Carbon Nanomaterials Based Membranes

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Abstract

In the past few years, there is impressive breakthrough for the research on nano structured materials to solve global significant challenges like, water, energy, environment, medicine etc. Among various nanomaterials, carbon nanomaterials (CNMs) are gaining significant interest to the material scientists to develop advanced membranes for novel separation processes. It is believed that CNM based membranes have the potential to overcome the inherent limitations of conventional membranes separations.

Keywords: Carbon nanotube; Gas separation; Graphene oxide; Membrane; Nanocomposite; Water treatment

Introduction

As a low cost, easy to scale up, simple in operation and efficient method, membrane based separations have been widely used in many separation processes e.g. water treatments (desalination and wastewater treatment) and gas separation [1-2]. Separation through membranes is usually achieved based on the selective transport phenomenon of the molecules through the membrane matrix [3]. Reverse osmosis and nanofiltration membranes are widely used for water treatment. However, thick active separating layer of the pressure driven membranes restricts the water flux. Solution could be the reinforcement of nanomaterials in the membrane matrix to enhance the flux while achieving the targeted molecules to be separated [1].

Advanced membrane materials with excellent selectivity is required for controllable separation process of gas purifications and water treatments [4]. Among various nanomaterials, carbon nanomaterials (viz. carbon nanotube, graphene) have drawn tremendous interests in the advanced materials applications. Depending on the number of shell of graphene, carbon nanotube (CNT) can be classified as single walled carbon nanotube (SWNT) with single shell of graphene, similarly, double walled carbon nanotube (DWTN) and multi walled carbon nanotube (MWNT). Whereas, graphene is a one-atom thick sheet of graphite which contain sp2-hybridized carbon atoms nicely arranged in the hexagonal honeycomb lattices, and graphene oxide (GO) nano sheets are oxygen functional groups containing graphene which could be obtained by treating graphite with strong oxidizer [4-6]. One of the prime applications of the CNMs is reinforcing materials in the matrix (e.g. to prepare nanocomposite membranes) due to their unique physical, mechanical and other functional properties. Properties of the nanocomposite membranes depend on several factors such as nanomaterials dimensions, dispersion, distribution and interfacial interaction of nanofillers with the matrix [7]. Other common forms of CNM based membranes are vertically aligned CNT membrane, free standing CNT or graphene membranes etc. The impact of research on carbon nanomaterials for the membrane separation is growing tremendously which is reflected by number of review articles published in this area of advanced material applications [8-10].

Brief overview of CNMs based membranes

There are few approaches to fabricate CNT membranes [8]. Three common types of CNT membranes are schematically shown in Figure 1. Jenus polymer/CNT hybrid membranes can be obtained by grafting of hydrophilic and hydrophobic polymers on different sides of the CNT membranes (Figure 1a) [11]. Synthesized well aligned CNT on the substrate and subsequent filling of gaps between the CNTs, could serve as a novel membrane (Figure 1b). Filling materials could be impermeable materials such as epoxy resin, silicone nitrite, etc. [12]. The tips of the CNT can be opened by plasma treatment. The high aspect ratio, smooth hydrophobic wall and the hollow tunnel of CNT provides frictionless transport of water molecules to enhance flux though the membranes. Third type of CNT membrane is polymer matrix CNT reinforced nanocomposite membrane (Figure 1c). Reinforcement of CNT into the polymeric membrane could enhance performances such as high flux, improve permeselectivity, better mechanical properties and improvement of other functional properties for an example antifouling property [13-14]. Reinforcement of amino functionalized MWNT in the chitosan/polyvinyl alcohol (CS/PVA) matrix formed ensures better dispersion and distribution of functionalized MWNT, formed compact structure with improved mechanical property of weak pure CS/PVA adsorbive membrane [15].

Pure graphene membrane without pore is impermeable to small molecules due to the closely packed carbon atom in the lattice and repulsion of molecules by electron density of its hexagonal rings. Whereas, nanoporous graphene/graphene oxide with its high surface area can be used for advanced membrane separation due to its molecular sieving property [6,16]. Nanoporous membrane can be fabricated by arranging graphene (G)/graphene oxide (GO) with specific architecture and size. Graphene and graphene oxide based membrane could be fabricated by deposition of graphene on a substrate as and also reinforcing graphene/graphene oxide in the polymeric membrane matrix [17-18]. Graphene oxide membrane can be prepared by vacuum filtration of GO solution on a template support or spraying of GO solution on solid support by doctor blade and subsequent removing the solid support [16]. Thin and uniformly
aligned graphene oxide membrane can be obtained by spin coating [19]. Single layer GO membrane has few limitation for bulk production and uses, such as durability, stability and fragile, hence, difficult to handle [16].

![Diagram of CNT Membrane](image)

**Figure 1:** Schematics showing three common types of CNT membranes: (a) polymer1-g-CNT-g-polymer2 Janus membrane; (b) vertically aligned CNT membrane and (c) polymer-CNT nanocomposite membrane.

### Applications of CNM based membranes

Rapid rise of global population demands more energy, fresh water, and subsequent needs for waste water treatment facilities. The application of carbon nanomaterial based membranes are promising in many areas such as water treatment (viz. desalination, waste water treatment), gas treatment, fuel cells are few fields of many to states. Both gas separation as well as large-scale water treatment could be benefited by using CNMs based membrane. Membrane prepared by using aligned encapsulated CNT with open both ends allows low resistance flow of fluids, and this could be used to develop energy efficient membrane as compared with the energy intensive reverse osmosis membrane to desalinate sea water, and for gas separation as well [7]. Functionalized MWNT reinforced adsorptive membrane could be used to remove metal ions from the aqueous solution. Functional groups on MWNT can provide additional functionalities for the metal ion adsorption further creation of nano channel by the nanofillers reduces diffusive hindrance and provide supplementary pathways for the transport of metal ion to the active sites for the effective adsorption [15].

Ultrathin composite membrane of SWNT/TiO$_2$ prepared by coating of TiO$_2$ on SWNT network via sol-gel technique. Membrane shows excellent performance for separating oil-in-water with high separation efficiency. Further, membrane shows excellent anti fouling and self-cleaning performance due to the photo-catalytic degradation of organic compounds by the TiO$_2$ nanoparticles [20]. Hydrophobic polymer/CNT hybrid membrane can be fabricated via grafting of hydrophobic polymers on the surface of CNT membrane which can separate wide range of organic solvent from the water with excellent adsorption capacity and good recyclability of membranes [21]. While, Janus polymer/CNT hybrid membrane with hydrophilic and hydrophobic polymers grafted on different sides of the membranes can separate both surfactant stabilized oil-in-water and water-in-oil emulsion due to the anisotropic wettability of membranes, membrane maintain high separation efficiency and good flux [11]. Single-layer or multilayer nano-porous graphene membranes are promising for the desalination of water [22].

Advanced membrane technology can offer economic, environmental friendly and high performance solution for the gas separation. CNT reinforcement in the polymeric membrane matrix demonstrated high transport rate due to the inherent smoothness of the carbon nanotubes. Up to a threshold value of CNT loading, all gas molecules pass through the CNT tunnel, hence, increases the permeability. Whereas, higher loading of CNT limits the increase of gas permeability due to the tortuosity of the agglomerated CNT [23]. Nano-porous graphene membrane can be used for high efficiency membrane separation due to its ultrafast molecular permeation rate which could be promising for the applications in energy, environment and water solution, including carbon sequestration, fuel cells, gas separation, desalination [4-6].

### Conclusion

Carbon nanomaterials have been received tremendous attention as potential in the advanced material applications including in the field of novel membrane science and technology. Application of CNM could improve the membrane separation process. However, homogeneous bulk fabrications of CNM based membranes are still at the premature stage and required further improvements. Major challenges for the CNMs reinforced membrane are poor dispersion and distribution, and weak interfacial interaction between the dissimilar surface of CNM and matrix. Further, some form of CNM based membranes are fragile and causes significant challenges for handling and uses. Considering
these challenges, however, it is very hard to predict how CNM based membranes will shape the future membrane processes.

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