

# Fabrication of Graphene-based Membranes for Solvent-resistant Nanofiltration

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**Abstract.** Solvent-resistant nanofiltration (SRNF) is a promising technology which developed rapidly in recent years, which exhibits broader application prospects in separation of industries organic solvent system. Among various materials used for SRNF-membranes, graphene-based nanomaterials have aroused great interests due to the unique molecular sieve properties and excellent tolerance to organic solvents and harsh chemical environments. This paper emphatically introduces the progresses of membrane preparation with graphene-based nanomaterials for SRNF and their application in separation processes. The performances including permeability and stability of different kinds of graphene-based SRNF membranes in the process of filtration are also evaluated and discussed.

## 1. Introduction

Membrane processes are typical advanced technology for selective separation and play an important role in water and wastewater treatment [1]. Among them, nanofiltration membranes usually show high performance in the rejection of bivalent and polyvalent ions under low operation pressure [2]. As we know, the amount of chemicals in the modern world and the conventional intensive energy in separation processes have caused the total quantity of energy for chemical products separation to be astonishing, accounted for 10-15% of the world's total energy consumption [3]. To deal with the multifarious and massive organic solution in practical applications, the solvent-resistant nanofiltration (SRNF) membranes with high permeability and stability are highly desirable [4-6].

In general, an ideal SRNF membrane should have the following characteristics: (1) high solvent flux and separation performance in organic solvent system; (2) high separation efficiency and structural stability during long-time operation; (3) the synthesized SRNF membranes are suitable for wide solvent separation in industrial application [7]. In recent years, in order to achieve SRNF membranes with high permeability and stability, many nanomaterials including graphene, Mxene, metal-organic frameworks (MOFs) have been applied to fabricate SRNF membranes [8]. Among these nanomaterials, MOFs often exhibit a poor chemical stability and more suitable for use in gas barrier applications [9-13]. Compared with MOFs, graphene-based materials have attracted numerous



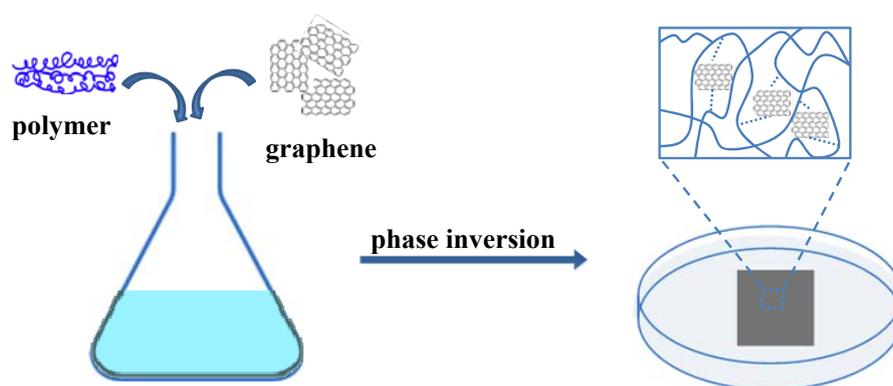
attentions due to their unique physicochemical properties, which has been proved in our experiments and elsewhere [14-20]. The unique two-dimensional (2D) structure and the good stability in organic solvents endow graphene nanomaterials to be an ideal candidate for creating novel membranes [15,21-23]. As a result of the uniform interlayer spacing, graphene membranes usually show superior solvents flux and precise molecular sieving for small organic reagents [8,17,18]. Herein, the methods of preparation of different kinds of SRNF membranes with graphene-based nanomaterials are introduced and the comparison of corresponding parameters of different graphene-based SRNF membranes during the filtration process are provided.

## 2. Graphene-based SRNF Membranes

Because of the excellent physicochemical properties and simple preparation method, graphene-based materials are widely used as versatile 2D component to fabricate molecule-selective membranes. Up to now, several approaches containing phase inversion and vacuum filtration methods have been used to successfully synthesize graphene-based membranes for SRNF. According to the microstructures, typically there are two kinds of graphene-based SRNF membranes: (1) graphene-based mixed-matrix membranes, (2) assembled graphene laminates.

### 2.1. Mixed-Matrix Membranes (MMMs)

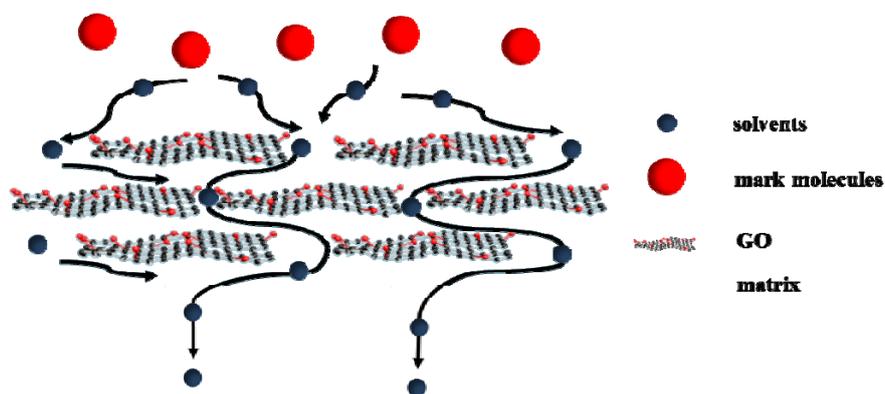
In general, traditional polymeric nanofiltration membranes possess a lot of advantages including good flexibility, simple preparation process and relatively low cost. However, the poor chemical resistance and membrane fouling problems seriously limit their development to some extent [5]. On the other hand, the inorganic membranes (such as ceramic membrane, metal membrane, zeolite membrane and glass membrane) with high flux and separation performance can be easily achieved through regular holes. Inorganic zeolite membranes usually exhibit good chemical stability, high temperature resistant, remarkable strength and long lifetime. Despite the progress achieved, inorganic ceramic membranes are brittle and high-cost in practical applications [24,25]. Therefore, MMMs which combine the advantages of organic and inorganic membranes can be a promising approach to prepare high-performance SRNF membranes [26-28]. The preparation process for graphene-based MMMs is schematically shown in Figure 1.



**Figure 1.** Schematic diagram of the graphene-based MMMs.

Since mixed matrix membranes combine the advantages of polymer and the unique characteristics of inorganic filler, graphene-based MMMs have attracted much more attention in membrane separation [29,30]. Besides, graphene can interact with polymers to form hydrogen bonds or chemical bonds, so the structure of graphene-based MMMs become very stable, which restricts its segmental mobility and improves the separation performance of SRNF membrane. For instance, Shao et al. prepared GO-polypyrrole (GO-PPy) composite SRNF membrane, which greatly enhanced the solvent permeance of methanol, ethanol and isopropanol without compromising Rhodamine B (RB) rejection, the retention rate of RB in the above organic solvents can still exceed 99% [14]. Wang et al. made

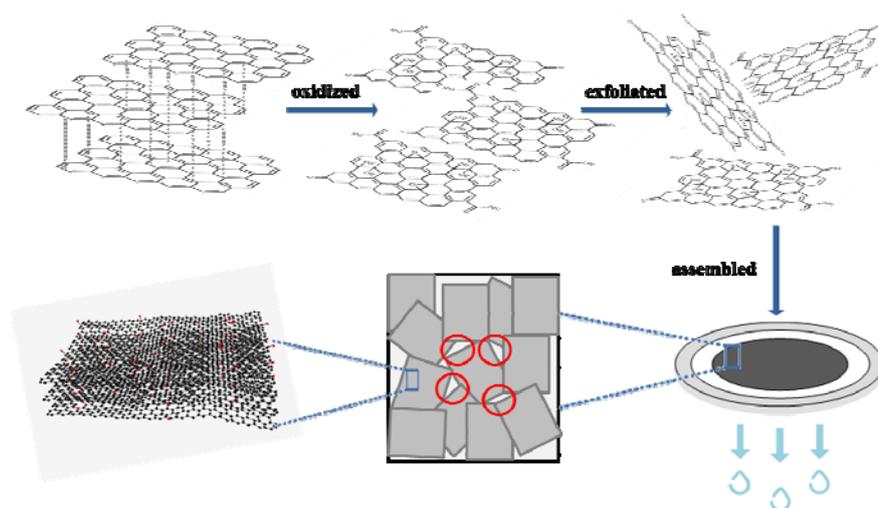
graphene oxide (GO) hybrid membrane by embedding GO sheets into polyethyleneimine (PEI) matrix. It was found that the created transport path through the GO side, the molecule rejection and solvent flux were improved largely [16]. As shown in Figure 2, solvents would pass through MMMs quickly while mark molecules would be blocked. The addition of graphene into polymer membranes is helpful for long-term stable operation and good solvent resistance.



**Figure 2.** Scheme of the separation process of the MMMs for SRNF.

### 2.2. Assembled Graphene Laminates

Up to now, the porous graphene layer is still facing many challenges. Instead, graphene derivatives can be easily prepared into ordered 2D channel structure by flow-directed (like filtration) and various coating approaches (including spray-coating, spin-coating, drop-casting, dip-coating) to assemble GO sheets [27]. The nanoscale channel of layered structure, narrower size distribution and good flexibility promise the practical utilization of such GO laminates for molecular separation. In addition, GO can easily be stripped from graphite, thus greatly reducing the cost. In particular, the rich oxygen group on GO provides active sites and can be further functionalized to enhance performance. These properties have opened up a more practical way for the large-scale production of graphene membranes [28].



**Figure 3.** Schematic illustration of assembled graphene laminates.

Huang et al. found that GO membrane has good stability in various organic solvents. Therefore, GO membrane was suitable for organic solvent nanofiltration, which can effectively improve the

versatility and stability of SRNF membranes [15]. Li et al. reported that the permeation flux of acetone and methanol of graphene oxide membranes (GOMs) on the hollow fiber ceramic substrate was higher than that of most commercial SRNF films and the molecular weight cut off (MWCO) was larger than 300Da. In order to further explore the mechanism of graphene-based membranes for SRNF, Nair et al. prepared highly laminated GO (HLGO) membranes with fluent 2D network prepared from large (10-20  $\mu\text{m}$ ) sheets and ordinary conventional GO (CGO) membranes made from smaller (0.1-0.6  $\mu\text{m}$ ) sheets. The preparation process was shown in Figure 3. They found that the permeation rate of organic solvents attenuated exponentially with the increase of membrane thickness, but the water continues to permeate rapidly. Based on the results, they supposed that organic solvent and sieving properties might be caused by the random pinholes of short interconnected channels in graphene [20].

Although Graphene-based membranes show great potential in the process of separation, most parts of the post-processing can only be carried out in a dry environment, predicting that it is far from the actual industrial application. In practice, GO membrane were easily shrunk during the drying process and then huge tensile stresses were produced in the membrane which causing obvious defects. More recently, an effective way to solve the stability problem by using the sacrificial layer in the process of membrane preparation was tried by Li et al. When the sacrificial layer was washed out, the gap between the GO layers and substrate allowed the GO membrane to shrink freely without pressure [18].

**Table 1.** SRNF Performance Comparison of Different Graphene-based Membranes.

| Membranes     | Solvents    | Mark molecule (g/mol) | Rejection (%) | Flux ( $\text{L m}^{-2}\text{h}^{-1}\text{bar}^{-1}$ ) | Duration | Ref. |
|---------------|-------------|-----------------------|---------------|--|----------|------|
| S-rGO         | methanol    | EB, 960.8             | 100%          | 75.3   | 24h      | [8]  |
|               |             | BY, 624.55            | 86.2%         | 76   |          |      |
|               |             | MB, 373.9             | 0             | 77.2   |          |      |
|               |             | BF, 377.85            | 0             | 76.9   |          |      |
|               | water       | EB, 960.8             | 100%          | 87.6   |          |      |
|               |             | BY, 624.55            | 99.2%         | 88.3   |          |      |
|               |             | MB, 373.9             | 12.6%         | 90.2   |          |      |
|               |             | BF, 377.85            | 13.1%         | 91.3   |          |      |
| GO/PMMA/YSZ   | water       | MR,269.3              | 90%           | 0.07-2.8   | \        | [18] |
|               | acetone     | MR,269.3              | 90%           | 0.14-7.5   |          |      |
| DPAN/PEI-GO-X | ethanol     | PEG <200              | 90%           | 1.5  | 10h      | [16] |
|               | acetone     | PEG <200              | 90%           | 3.5  |          |      |
|               | ethyl       | PEG <200              | 90%           | 2.7  |          |      |
|               | heptane     | PEG <200              | 90%           | 0.8  |          |      |
| GO-PPy/PAN    | isopropanol | RB,1017               | 98.5%         | 3.17   | 100h     | [14] |
| PAN/PA /GO    | ethanol     | BB,854                | 95%           | 1.9  | \        | [19] |
| HLGO          | n-butanol   | CG,249                | 95%           | 2.5  | 5h       | [20] |
|               | hexane      | CG,249                | 95%           | 18   |          |      |

### 3. Performance Comparisons of Different Graphene-based Membranes

As graphene has many adjustable spaces to enhance the properties, graphene-based membranes can achieve high flux and good performance in separation of small molecules. However, the permeances of reported graphene membranes for organic solvents were extremely low [8], especially for MMMs. Although the sacrificial layer can be used to solve the problem of shrink, the flux still remains low. The assembled graphene laminates are facing some technical challenges in practical application, such as the long-term stability during operation. In order to solve the problem of instability, the GO

membrane can be retained in the wet condition to avoid further shrink, thus effectively preventing defects [17]. Huang et al. prepared ultrathin S-rGO membranes and soaked it in the solvent when it was wet to keep its solvated state. These SRNF membranes showed high rejections while retaining their super high permeances to organic solvents [8]. But this membrane with ultrafast organic solvent permeance was aged easily under external stress. From the performance comparison (Table 1), it can be observed that graphene membranes with different characteristics and performances were well developed through different methods.

#### 4. Conclusion

In this paper, the preparation of two main types of graphene-based SRNF membranes has been presented and the performances of related graphene-based membranes have been discussed. Moreover, the characteristics and parameters of different graphene-based membranes during SRNF process are also provided in detail. On account of the rapid development of organic solvent nanofiltration technologies, graphene-based SRNF membranes have shown great potential in molecular sieving process of various industrial applications.

#### Acknowledgments

This work was supported by the National Natural Science Foundation of China (21736009, 21506193 and 21476206) and Fujian Provincial Department of Ocean (Grant No. 2014-06).

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