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Graphene Enhanced Nano-porous Ultrafiltation Membrane for Water Treatment

Technical Note

The World Heath Organisation (WHO) published the following key facts in 2019:

https://www.who.int/news-room/fact-sheets/detail/drinking-water

- 785 million people lack even a basic drinking-water service, including 144 million people who are dependent on surface water.
- Globally, at least 2 billion people use a drinking water source contaminated with faeces.
- Contaminated water can transmit diseases such diarrhoea, cholera, dysentery, typhoid, and polio. Contaminated drinking water is estimated to cause 485 000 diarrhoeal deaths each year.

Cleaning up polluted water for safe drinking and for industrial waste-water disposal is a key challenge in both developed and developing countries. The classical methods for water treatment include coagulation[1], absorption[2], biological treatment[3] and sand filtration[4]. The filtration capability is mainly restricted by the filtration system pore size (typically above 1 μm). They are not suitable for filtering out nano scale contaminations such as viruses and harmful nanoparticles, nanowires and nano-plastics. Pressure driven membranes are the most promising techniques, which can remove a wide range of nano particulates and heavy metal ions[5]. The pressure driven membrane processes include microfiltration [6], ultrafiltration [7], nanofiltration [8] and reverse osmosis [9], which are distinguished by pore sizes in the membranes, electrical charge of the retained particles or molecules, and pressure exerted on the membrane [10]. Membrane selection is according to the diverse water quality, cost and efficiency.

Microfiltration (MF) membranes have the largest pores, ranging from 0.1 μm to 10 μm, which enable high water permeability. Large contaminating components, including suspended solids, colloid and bacteria, can be removed by MF sieving[11]. Ceramic MF membranes with above 500 nm pores can work as sub-micro filtration with a high chemical, thermal and mechanical stability compared to polymeric membranes [12].

Reverse osmosis membrane is a dense membrane without predefined pores. It filtrates polluted water by a solution diffusion mechanism, which has very low water permeability and requires the highest pressures compared with other filtration approaches. Its high cost for energy consumption limits its widely use [13].

Ultrafiltration (UF) membranes have smaller pores (2-100 nm) to filter out particles in the sub-micro to nano scales. Their permeability is much lower than that of MF and the water pressure required is higher. Water contaminants with a size above the pore size are sieved [11].

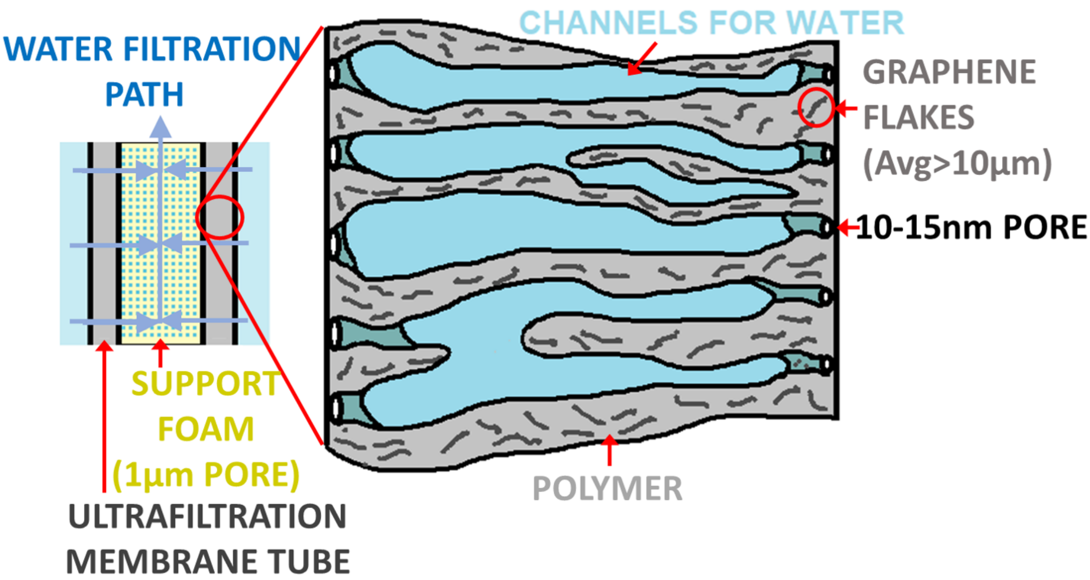
Graphene oxide imbedded UF membranes have been shown to enable water purification with controllable nano-pores through unfocused beam of gallium ion irradiation [14] or in-situ/post-process chemical doping [15]. These membranes normally have low porosity density, but good mechanical property against high water pressures [16]. Structured channels or pores can facilitate water flow and thus increase the permeability. Ions and solute molecules rejection can be achieved by controlling the pore size, electric charge and hydrophobicity characteristics of the membranes[17]. The main drawbacks of the graphene oxide based membranes are the low permeability as the water flow is proportional to the numbers of pores, and the mechanical stability of membrane which decreases with the increase of number of pores[18]. The nano-capillaries on a graphene oxide (GO) laminate is a recent approach used to enable small ions to pass through the membrane without a high pressure [19]. The low permeability presents a challenge. Another challenge is the high cost of membranes due to the use of graphene oxide.

Nano-filtration (NF) membranes have smaller pore sizes than that of UF, typically around 1 nm, which corresponds to dissolved compounds with a molecular weight about 300, thus it can remove relatively small organics, such as organic nano-pollutants and dyes. Additionally, NF has surface charge containing ionisable groups. This feature enables the removal of ions with a size below the pore size by Donnan exclusion mechanism [20].

The typical approach for UF/NF fabrication is based on phase inversion [21]. Polyvinylidene fluoride (PVDF) has a high anti-oxidation activity, excellent chemical resistance, thermal stability, and good membrane-forming properties[22]. However, PVDF membrane is susceptible to contamination by impurities in water treatment systems. A sharp drop in water flux often occurs. This is being overcome by various approaches including physical blending[23], plasma treatment[24], surface modification[25] and chemical grafting [26]. Among these approaches, physical blending is facile and effective. Additives are used to increase permeability, selectivity, antifouling and bactericidal abilities. Due to the hydrophilicity and remarkable resistance against protein adsorption, polyethylene glycol (PEG) is commonly used for improving hydrophilicity and antifouling properties [27]. Water flux increment is directly related to the enhanced surface hydrophilicity. Several studies focus on incorporating graphene oxide (GO) to improve properties of membranes. However, the complicated Hummer's method for graphene oxide synthesis takes long time, high cost, and requires the use of hazardous chemicals [28]. The water filtration system can work properly at a normal range of ambient temperatures from 10 to 40 °C. When a water filtration system is required to operate at close to freezing temperature, the increase of water's viscosity leads to a large amount of water flux loss. It is a common challenge in the water industry [29]. Collapsing the walls of membrane pores causes the direct loss of water flux during post process drying procedure in filtration membrane fabrication processes. A glycerin post-immersion is commonly used to avoid shrinkage of pores. However, the subsequent removal of the non-environmental friendly glycerin residual has been a challenge [30]. Nitrogen doped graphene has been demonstrated to be hydrophilic due to the increase of surface energy [31]. Compared with the widely studied GO, nitrogen doped graphene has not yet been previously reported for the modification of membranes for water treatment, until now.

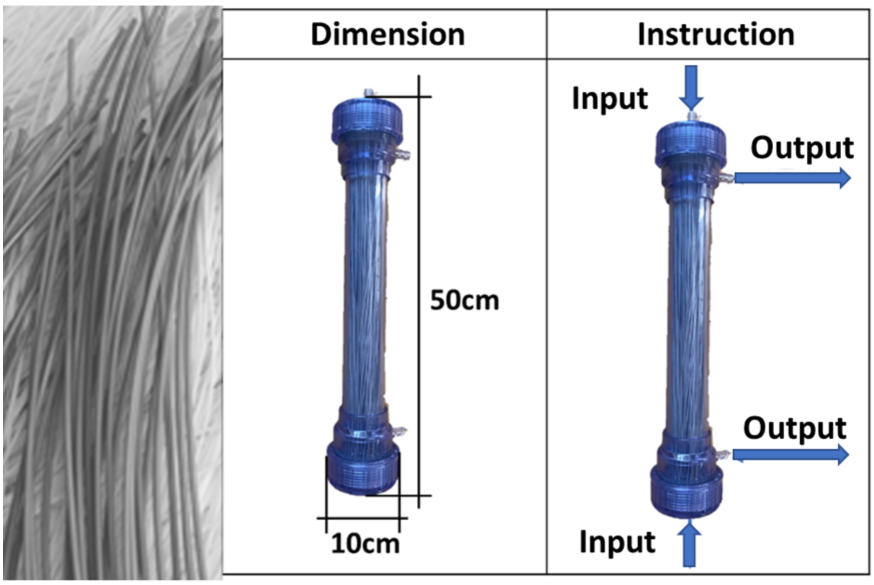
The existing nano-scale water filtration techniques are facing the challenges of low water flow flux, high cost and failure to work effectively at close to freezing temperatures.

At LIG Nanowise Ltd, a new type of N-doped graphene imbedded ultra-filtration membrane demonstrates better water flux, better stability than standard ultrafiltration membranes, and can work for close to freezing water. The structure of the filtratration system is shown in the following figure.



Graphene Enhanced Ultrafiltration (UF) Nano-porous Hollow Fibre Membrane for Water Treatment

<u>Standard Product Specification</u>



Item or parameter	Value or specification
Filter length	50 cm
Filter diameter	10 cm
Number of water inlets	2

Number of water outlets	2
Inlet port diameter	0.6 cm
Outlet port diameter	1 cm
Total membrane surface area	0.2 m^2
Operating water pressure	0.1-0.3 Mpa
Operating temperature range	0-40 ^{o}C
Casing material	Unplasticized Polyvinyl chloride (UPVC)
Casing colour	Light blue (partial transparent) or light grey (partial transparent)
Membrane hollow fibre diameter	1.3 mm
Membrane hollow fibre wall thickness	0.6 mm
Average hollow fibre pore size	10-20 nm
Membrane host material	polyether sulfone
Imbedded graphene	N-doped graphene
Membrane colour	Grey
Application	Water filtration

Other customized filter module dimensions, filtration pore sizes, membrane surface areas and material specifications could be tailored on request.

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