

## Grand Challenges in Fabrication of Nanocomposite Hollow Fiber Membranes

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### ABSTRACT

Membrane processes allow scalable and energy-efficient separation of gas and liquid, advance low-carbon purifications in various industrial and environmental applications and enable more resilient economy and society. In pursuit of developing more advanced membranes with continuously improved separating performances, nanofillers have been commonly incorporated into membranes to upgrade membrane properties such as mechanical robustness, antifouling ability, and permeability etc., across all types of popular membrane geometries from flat sheet and spiral wound to hollow fiber. Nanofillers inside hollow fibre membranes have received more attentions due to the unique structural advantages such as a large surface area/volume ratio and compact module designs. The resultant nanocomposite hollow fiber membranes thus combine the structural superiority with specific functions of nanomaterials such as superhydrophilicity or catalytic activity, whereas the development of dual layer hollow fiber membrane allowed further design of both the inner and outer membrane layers with innovative functions. On the other hand, greener and more environmentally friendly membranes fabrication are increasingly important to sustainable membrane technology, for example topics of using natural polymers, solvent free membrane fabrication and nano-pollutions are fervently investigated.

*Keywords:* Hollow fiber membranes, nanocomposite membranes, nanomaterials, separation process

### INTRODUCTION

Separation is highly important to both the industry and scientific community and consists of various technologies which are conventionally, chemically or thermally intensive. In contrast, membrane separation relies on designing specific physical and chemical properties of membrane materials to enable more energy-efficient gas and liquid separations. One important class of such membranes which has garnered intense research attention is nanocomposite membranes, where membranes are modified with nanomaterials [1]. In the field of membrane research, the development of

nanocomposite-based membranes is desired since various nanomaterials can be incorporated into the membrane matrix for enhanced separation performance. In addition to this, unique features of nanomaterials can also be imparted upon them. These modifications can be implemented upon both flat sheet and hollow fiber membrane configurations. Some of the unique features imparted onto membranes include anti-fouling propensity, anti-bacterial, super hydrophilicity, super hydrophobicity, catalytic activity, and adsorbents [2, 3]. Hollow fiber membranes, which are fabricated with polymeric or ceramic based precursor materials, have been

intensely researched upon due to several advantageous properties, such as higher packing density, larger surface area and higher flux rates at lower operating pressures. The hollow fiber membrane has a large market size, valued at more than USD 9 billion in 2019 with an expected annual growth projected at 9.4% yearly till 2026 [4]. The rapid pace in which technological advancement in the field of wastewater treatment as well as the growing demand for such technology in regions facing water scarcity issue will increase product penetration in the membrane industry by 2026.

Different modifications have been attempted to improve or impart unique features to the hollow fiber membranes. These can be done by incorporating various nanomaterials inside the membrane matrix. On the other hand, modification of the physical structure of the membranes has been attempted, namely dual layer membranes where the selective layers were tailored according to the separation needs of various wastewater and gas streams. However, each method does pose specific challenges and limitations. Agglomeration of nanomaterials, loss of nanomaterial function due to even dispersion, use of hazardous solvents and delamination of layers are some challenges. Additionally, the use of biomaterials as base material for a greener approach of nanocomposite membranes has recently garnered great attention. In this article, the challenges faced in developing such nanocomposite hollow fiber membranes are discussed as well as some recommendations for future research.

## **NANOCOMPOSITE HOLLOW FIBER MEMBRANES**

Nanomaterials incorporated inside membrane matrices play a significant role in enhancing the properties as well

as separating performance of membranes. Commonly, nanomaterials are incorporated into hollow fiber membranes for several purposes, including enhanced hydrophilicity (water separation), enhanced hydrophobicity (gas separation, membrane distillation), enhanced adsorption (metal ion capture, pollutant adsorption), catalytic activity (pollutant degradation), and enhanced selectivity (gas separation). For such improvements, various types of nanomaterials have been incorporated into hollow fiber membranes. They consist of metal oxides ( $\text{TiO}_2$ ,  $\text{CuO}$ ,  $\text{Fe}_3\text{O}_4$ ), non-metallic 2D nanomaterials such as graphene oxide (GO) and graphitic carbon nitride ( $\text{g-C}_3\text{N}_4$ ), as well as metal-non-metal nanocomposites such as ( $\text{GO-TiO}_2$ ,  $\text{Si-TiO}_2$ ) [5–7]. The unique features of materials in nanoscale can be incorporated on the membrane itself, providing improved properties and performances which would not be achieved by pristine hollow fiber membranes.

Commonly, the method used to prepare such nanocomposite membranes is by blending the nanomaterials in polymeric solution or ceramic suspension before the fabrication process. During incorporation, techniques such as ultrasonication are used to ensure good dispersion of nanoparticles throughout the matrix. However, one common problem faced when dispersing nanoparticles in membrane matrices is agglomeration. Several researchers have reported that nanomaterials have a threshold loading capacity before agglomeration initiates [8, 9], which limits the effectiveness of nanofillers in improving the membrane performance. Agglomeration of nanomaterials can lead to several issues, such as non-uniform membrane pore size, formation of defects and non-selective interfacial

voids, which all reduce selectivity of membrane separation. However, several different ideas have been investigated to mitigate such agglomerations. Vu *et al.* attempted to decorate nanomaterials with polyetherimide (PEI) as an interface agent to improve dispersion, while Sadeghi modified the surface functional group of nanomaterials to enhance interaction between nanofiller and polymer matrix [10, 11]. Such modification was able to improve the liquid separation properties of membranes prepared. Several other modification methods have also been attempted to avert agglomeration of nanomaterials in membranes, including growth of nanomaterials on membrane surface and coating nanomaterials on membrane surfaces. A second potential pitfall of nanocomposite membranes is leaching of nanomaterials during fabrication and/or separation process. Kajau *et al.* discussed that nanomaterials leaching into the water source is a major problem during separation processes [12]. Changes in surface charge, surface pressure and incompatibility of nanomaterial with polymeric/ceramic material during fabrication are all issues that occur due to leaching. Leached nanomaterials result in secondary pollution and pose health risk to non-target organisms.

### **DUAL LAYERED HOLLOW FIBER MEMBRANE**

While incorporating nanomaterials into membrane matrix can improve the overall membrane performance, it is less effective to modify membrane surfaces where selective separation occurs. As a result, researchers investigated the possibility of applying concentrated nanomaterials on surfaces of the membranes via a dual co-extrusion method. In co-extrusion, two

different solutions are extruded concurrently to produce membranes of laminated layers. Here, the outer and inner layers can be tailored according to the separation requirements for enhanced selectivity and permeation performance. This was evident in the research published by Grünig *et al.*, where hydrophilic alkyl poly (ethylene glycol) blocks were used as the outer layer of membrane which improved membrane hydrophilicity as well as antifouling propensity of the membrane surface which assisted in enhancing the liquid separation properties of membranes developed [13]. Researchers also added nanomaterials only on the membrane outer layer to enhance photocatalytic activity as well as improving membrane selectivity. Yaacob *et al.*, fabricated a dual layered hollow fiber membrane where ZrO<sub>2</sub>-TiO<sub>2</sub> photocatalyst was incorporated on the outer layer of the membrane only [14]. The results indicated that the performance of the dual layer was better compared to the mixed matrix membrane due to the improved contact between catalyst and pollutant. While such membranes can focus the concentration of nanomaterials on specific layers, compatibility/adhesion between membrane layers need further attention. The use of single polymer base for both layers are recommended. Different base materials may lead to delamination of membrane layers. This is particularly a problem when designing membranes with layers of opposite characteristics (hydrophilic/hydrophobic) which commonly requires different base materials [15].

### **GREEN MEMBRANES**

Environmentalists have placed great emphasis in decarbonisation and adopting measures to reduce atmospheric carbon to mitigate climate

change. Sustainability is key for emerging and current technologies to adopt. In that sense, adoption of greener and more sustainable methods to fabricate hollow fiber membranes without sacrificing its performance is one of the emerging challenges faced by researchers. The solvents commonly used to produce hollow fiber membranes are dimethylformamide (DMF), n-methyl-2-pyrrolidone (NMP) and dimethylacetamide (DMAC). Reports have shown that the membrane industry produces more than 50 billion litres of wastewater each year during membrane fabrication process via rinsing while their recycling is difficult or uneconomical [16]. Hence, there is an urgent need to reduce or remove the use of such hazardous solvents when preparing hollow fiber membranes. One of the emerging techniques in producing hollow fiber membranes in a sustainable way is via melt/solution integrated homogeneous-reinforcement method. This method uses a reinforced thread as a support which does not partake in the separation process while polymers like polyvinylidene fluoride (PVDF) are casted on it to tailor the selective layer. Melt spinning-stretching is another solvent free method used to produce hollow fiber membranes using polymers that have stacked crystalline lamellar and micropores. Another method gaining prominence is the utilisation of electrospinning. This solvent-free process produces a continuous and interconnected nanofibers using different polymeric materials. They are advantageous as they have high porosity, high specific surface area and the fabrication mechanism which allows researchers to control the pore size of hollow fiber membrane prepared. Su *et al.* successfully fabricated a nanocomposite electrospun hollow fiber membrane using

hexafluoropropylene (FEP) and Polytetrafluoroethylene (PTFE) composite material [17]. Electrospinning proved advantageous as it allowed the formation of a porous, 3D network structure with uniform pore size and large surface area [18]. Such membranes are able to provide a platform as substrate to support nanomaterials via deposition or assembly method. Moving forward, there is also a literature gap in research conducted in fabricating hollow fibre membranes using biopolymers which are more environmentally friendly [19].

## FUTURE OUTLOOK

The membrane research has experienced a rapid rise in interest among researchers worldwide. Its wide range application, ease of scale up, facile modification, and easy fabrication means research for membranes with high flux, high rejection and low fouling tendencies are desired among researchers and industry as well as to improve throughput and reduce operating cost. It is clear that the incorporation of nanomaterials can significantly improve performance and characteristics of membranes. Further manipulating physical fabrics of the membrane, itself by producing multi-layered hollow fiber membranes allow more room for specification. However, at the field of membrane science is still in its infancy and there are plenty of scope that can be investigated to push the boundaries further. Some of the outlook that can be pursued further are listed below;

- More emphasis on research to control dispersion of nanomaterials in membrane matrix is required. Additionally, methods to concentrate nanomaterials in specific parts of membrane matrix would improve efficiency of

nanomaterials used (magnetic controlled dispersion, coating, template growth). More studies are also required to develop polishing steps to mitigate leaching of nanomaterials into source stream (encapsulation). Thin polymer coating or enhancing interaction between nanomaterial and base material can be looked into to better anchor the former to stay in the membrane matrix.

- Delamination when using polymers of different characteristics when fabricating dual layered hollow fiber membranes is a pertinent problem. Exploration on binders between layers or interconnected pathway between layers which can improve transport mechanism as well as mitigate delamination can be looked into.
- Solvent free membrane fabrication processes as well as using biopolymers to produce green membranes which can exhibit comparable or superior membrane performance. This is applicable for ceramic hollow fiber membranes, where use of natural clays to replace alumina powders can enhance the sustainability of the fabrication process. Most research on biopolymer-based membranes are focused on flat sheet membranes, which could be due to the poor structural strength of such polymers. The use of nanomaterials to strengthen the biopolymer matrix for fabrication of hollow fiber membranes can be considered.

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