

## Graphene Oxide Membranes: A Review

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**Abstract:** A perfect molecular level separating unit for any kind of species to be filtered is on very high demand. In recent years, graphene oxide has emerged as an important material which can filter ions and molecules. This is an emerging field of research which has drawn extensive attention. Membrane-based separation technology has attracted great interest in many separation fields due to its advantages of easy-operation, energy-efficiency, and easy scale-up, and environmental friendliness. The development of novel membrane materials and membrane structures is an urgent demand to promote membrane-based separation technology. Graphene oxide (GO), as an emerging star Nano-building material, has showed great potential in the membrane-based separation field. In the past few decades, membrane-based separation technology has attracted considerable attention in many separation fields due to its advantages of easy-operation, energy-efficiency, and environmental friendliness.

**Keywords:** Membrane-based separation, Graphene oxide membranes, water purification, Nano-building material

### 1. INTRODUCTION

Since, the industrial revolution, there has been significant changes in agriculture, mining, and manufacturing sectors. Almost 71% of the Earth's surface is made up of water out of which only 2.5% is fresh water, out of which less than 1% is available for human consumption. The inaccessibility to adequate clean water is one of the most serious problems affecting large numbers of people worldwide. [1]

Numerous technologies have been employed in remediation of heavy metals in water. These technologies can be broadly classified into three processes namely: a) physio-chemical, b) biological and c) membrane processes. Among the range of appropriate technologies, membrane separation has many advantages as the chemical and energy requirements maybe less than conventional processes and treated water of high quality can be obtained.

A combination of these processes is also used to improve the treatment efficiency. So far water treatment has been mainly carried out by multiple flash distillation and reverse osmosis. Graphene is considered as an ultimate material for membrane formation because it is stronger, thinner and more chemically resistant. It is a layer of strongly packed pure carbon atoms joined together in a hexagonal honeycomb, but it is not scalable to areas required for membrane applications. There is a strong Van Der Waals force between the graphene sheets, which leads to the difficult application of graphene materials directly. Graphene oxide is the most common derivative of graphene. It has been suggested that Graphene oxide membranes, with all their favorable properties, are ideal for contaminant filtration, sieving and separation in water treatment [2]. Graphene oxide membranes continue to attract interest due to their unique molecular sieving properties combined with fast permeation rates. Graphene oxide has hydrophilicity and has been tried to use it into thin films for water treatment in recent years. [1] Membranes prepared from layers of graphene oxide offer substantial advantages over conventional materials for water treatment. However, for applications of GRAPHENE OXIDE membranes in water desalination, the Graphene Oxide interlayer spacing within the laminates has to be reduced to less than 0.7 nm to sieve the hydrated  $\text{Na}^+$  ions from water. But due to reduction in spacing between Graphene Oxide membranes, permeation of water is significantly reduced due to reduction in hydrophilic groups, sometimes leading to formation of impermeable barrier membranes.

On treating Graphene Oxide Membranes with HydroIodic acid; or intercalating Titania Nano sheets followed by Ultraviolet Reduction; or coating Graphene Oxide Membranes by Poly-Dopamine we can obtain Reduced Graphene Oxide Membranes. These Reduced Graphene Oxide Membranes have high permeability for water and high salt/ion rejection properties. However, PDA- Graphene Oxide membranes are environment friendly having abundant hydrophilic properties of PDA. [4]

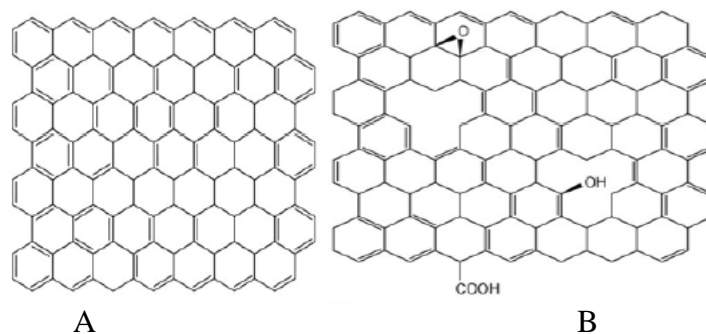


Fig1.1. Structure of A) Graphene B) Graphene Oxide

Graphene Oxide is hydrophilic and its surface can be easily modified with a host of biocompatible polymers such as chitosan, polyethylene glycol (PEG), poly (ε-caprolactone), poly-L-lysine (PLL), and polyvinyl alcohol. These properties make it extremely attractive to a large number of scientists who apply it in the fields of drug delivery. Functionalized Graphene Oxide sheets and nanoparticles are frequently used as tissue scaffolds, fillers, and composite meshes in many areas of regenerative medicine. The membranes easily combine with host of other nanoscale materials leading to new applications in the fields of drug delivery, Tissue Engineering, cancer therapeutics, bio imaging, and diagnostics. [5] The reactive COOH and OH groups Graphene Oxide bears facilitate conjugation with various systems, such as polymers, bio molecules, quantum dots, Fe<sub>3</sub>O<sub>4</sub> nano particles, etc. imparting Graphene Oxide Membranes with multi-functionalities and multi-modalities for diverse biological and medical applications. [6] Melanoma skin cancer in mice has been treated using photo thermal therapy with a near infrared laser and Graphene Oxide that was functionalized with poly- Ethylene Glycol and hyaluronic acid.[7]

## 2. PREPARATION OF GRAPHENE OXIDE

Graphite oxide was first prepared by Oxford chemist Benjamin C. Brodie in 1859, by treating graphite with a mixture of potassium chlorate and fuming nitric acid. He reported synthesis of "paper-like foils" with 0.05 mm thickness. [9]

In 1957 Hummers and Offeman developed a safer, quicker, and more efficient process called Hummers' method, using a mixture of sulfuric acid H<sub>2</sub>SO<sub>4</sub>, sodium nitrate NaNO<sub>3</sub>, and potassium permanganate KMnO<sub>4</sub>, which is still widely used, often with some modifications. Graphene oxide has also been prepared by using a "bottom-up" synthesis method (Tang-Lau method) in which the sole source is glucose, the process is safer, simpler, and more environmentally friendly compared to traditionally "top-down" method, in which strong oxidizers are involved. Another important advantage of Tang-Lau method is control of thickness, ranging from monolayer to multi layers by adjusting growth parameters. [10]

### 2.1. Synthesis of Graphene Oxide: Top Down Approach

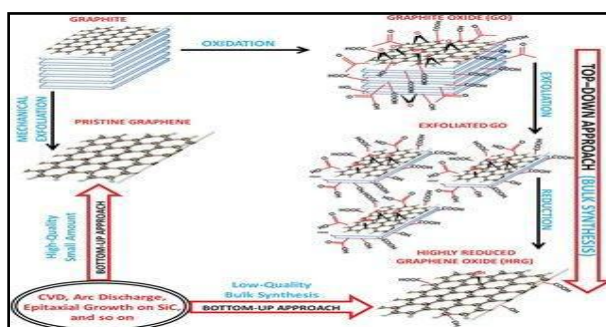


Fig1. Top –Down Approach for Synthesis of Graphene Oxide approach

- The main drawbacks of this top-down approach are the use of strong oxidizing agents and small lateral size of Graphene Oxide Nano sheets.
- The Graphene Oxide Nano Sheets are prepared by a hydrothermal method using glucose as a sole reagent. The method is environmentally friendly, facile, low-cost as well as capable of scaling up for mass production.

## 2.2. Synthesis of Graphene Oxide: Bottom Up Approach

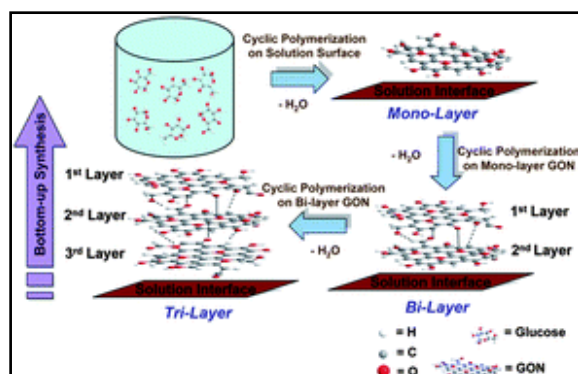


Fig2. Bottom down approach for synthesis of Graphene oxide sheets

## 2.3. Various Materials Suitable for Graphene Oxide Membranes

Normally, membrane material is manufactured from a synthetic polymer, although other forms, including ceramic and metallic “membranes,” may be available. Almost all membranes manufactured for drinking water are made of polymeric material, since they are significantly less expensive than membranes constructed of other materials. Membranes constructed of polymers that react with oxidants used in drinking water treatment should not be used with chlorinated feed water. Mechanical strength is another consideration, since a membrane with greater strength can withstand larger trans-membrane pressure (TMP) levels, allowing for greater operational flexibility and the use of higher pressures. Membranes with bi-directional strength may allow cleaning operations or integrity testing to be performed from either feed or filtrate side of the membrane. Membranes with a particular surface charge may remove particulate or microbial contaminants of the opposite charge due to electrostatic attraction. Membranes can also be hydrophilic (water attracting) or hydrophobic (water repelling). [13]

## 3. CHARACTERIZATION OF GRAPHENE OXIDE MEMBRANES

The physical chemical characterization of graphene oxide is not often of easy interpretation because this material is made of carbons and oxygen as the majority of organic molecules. Thus, the peculiar spectroscopic signals are blended by conventional carbon and oxygen signals.

### 3.1. FTIR

The FTIR is an efficient tool for a rapid characterization of Graphene Oxide. It becomes common to interpret FTIR signals as referred to hydroxyl (OH), epoxy (C–O–C) and ketone (C=O) groups. A typical FTIR spectrum is reported as below (fig3).

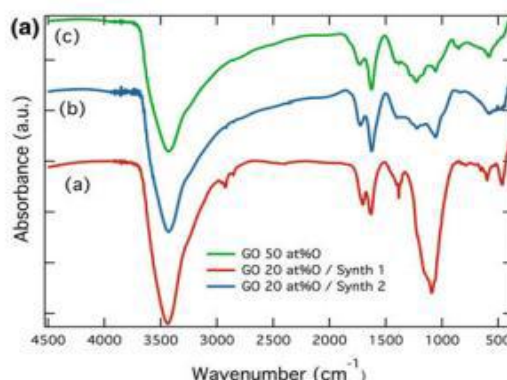


Fig3. FTIR Spectra of Graphene Oxide Membrane

### 3.2. Raman Spectrum

Raman spectrums for the GO shows only two broaden peaks which represent the G and D band. (Fig4)

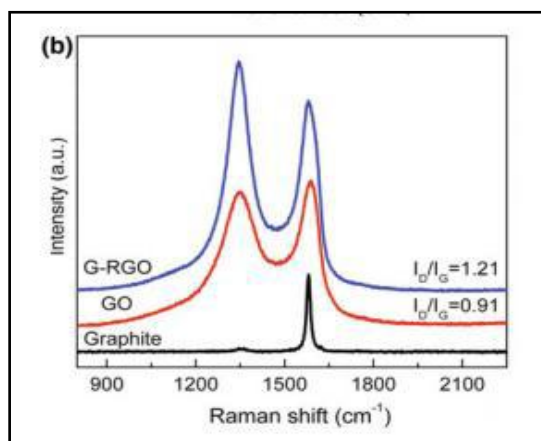


Fig4. Raman Spectrum for Graphene Oxide Membranes

### 3.3. XRD

X-ray diffraction (XRD) pattern of pristine graphene oxide shows only a broad peak around 11° (Fig5).

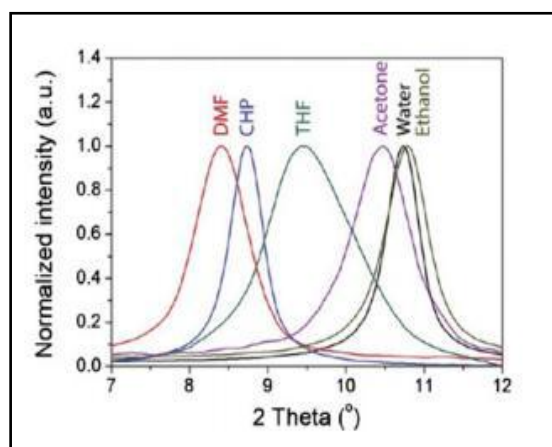


Fig5. XRD for Graphene Oxide Membranes

Various Methods for Characterization are discussed below in Table1.

Table1. Method of characterization of GO membranes

Characterization Method	Characterization Information	Reference
Stress–strain curves	Mechanical stability of the membrane, tensile strength, Young’s modulus	17
SEM	Surface morphology and cross-section structure	18
AFM	Surface roughness of membrane, membrane uniformity	18
CA	Surface hydrophilic or hydrophobic property of membrane	19
FTIR	Chemical structure of membrane, surface functional groups of membrane	20
XRD	Crystalline structures, d-spacing of membrane	20
Raman Spectroscopy	Identified the existence of GO in composite membrane	22

## 4. TYPES OF GRAPHENE OXIDE MEMBRANES

There are 3 types of GO membranes:

- Free-standing GO membrane
- Supported-GO membrane
- GO-modified composite membrane

**4.1. Free-Standing**

At present, a variety of approaches have been employed to fabricate free-standing Graphene Oxide membrane, such as vacuum filtration, evaporation-driven self-assembly, self-assembly process under ambient conditions, drop casting, and pressurized ultra filtration (UF) method. Sun et al. developed free-standing Graphene Oxide membranes via a drop-casting method and investigated their water purification performance. [23]

**4.2. Supported-GO Membranes:**

Although free-standing Graphene Oxide membranes have achieved great progresses in membrane separation applications, a Graphene Oxide membrane supported on desired mechanical support for high-pressure application is rather necessary. Additionally, depositing Graphene Oxide layers onto certain polymeric or inorganic membrane surface could also improve the separation performance and antifouling property of pristine membranes.

**4.3. GO-Modified Composite Membranes:**

Apart from the two types of GO-based membrane described above, in which Graphene Oxide nano sheets were directly used as the active separation layers, researchers also focused on modifying polymeric membranes with Graphene Oxide nano sheets via different methods. By now, various Graphene Oxide-modified polymeric composite membranes have been developed and presented improved water permeability, selectivity, and anti-microbial performances.

**Table2.** Application of GO-based membranes.

Types of Graphene Oxide Membrane	Name of Graphene Oxide Membrane	Application
Free-standing	Cross-linked GO membrane	Ion dialysis separation
	GOP nano hybrid membrane	Oil/water separation
	GO membrane	Ion penetration
	GO membrane	Dehydration of 85 wt % ethanol
Supported	GO/PES	Gas separation
	GOF/Al <sub>2</sub> O <sub>3</sub>	3.5 wt % seawater desalination
	GO/PAN	Water purification
	GO/Nylon	Water treatment
	GO/PES	Humic acid removal
	GO/ceramic	Pervaporation separation of water/ethanol mixtures
	IRMOF-3/GO/PDA-PSF	Heavy-metal removal
GO-modified	GO/PSF	Water purification
	Pebax/GO/PVDF	Gas separation
	GO/PEI/DPAN	Solvent resistant NF

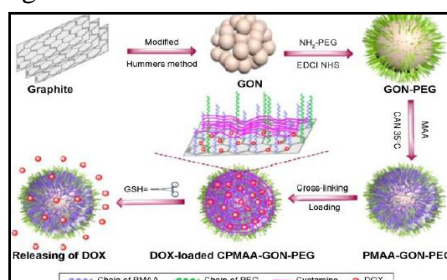
**5. APPLICATIONS OF GRAPHENE OXIDE MEMBRANES**

Graphene Oxide (GO) Membranes finds its application in various ways. For example, it can be used for Desalination of water, Waste Water Treatment, Gas Separation, Nano Medicines, Molecular Separation, etc.

**5.1. Nano Medicine:**

Graphene Oxide is hydrophilic and its surface can be easily modified with a host of biocompatible polymers such as chitosan, polyethylene glycol (PEG), poly (ε-caprolactone), poly-L-lysine (PLL) and polyvinyl alcohol. Graphene Oxide contains a large amount of hydrophilic groups on its edge or basal planes. [5]

These properties make Graphene Oxide extremely attractive to a large swath of scientists with new applications in the fields of drug delivery, parasitology, tissue engineering (TE), antibacterial, cancer therapy, sensors imaging, and diagnostics



**Fig6.** Application Of Graphene Oxide Membrane in Drugs & Medicines

### 5.2. Desalination of Water:

Desalination is one of the most important and promising methods for fresh water augmentation. Permeation of water through the membrane was attributed to swelling of Graphene Oxide structures, which enables a water penetration path between individual Graphene Oxide layers. The interlayer distance of dried Hummers graphite oxide was reported as 6.35 Å, but in liquid water it increased to 11.6 Å. [7]

Retention rates more than 90% were reported in this study for NaCl solutions using stabilized Graphene Oxide membranes in a reverse osmosis setup. Graphene Oxide membranes could be used for the filtration of sea water.

### 5.3. Coating Technology:

Multilayer Graphene Oxide films are optically transparent and impermeable under dry conditions. Exposed to water (or water vapor), they allow passage of molecules smaller than a certain size. The films consist of millions of randomly stacked flakes, leaving Nano-sized capillaries between them. Graphene-coated plastic films could be used in medical packaging to improve shelf life.

### 5.4. Graphene Oxide Composites and Paper-Like Materials:

Graphene Oxide mixes readily with many polymers, forming nanocomposites, and greatly enhances the properties of the original polymer, including elastic modulus, tensile strength, electrical conductivity, and thermal stability. Free-standing Graphene Oxide films are considered for applications including hydrogen storage applications, ion conductors, and nanofiltration membranes.

### 5.5. Energy Storage Device:

Graphene Oxide has an extremely high surface area; therefore, these materials are considered for usage as electrode materials in batteries and double-layered capacitors, as well as fuel cells and solar cells.

## 6. CONCLUSION

Graphene Oxide is new emerging term in carbon nanotechnology. Graphene Oxide refers to Graphene sheet having oxygen containing groups mainly –OH, Epoxy, carboxylic groups etc. Decorating Graphene with functional groups facilitates it to keep them detached from each other. Graphene Oxide has hydrophilic nature and can be easily dispersed in water at concentration up to 3mg/ml. Attachment of functional groups causes“ disturbance in electronic structure yielding in poor electrical properties and reduced mechanical strength of individual Graphene sheet. On the other hand there is hope that functional groups can enhance strength of composite by good adhesion with matrix. [13]

- Good physical and mechanical properties make graphene oxide as leading material for future applications. It became subject of interest for researchers to explore and utilize its properties for various applications ranging from civil to defense and aerospace applications etc.
- High strength and modulus of graphene oxide promises its application for structural composite reinforcement
- XRD characterization confirms that along with it some trace amount of planer stacking were found even upon exfoliation
- FTIR analysis shows increase in functionality as degree of oxidation increase. Modified Hummers Method mainly attaches carboxylic groups and phenolic groups.
- In TEM analysis, it was found that graphite oxide is bunch of planes instead of single layer of graphene.
- Based on the unique single-atomic-thick and two-dimensional structure, together with excellent physicochemical property, Graphene Oxide as an emerging star Nano-building material has attracted great interest in the membrane-based separation field.

- The separation performance of Graphene Oxide membranes could be effectively and successfully improved by different approaches, including physical approach, chemical approach, and some other novel approaches

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