the layer-by-layer nano-manipulation of the elemental carbon architectures embedded in its hierarchical structure. The FCM operates in the nanofiltration regime similar to polymeric and, concurrently display the chem-
Chapter 6. Fully Carbon Membranes

ical and thermal stability typical of ceramic membranes. Specifically, FCM have a nanoscale pore size (< 2 nm), which effectively reject polyvalent ions, and are also resistant to chlorine oxidants, high pH, organic solvents, and elevated temperatures (> 150 °C). The investigation also displayed the ability to use externally applied pressure as a potential stimulus to control performance in situ, highlighting the structurally-active and reversible behavior of the FCM. Through the development of an FCM we are hoping to spark a new direction of research in membrane materials displaying polymer-ceramic hybrid properties, cultivating new material ideas, promoting membrane progress, supporting continued AWWT efforts, and thus ultimately contributing to the increase of global water resources.
7.1 **Introduction**

In the last chapters, I discussed the environmental applications of GO. If a killer application of GO is to be found in the future, we might expect a significant ramp-up of production. In turn, this could lead to an increase in the amount of GO released into the environment, raising the concern of potential toxicological impacts and risks associated with GO exposure.Researchers should begin to assess GO toxicity in order to limit risks connected to human exposure. This line of research falls under recent EPA efforts to address the toxicity and the presence in the environment of contaminants of emerging concerns, including nanomaterials (NMs), which are also regulated by the Toxic Substances Control Act (TSCA). The EPA defines carbon NMs to be stable, have limited reactivity, composed entirely of carbon, and be strong antioxidants. GO cannot be included in this category due to its oxy-functionality and its metastability and might require an additional category.

7.2 **Graphene Oxide Toxicity**

There are two main mechanisms of GO-induced toxicity and cell damage (Fig. 7.1). The first one relies on the physical interactions between the 2-D GO morphology and the cell membrane. In this mechanism, the sharp edges of GO can cut, penetrate, and disrupt the cell membrane. The second mechanism is oxidative stress that can increase the generation of intracellular reactive oxygen...
species (ROS) and charge transfer. This process can cause lipid peroxidation and DNA damage, thereby disrupting cell membranes, inhibiting important metabolic functions of macromolecules, and leading to toxic effects in the cells.\textsuperscript{109}

Both mechanistic explanations (\textit{i.e.}, physical damage and oxidative stress) were reported to have bactericidal effects. For example, it has been proposed that a higher defect surface density in small GO flakes as compared to large flakes will induce oxidative stress and reduce bacterial adhesion. Other studies noted that damage of the model bacterium (\textit{E. coli}) by GO requires nanosheets penetration of the cell membrane, suggesting that a vertically aligned GO structure can lead to a greater antibacterial effect.\textsuperscript{151} The importance of the structure and morphology was also corroborated by another finding showing that the bactericidal activity was dependent on the morphology and the size of the GO flakes being similar to those of the bacteria.\textsuperscript{11} The range of possible interactions depends on the environment and the medium in which GO is immersed, highlighting once again the importance of the presence of surface functionality.\textsuperscript{109} The toxicity mechanisms might be largely distinct when applied to different cell lines in vitro, especially for eukaryotic cells that are more relevant to humans. Recently, carbon radicals were found to be the dominant surface functionality that induces cytotoxicity in lung cells.\textsuperscript{109} Other investigations reported that GO exposure can lead
to lung cell apoptosis and granuloma formation only at high concentrations. The compatibility of GO with different oxidation states was studied in vivo, demonstrating that a reduced GO leads to rapid immune cell infiltration, uptake, and clearance from the injection site. Since GO toxicity seems to be a function of GO purity, size, surface charge, functionalization and aggregation state, one could imagine mitigating GO toxicity by controlling its chemo-morphological properties. However, knowledge of GO fate and interaction in the human body is still limited and more investigations are needed to fully understand the mechanisms of toxicity.

7.3 Proposed Experiments

Human exposure to GO and nanomaterials, in general, can occur in several ways (e.g., ingestion, inhalation, injection, and dermal exposure) depending on the GO source and activities of the person. Since this thesis focuses on GO for water treatment applications, we identify ingestion as the main exposure mechanism.

As specified multiple times throughout this dissertation, GO is a metastable material, with a high potential for chemical interactions upon immersion in biological fluids. These interactions can induce phase transformation and dramatically modify GO chemo-morphological properties. In this sense, the relevant biological response and toxicity are not the ones of the original material, but rather, of its transformed configurations. Transformations can also occur in the human body, which interacts with the nanomaterial and its intermediate states that arise during the transformation process.

To study the gastrointestinal fate of GO, we proposed an experiment in which GO is passed through a three-stage gastrointestinal tract (GIT) simulator that includes the mouth, stomach, and small intestine (see Fig. 7.2). The design assumes ingestion as the main exposure mechanism and is based on the GIT simulator developed earlier by Deloid et al.

The initial GO concentration was 0.50 mg/mL. After digestion, the samples were diluted in
serum-free DMEM cell culture medium so that the final concentration of the digested GO reached 10 µg/mL. One hundred (100) µL of the diluted digest was used to expose a near confluent cell monolayer. The GO concentration was calculated from the mass of GO released if a GO-based membrane would break. Nanotoxicity was evaluated by exposing digested GO to human cells and evaluating cell viability, using Invitrogen™’s PrestoBlue™ cell viability assay. The resazurin dye in the PrestobeBlue™ reagent is cell permeable. Once inside cells, it can be irreversibly reduced to the fluorescent resorufin. Since redox reactions are an indication of cell proliferation and cell viability, this dye can be used as an indicator of nanomaterial toxicity. Per manufacturer’s guidelines, 24 hours after exposure, the diluted digest was carefully aspirated and the cells were washed with 100µL of PBS. Then, fresh Dulbecco’s Modified Eagle Medium (DMEM) with 10% PrestoBlue™ reagent was added to the cells. The well plate was incubated at 37°C for 1 hour, and the fluorescence of the cells was measured at 560/590 nm (excitation/emission wavelengths). Any potential interference of GO with the assay were also measured. Cells were also exposed to a digest of phosphate buffer to measure the impact on viability due to the native composition of the digest. Ten (10) wells were allocated to each exposure condition. The statistical significance was set at $p = 0.05$ and was tested.
using an unpaired, parametric, two-tailed t-test.

Concurrently, the morphology and the chemistry of digested GO were characterized with surface science techniques in order to highlight possible transformations from the original (i.e., not digested) material.

7.4 Preliminary Results and Future Investigations

The chemical transformation of the digested GO is displayed in the C1s XPS spectra (Fig. 7.3a). The GO before digestion is characterized by O/C ≈ 0.5 with oxygen functionalities (epoxide, hydroxide, and carboxylate groups) previously observed throughout this thesis. On the other hand, we notice a strong reduction of the digested GO with a 50% decrease in the O/C. The reduction process is also confirmed by the change in the oxygen functionality with an increase of the sp² bonding (C-C and C=C) centered at 295 eV and a decrease of the single C-O bond (O-C-O and C-OH) centered at 297 eV. The reduction process could be connected to reducing agents present in the GIT. In particular, citrates and bases (NaOH) have been previously reported to reduce GO oxygen content. (reference deoxygenation, Facile synthesis of well dispersed ). We also notice the presence of ≈ 3% nitrogen, which could be the residue of adsorbed proteins and urea acid used to simulate the GIT. Fig. 7.3b shows the GO size distribution obtained by SEM before and after digestion and we did not observe a significant change in size.

Fig. 7.4 shows the viability of human epithelial colorectal adenocarcinoma (Caco-2) cells, previously seeded in 96-well plate. From Figure 4 we can observe that there is not a significant effect of the GO (digested or not) on cell toxicity. Cell viability is close to 100% and similar to the control (CM or blank digest). Thus, GO at that concentration does not represent a meaningful biological concern.
Figure 7.3: Characterization of pristine and digested GO. (a) XPS C1s spectra and size distribution analysis by SEM.

These preliminary results form the foundation for a more robust study that will include: i) size distribution of the digested GO through laser diffraction in order to highlight possible agglomeration of the material in the GIT; ii) different combinations of GO chemistry and morphology in order to evaluate the effect of GO nanoproperties on toxicity; iii) conducting the nanotoxicity study on a co-culture model of the human gut epithelium (Caco-2 + HT29 cells) to more accurately mimic the intestinal environment.

Further assays, including the production of ROS and cellular integrity, will also be considered.
Figure 7.4: Cell viability exposed to different media.
Conclusions

GO’s metastability is a clear hurdle for researchers who want to reach a common vision of this nanomaterial. The plethora of GO configurations prevents researchers from reaching an agreement on underlying basic principles in the field, thus creating bottlenecks that prevent further progress.

This dissertation attempts to build a solid foundation in the field to address and resolve some of the debates that have arisen in the last five years. In particular, this work offers:

• A standardization of GO offering high-throughput characterization techniques and clustering algorithms that are able to identify six classes of GO based on its properties. The experimental work shows that applications based on GO from the same class tend to have the same macroscopic performance. The GO classification scheme aims to support researchers by enabling a fair comparison among scientific investigations.

• The resolution of water transport in GO through novel Lattice-Boltzmann simulations, which highlight the friction-like water transport inside GO nanochannels. The simulations are supported by experimental results that identify separation distance between neighboring flakes as the dominant property dictating water transport inside GO.

• Evidence of the ability to fine-tune GO properties by creating GO nanoarchitectures: i) graphene oxide nanoscrolls (GONS) whose dimensions can be regulated via ultrasound power; ii) graphene oxide architectural laminate (GOAL) membrane whose water transport can be
controlled by chemically modifying the GO surface functionality; iii) fully carbon membrane (FCM) showing the potential of GO in nanofiltration applications for water reclamation processes.

For future investigations, we establish a line of research aimed to elucidate GO nanotoxicity through ingestion exposure. This methodology can be extended to other nanomaterials and represents a call to action for other research groups to monitor the toxicity of a nanomaterial concurrently with its development.
Appendix A

Apart from minor modifications, this chapter originally appeared as supplementary information for:

“Graphene oxide standardization and classification: Methods to support the leap from lab to industry”. Carlo A. Amadei, Paula Arribas, and Chad D. Vecitis, Carbon, 2018, 133, 39-409.

Table 9.1 summarizes the results of the XPS analysis. Note that O/C atomic ratio in Figure 1 in the manuscript is obtained by calculating the average for each of the samples. Some of the samples contained Sulphur, which might be a residual of the oxidation process. The nitrogen can be connected to atmospheric adsorption.

Fig. 9.1 left represents an SEM image of GO flakes cast on silica. Fig. 9.1 right represents the same image analyzed by ImageJ in order to determine the size distribution of the GO flake.
Table 9.1: XPS percentage peak area data for the six samples. The standard deviation for the atomic ratio of each element is ±1%.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Test</th>
<th>C1s (%)</th>
<th>Atomic Percentage (%)</th>
</tr>
</thead>
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<tr>
<td></td>
<td></td>
<td>C-OH</td>
<td>C-C</td>
</tr>
<tr>
<td>1</td>
<td>a</td>
<td>24.36</td>
<td>70.29</td>
</tr>
<tr>
<td>1</td>
<td>b</td>
<td>23.39</td>
<td>71.83</td>
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<tr>
<td>2</td>
<td>a</td>
<td>53.33</td>
<td>46.67</td>
</tr>
<tr>
<td>2</td>
<td>b</td>
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<td>47.67</td>
</tr>
<tr>
<td>2</td>
<td>c</td>
<td>53.44</td>
<td>46.56</td>
</tr>
<tr>
<td>3</td>
<td>a</td>
<td>56.49</td>
<td>40.69</td>
</tr>
<tr>
<td>3</td>
<td>b</td>
<td>56.63</td>
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</tr>
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<td>4</td>
<td>a</td>
<td>64.45</td>
<td>33.01</td>
</tr>
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<td>4</td>
<td>b</td>
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<td>4</td>
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<td>63.25</td>
<td>32.99</td>
</tr>
<tr>
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<td>a</td>
<td>62.94</td>
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</tr>
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<td>b</td>
<td>64.9</td>
<td>32.84</td>
</tr>
<tr>
<td>5</td>
<td>c</td>
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<td>6</td>
<td>b</td>
<td>59.82</td>
<td>34.72</td>
</tr>
<tr>
<td>6</td>
<td>c</td>
<td>61.6</td>
<td>33.4</td>
</tr>
</tbody>
</table>

Figure 9.1: SEM of monolayer GO and flake size distribution via ImageJ analysis.

Fig. 9.2 presents the settling of GO flakes in Sample 1. The photo was taken 10 minute after the injection of GO and highlights the pure colloidal stability of Sample 1.

Fig. 9.3 represents the technique used for determining the GO layer percentage. In the first step,
Figure 9.2: GO flakes settling.

The substrate (silica) is changed to white. Then an intensity histogram is generated followed by deconvolution of the histogram into monolayer and multilayer peaks. The monolayer percentage is then calculated by considering the relative area under each peak in the histogram.

Fig. 9.4 collects representative SEM images of bacterial adhesion for Sample 1, 2, 3, 5. Please refer to Figure 7 in the main manuscript for Sample 4 and 6.

Fig. 9.5 represents the elbow method used to determine the optimal number of clusters used in Fig. 3.6. Six is the lowest number of clusters to achieve 90% of variance explained.
Figure 9.3: GO monolayer percentage evaluation
Figure 9.4: Representative SEM images of *E. coli* bacteria adhesion onto GOM surfaces. The samples are identified by numbers.

Figure 9.5: Elbow method to determine the optimal number of clusters.
Appendix B

Apart from minor modifications, this chapter originally appeared as supplementary information for:


As discussed in the main text, the GO solution was prepared using a modified Hummers’ method with additional pre-processing of the graphite powder. The preoxidation of the graphite powder (5 g; d = 45 µm) was completed using sulfuric acid (30 mL; 97% H₂SO₄), phosphorus pentoxide (4.2 g; P₂O₅), and potassium persulfate (4.2 g; K₂S₂O₈) in a water bath at 75°C for 4.5 h. The mixture was then cooled to room temperature and diluted with 700 mL of deionized water (DI) and vacuum filtered through a poly(tetrafluoroethylene) membrane (pore size 5 µm). After pre-oxidation, the graphite was subjected to a modified Hummers’ method during this process, the pre-oxidized material was suspended in H₂SO₄ (150 mL; 97%) in an ice bath for 20 min. Potassium permanganate was slowly added (15 g; KMnO₄) and the mixture was heated to 35 °C for 2 h. Hummers’ method was completed by adding 250 mL of DI water and heating the mixture to 70°C for an additional 2 h. After quenching the reaction with hydrogen peroxide (30 mL; H₂O₂) and DI water (750 mL), it was allowed to cool to room temperature. In order to quench the unreacted reagent and clean the solution, the product was then filtered through a 300 µm testing sieve, then through glass fiber and centrifuged for 2 h at 5000 RPM (Sorvall RC-5C plus). The supernatant was then washed with hydrochloric acid (400 mL, 10% HCl). The sieving, centrifugation, and washing process was then repeated using DI (two times) and ethanol (EtOH, two times). The final solution
was then dispersed in 300 mL of EtOH at a concentration of $\approx 0.1$ wt%.

Various stages of the formation of three different GONS are displayed in Fig. 10.1. In Fig. 10.1a, a large portion of the GO sheet has not scrolled, indicating an early stage of GONS formation. Fig. 10.1b is GONS in a more advanced state, in which the majority of the GO sheet is scrolled around the main structure. Fig. 10.1c is near the end of the formation of GONS as characterized by an almost complete scrolling of the GO.

**Figure 10.1: Different stages of GONS formation.** (a) Early stage formation. (b) Advanced stage formation. (c) Final stage formation.
The different geometries depicted in Fig. 3 in the main text can originate from the same GO flake. Fig. [10.2] represents a scrolled GO flake where it is possible to recognize two T-GONS and one C-GONS.

![Diagram of GO flake with T-GONS and C-GONS]

**Figure 10.2: Formation of a scrolled GO flake displaying simultaneously T- and C-GONS.**

Fig. [10.2] demonstrates the hollow nature of the GONS acquired \textit{via} transmission electron microscopy. Fig. [10.2a] presents GONS whose tail (right side) is not scrolled in accordance with the multi-layer structure. Fig. [10.2b] presents open-structure GONS, characteristic of an incomplete scrolling process.

![TEM images of GONS](a) TEM image of GONS with a defective (wrinkled) tail. (b) TEM image of open-structure GONS formed by partial scrolling.

**Figure 10.3: Transmission electron microscopy (TEM) of GONS.** (a) TEM image of GONS with a defective (wrinkled) tail. (b) TEM image of open-structure GONS formed by partial scrolling.
Fig. 10.4 represent the statistical analysis of the GONS diameters for different geometries. Statistical data is based on a population of 10 – 15 GONS for each geometry. Fitting with normal distributions shows that the diameter of the narrow tube-like GONS is $225 \pm 85 \text{ nm}$ ($R^2 = 0.9964$) while the diameter of the wide tube-like GONS is $1.802 \pm 0.273 \mu\text{m}$ ($R^2 = 0.99$). Also, the Gaussian fits show that the minimum diameters of the cone-like GONS are $193 \pm 1 \text{ nm}$ ($R^2 = 0.9999$) for the narrow cone and $0.948 \pm 0.317 \mu\text{m}$ ($R^2 = 0.8722$) for the wide cone, while the maximum diameters are $1.65 \pm 0.391 \mu\text{m}$ ($R^2 = 0.9668$) for the narrow cone and $1.84 \pm 0.331 \mu\text{m}$ ($R^2 = 0.9548$) for the wide cone.
Figure 10.4: Histograms of the GONS diameters and normal distribution. (a) Diameter distribution for narrow tube GONS. (b) Diameter distribution for wide tube GONS. (c) Minimum diameter distribution for narrow cone GONS. (d) Maximum diameter distribution for narrow cone GONS. (e) Minimum diameter distribution for wide cone GONS. (f) Maximum diameter distribution for wide cone GONS.
Fig. 10.5 represents an AFM image of GONS. The cross-section line highlights its multilayered structure. On the left side of the image, it is possible to notice a GO flake not wrapped around the GONS characterized by a thickness of $\approx 2$ nm. The GONS maximum thickness is $\approx 12$ nm and it displays a noticeable wrinkle on the outer most layer.

![AFM image of GONS and cross-section line that illustrates its multilayer structure.](image_url)

**Figure 10.5:** AFM image of GONS and cross-section line that illustrates its multilayer structure.
Fig. 10.6 represents the C1s peak for the parent GO flake (Fig. 10.6a), after 5 minutes of LF irradiation (Fig. 10.6b), and 5 minutes of HF irradiation time (Fig. 10.6c). The post-treatment XPS shows a reduction in the C-O peak from 65% to $\approx 25\%$, and increase in C-C/C=C from 30% to $\approx 60\%$ which is related to the cleavage of GO sheet at oxygen defects in the basal plane as explained in the main text.

Figure 10.6: XPS before and after ultrasonic treatment. (a) XPS pre-treatment. (b) XPS after 5 min ultrasonic treatment at low frequency (LF). (c) XPS after 5 min ultrasonic treatment at high frequency (HF).
Figure 10.7: Picture taken from the built-in color threshold function of *ImageJ* used for analyzing the GO flake area.

Fig. 10.7 represents an SEM image analyzed by *ImageJ* in order to determine the size distribution of the GO flake. The statistical analysis is based on 300 GO flakes taken from 5 different SEM images for each processing time.
Table 10.1 and Table 10.2 present the experimental data for the GO flake area (A_GO) and the length of the produced GONS (L_{GONS}). See Fig. 4 and Fig. 5 in the main text for plots.

**Table 10.1:** Experimental data for the evolution of the GO flake area (A_GO) as a function of the treatment time (t) for both the low frequency (LF) and high frequency (HF) treatments. The values reported are the mean values and their standard errors.

<table>
<thead>
<tr>
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</thead>
<tbody>
<tr>
<td>0</td>
<td>52.8 ± 3.9</td>
<td>52.8 ± 3.9</td>
<td>52.8 ± 3.9</td>
<td>52.8 ± 3.9</td>
<td>52.8 ± 3.9</td>
</tr>
<tr>
<td>5</td>
<td>53.4 ± 6.4</td>
<td>44.4 ± 4.9</td>
<td>45.5 ± 1.8</td>
<td>17.3 ± 1.1</td>
<td>3.7 ± 0.1</td>
</tr>
<tr>
<td>10</td>
<td>51.0 ± 4.5</td>
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<td>25.7 ± 1.5</td>
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<td>3.5 ± 0.4</td>
</tr>
<tr>
<td>20</td>
<td>57.1 ± 5.9</td>
<td>30.8 ± 2.4</td>
<td>13.3 ± 1.2</td>
<td>10.6 ± 0.7</td>
<td>2.7 ± 0.2</td>
</tr>
<tr>
<td>30</td>
<td>47.5 ± 5.2</td>
<td>26.0 ± 1.5</td>
<td>16.1 ± 1.1</td>
<td>8.1 ± 0.7</td>
<td>2.0 ± 0.2</td>
</tr>
<tr>
<td>60</td>
<td>51.3 ± 4.2</td>
<td>31.9 ± 1.7</td>
<td>14.6 ± 0.9</td>
<td>6.7 ± 0.7</td>
<td>1.7 ± 0.2</td>
</tr>
</tbody>
</table>

**Table 10.2:** Experimental data for the evolution of the GONS length (L_{GONS}) as a function of the treatment time (t) for both the low frequency (LF) and high frequency (HF) treatments. The values reported are the mean values and their standard errors.

<table>
<thead>
<tr>
<th>t [min]</th>
<th>HF(1 W) L_{GONS} [µm]</th>
<th>HF(10 W) L_{GONS} [µm]</th>
<th>HF(20 W) L_{GONS} [µm]</th>
<th>LF(10 W) L_{GONS} [µm]</th>
<th>LF(100 W) L_{GONS} [µm]</th>
</tr>
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<tr>
<td>5</td>
<td>10.3 ± 1.2</td>
<td>11.3 ± 1.2</td>
<td>10.9 ± 1.8</td>
<td>6.8 ± 0.8</td>
<td>2.5 ± 0.4</td>
</tr>
<tr>
<td>10</td>
<td>9.2 ± 0.8</td>
<td>8.3 ± 0.8</td>
<td>8.2 ± 1.5</td>
<td>5.7 ± 0.6</td>
<td>2.3 ± 0.4</td>
</tr>
<tr>
<td>20</td>
<td>8.7 ± 1.0</td>
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<td>7.2 ± 1.2</td>
<td>5.4 ± 0.5</td>
<td>1.4 ± 0.2</td>
</tr>
<tr>
<td>30</td>
<td>9.0 ± 0.8</td>
<td>6.5 ± 0.6</td>
<td>7.2 ± 1.1</td>
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<tr>
<td>60</td>
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<td>7.2 ± 0.9</td>
<td>2.8 ± 0.2</td>
<td>1.0 ± 0.1</td>
</tr>
</tbody>
</table>
Since the volume of the GO solution used during HF and LF processing could affect the $A_{GO}$ and $L_{GONS}$, but this effect will be more pronounced in the highly destructive LF treatment method, and may alter the $A_{GO}$ and $L_{GONS}$ evolution kinetics presented in Eq. 1 and Eq. 2 in the main text. As Fig. 10.8 illustrates, reducing the volume of the solution used in the LF(10W) treatment leads to a faster reduction in $A_{GO}$ ($A_1 = 101.7 \text{ \mu m}^2$, $k_{GO} = 0.538$, $A_2 = 5.99 \text{ \mu m}^2$, $s_1 = 0.50$, and $t_{crit} = 7.1$ min) and $L_{GONS}$ ($L_2 = 5.1 \text{ \mu m}$, $s_2 = 0.518$, and $t_{crit} \leq 5$ min), but the general kinetics are very similar to the ones observed for LF(100W) and are consistent with Eq. 1 and Eq. 2 in the main text.
Appendix C

Apart from minor modifications, this chapter originally appeared as supplementary information for:


Figure 11.1: Periodic cell used in the LB simulations.

Fig. 11.2 illustrates the dead-end filtration system, which is characterized by a reservoir (i.e., pressurized pot), allowing the filtration experiments to be performed with large volume (i.e., more than 3 L). The pressure taken from the wall was regulated with a pressure gauge from Ingersoll. The membranes were placed in a stainless steel EDM Millipore holder.

Table 11.1 reports the oxygen and carbon footprints for the GOAL membranes. It is important to underline that the HI treatment is the most effective reduction technique among the ones tested and it allows achieving O/C ratio of 21%. Regarding the UV irradiation, longer irradiation times lead to stronger reduction and the vacuum dictates more effective reduction compared to air.

AFM analysis of the GOAL surface at the boundary of the bare PVDF is displayed in Fig. 11.3. Fig. 11.3a represents the topography of the GOAL surface obtained and the dashed line section indicates a < 50 nm topography variation (Fig. 11.3c) at the interface between GO and PVDF, corrobor-
Figure 11.2: Dead-end filtration set-up.

Table 11.1: XPS percentage peak area data for the six samples. The standard deviation for the atomic ratio of each element is ±1%.

<table>
<thead>
<tr>
<th>Treatment</th>
<th>Time (min)</th>
<th>C-OH</th>
<th>C-C</th>
<th>C=C</th>
<th>O-C-O</th>
<th>O/C</th>
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<td>Untreated</td>
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<td>3.51</td>
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<tr>
<td>UV vacuum</td>
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<td>37.16</td>
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<td>0.65</td>
<td></td>
</tr>
<tr>
<td></td>
<td>360</td>
<td>38.12</td>
<td>51.05</td>
<td>10.83</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1440</td>
<td>19.28</td>
<td>66.21</td>
<td>14.51</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>HI</td>
<td>1</td>
<td>11.69</td>
<td>76.46</td>
<td>11.85</td>
<td>0.21</td>
<td></td>
</tr>
</tbody>
</table>

orating the SEM observations and mass analysis calculations on the thickness of the GO layer. The distinction between the two domains (GO and PVDF) is also visible in the phase image (Fig. 11.3b) highlighting the different chemistry of the two materials. Fig. 11.4a displays the evolution of the C1s spectrum with UV irradiation time in air. As explained in the main text, longer irradiation time leads to a more efficient graphitization of the GOAL. The intensity of the single (C-C) and double
carbon (C=C) bond binding increases from 28% to 51%. This is also confirmed by the oxygen to carbon mass ratio (i.e., O/C) which decreases from 72% to 56% for untreated GOAL and the UV-GOAL irradiated for 360 min in air, respectively. Fig. 11.4b represents the evolution of the XRD signal of GOAL with different UV irradiation times. We observed that the decrease in the number of functional groups with an increase in the exposure time leads to a shift of the peak of circa 1 Å. However, as explained in the main text, the air treatment leads to a nosier XRD signal.

Fig. 11.5 represents the XPS and XRD spectra for HI-GOAL. We did not succeed in reducing the GO on Al₂O₃ with HI and for this reason, we used PVDF as the substrate. As explained in the main text, the PVDF exhibits peaks in the same region of GO. However, in Fig. 11.5a it is possible to notice the appearance of a peak centered at circa 16°. This peak, which was not as strong in the

Figure 11.3: AFM analysis of the GOAL surface. (a) Topography, (b) phase image, (c) section line (in red) acquired at the boundary between the GOAL and the bare PVDF.
bare PVDF, can be related to the presence of the HI-GOAL and corresponds to a spacing of 5.5 Å.

Fig. 11.6 represents the effect of the sonication treatment on the GO flake size. In particular, with 23 min of bath sonication, the flake size varies from 52.2 ± 18.9 µm$^2$ to 1.3 ± 0.4 µm$^2$.

Fig. 11.7 represents the independence between the variation of the dimensions of the GOAL
architecture. Fig. 11.7a displays the variation of the GO flake size versus the UV treatment time in vacuum. Although the UV treatment is responsible for the changing of the GOAL chemistry (i.e., the GOAL spacing), it is possible to notice that even 360 min of UV irradiation does not lead to a significant variation of the GO flake size. At the same time, the bath sonication treatment, responsible for the changing of the GO flake size, does not significantly change the chemical composition of the GOAL (Fig. 11.7b). Moreover, the sonication does not change the spacing between the GO laminates as highlighted in the XRD spectra in Fig. 11.7c. It is important to note that the sonication does not increase the GO defect density, which could lead to larger water permeability results. This is confirmed by three Raman intensity maps (4.096 acquisition points/spectra for an 80 x 80 µm² image with acquisition time 0.05 s/spectra) acquired for the sonicated and not-sonicated GO samples. The average D/G area ratio ($A_D/A_G$) for the three images was evaluated to be 1.36 ± 0.08 and 1.38 ± 0.05 for the non-sonicated and the sonicated sample, respectively.

Fig. 11.8 represents the water permeation through a 0-GOAL membrane versus time. The initial permeability is characterized by higher values compared to the permeability at steady state conditions, which are reached after circa 700 min of filtration. In particular, during the membrane compaction stage, the permeability reduces by circa three-fold. The Darcy behavior of the mem-
Figure 11.7: Absence of interdependency between the tuning of flake size and oxygen content. (a) Variation of the GO flake size with UV irradiation in vacuum, and (b) Photo of GOAL obtained with sonicated and not-sonicated GO solution and their atomic composition. (c) XRD spectra for GOAL obtained via GO sonicated for 23 min and not-sonicated.

brane can also be observed with a pressure decrease from 3 to 1.2 bar, which leads to a reduction of permeability of almost a factor of three. The membrane permeability is also influenced by the GO thickness. Table 11.2 reports permeability results for different amount of GO used for fabricating the membrane, which leads to different thickness.

Figure 11.8: Water permeation through 0-GOAL versus time.
Table 11.2: Effect of the GO load (thickness) on the membrane permeability.

<table>
<thead>
<tr>
<th>GO Amount</th>
<th>Permeability (LMH-bar)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1x</td>
<td>2.18</td>
</tr>
<tr>
<td>3x</td>
<td>0.92</td>
</tr>
<tr>
<td>4x</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Fig. 11.9, the GOAL structure was characterized via Raman spectroscopy and display a D-band ($A_{1g}$ symmetry) at $\approx 1350$ cm$^{-1}$ representative of defects/disorder in the basal plane and a G-band ($E_{2g}$ symmetry) at $\approx 1590$ cm$^{-1}$ corresponding to the in-plane sp$^2$ bond stretching, thus proportional to the extension of the graphitic domains. The longer exposure to UV irradiation leads to a smaller D/G peak intensity ratio ($I_D/I_G$). In particular, the $I_D/I_G$ is equal to 0.95 and 0.90 for 15 min and 720 min UV irradiation, respectively, confirming the restoring of the graphitic domains via the reduction of GOAL.

![Figure 11.9: Raman D- and G-bands for 15minUV-GOAL and 720minUV-GOAL.](image)

Fig. 11.10 represents XRD spectra for reduced (UV-GOAL) and not reduced GOAL in a dry
Table 11.3: Effect of the GO nanochannels interlayer spacing \( (2h) \) on the permeability.

<table>
<thead>
<tr>
<th></th>
<th>15-GOAL</th>
<th>360-GOAL</th>
<th>HI-GOAL</th>
<th>15-GOAL-son</th>
<th>360-GOAL-son</th>
<th>HI-GOAL-son</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \Delta k ) (%)</td>
<td>56</td>
<td>74</td>
<td>91</td>
<td>43</td>
<td>66</td>
<td>86</td>
</tr>
<tr>
<td>( \Delta k_{2h} )</td>
<td>6.35</td>
<td>5.3</td>
<td>3.0</td>
<td>5.0</td>
<td>4.7</td>
<td>2.8</td>
</tr>
</tbody>
</table>

and hydrated state. As one can see, the hydration leads to smaller \( 2\theta \), which corresponds to a larger spacing \( (2h) \). In particular, when hydrated the spacing increased from 7.8 to 10.1 Å and from 8.1 to 10.5 Å for UV-GOAL and GOAL, respectively. It is important to note that hydration affects the spacing to a similar degree (20-25% increase) for both the oxidized and reduced GOAL in accordance with previously reported data.022

![Figure 11.10: XRD spectra for hydrated GOAL and UV-GOAL.](image)

Table 11.3 and Table 11.4 represent the variation in the permeability \( (\Delta k) \) due to the chemical reduction and sonication, respectively. The tables also report the normalized variations \( (\Delta k_{2h} \text{ and } \Delta k_l) \) for each scenario. As explained in the main text, the larger values of \( \Delta 2h \) highlight the importance of the nanochannels interlayer spacing in dictating the permeability, compared to the length of the nanochannels.
Table 11.4: Effect of the GO nanochannels interlayer spacing ($l$) on the permeability.

<table>
<thead>
<tr>
<th></th>
<th>0-GOAL-son</th>
<th>15-GOAL-son</th>
<th>360-GOAL-son</th>
<th>HI-GOAL-son</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\Delta k$ (%)</td>
<td>19</td>
<td>53</td>
<td>60</td>
<td>110</td>
</tr>
<tr>
<td>$\Delta k_f$</td>
<td>0.02</td>
<td>0.08</td>
<td>0.09</td>
<td>0.15</td>
</tr>
</tbody>
</table>
Appendix D

Apart from minor modifications, this chapter originally appeared as supplementary information for:


Figure 12.1: FCM fabrication process.

Table 12.1: Decomposition of the C1s peak of the FCM after each thermal annealing cycle.

<table>
<thead>
<tr>
<th>Functionality</th>
<th>Wavelength (eV)</th>
<th>1st (eV)</th>
<th>2nd (eV)</th>
<th>3rd (eV)</th>
<th>4th (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-C C=C</td>
<td>≈ 285</td>
<td>64.5 ± 1</td>
<td>66.3 ± 1</td>
<td>65.0 ± 1</td>
<td>64.3 ± 1</td>
</tr>
<tr>
<td>C-OH C-O-C</td>
<td>≈ 287</td>
<td>14.1 ± 1</td>
<td>10.2 ± 1</td>
<td>15.0 ± 1</td>
<td>16.5 ± 1</td>
</tr>
<tr>
<td>C=C-OH</td>
<td>≈ 289</td>
<td>21.4 ± 1</td>
<td>23.5 ± 1</td>
<td>19.0 ± 1</td>
<td>20.2 ± 1</td>
</tr>
</tbody>
</table>
Figure 12.2: Custom-made vacuum filtration device for FCM fabrication. (a) Photo of the 3D-printed vacuum filtration device. (b) SolidWorks representation of the 3D-printed vacuum filtration device.

Figure 12.3: Multi-cell cross-flow apparatus used for filtration tests. (1) Membrane cell lines; (2) feed tank; (3) circulation pump; (4) control panel to adjust flow and pressure flow control valves; (5) flow-meter; (6) pH and conductivity sensor.
Figure 12.4: SEM analysis of the hierarchical structure of FCM. SEM surface images of (a) CF paper (1st layer, substrate of the FCM), (b) intermediate CNT support layer (2nd layer) and (c) GO selective layer (3rd layer) at different magnifications.

Figure 12.5: Example of a mechanically-damaged FCM. (a) CNT layer and (b) CF layer. ImageJ software allows to recognized the superficial pores (in red) and calculate their areas.
Figure 12.6: Evaluation of the superficial mean pore size of the layers constituting the FCM. The FCM has a crack that reveals the underneath CNT layer.

Figure 12.7: FCM chemical stability to organic solvents. FCM after being immersed in acetone (top) or water (bottom) reveals the same morphology.
The untreated FCMs were not subjected to any annealing at 150 °C during the fabrication process whereas, the thermally treated FCMs were thermally reduced at 150 °C for 20 min during the fabrication process and then subjected to four sequential thermal annealing cycles of 15 min at 150 °C. TFC it was not treated before the annealing.

Figure 12.8: Mass change over temperature of an untreated FCM (red line), a thermally treated FCM (green line) and a polyamide thin film composite (TFC) membrane (dashed blue line). The untreated FCMs were not subjected to any annealing at 150 °C during the fabrication process whereas, the thermally treated FCMs were thermally reduced at 150 °C for 20 min during the fabrication process and then subjected to four sequential thermal annealing cycles of 15 min at 150 °C. TFC it was not treated before the annealing.
Bibliography


[100] H. Huang, Y. Mao, Y. Ying, Y. Liu, L. Sun, and X. Peng. Salt concentration, ph and pressure controlled separation of small molecules through lamellar graphene oxide membranes. *Chemical Communications*, **49**, 5963 (2013).


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