Recent developments on nanostructured polymer-based membranes

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Abstract

Advances in nanotechnology in recent years enhance the R&D in nanostructured membranes. This paper reviews the recent developments of the nanostructured polymer-based membranes, formed by incorporating nanomaterials and/or porous membranes with nanoscale pores, for gas separations, reverse osmosis, ultrafiltration, and other potential applications. Significant progress has been made on the development of nanostructured membranes for gas separations, particularly for CO₂ separations from H₂, N₂ and CH₄. Continued improvements on the nanostructured reverse osmosis polyamide membranes via interfacial polymerization have been made along with the efforts on developing novel nanostructured membranes for desalination. The modification of both the surface and bulk properties of the ultrafiltration membranes by nanomaterials can improve the membrane performance and open up the possibility of new applications in addition to those for the current ultrafiltration membrane processes.

Introduction

According to the International Organization for Standardization (ISO) [1], nanostructured material is defined as “material having internal nanostructure or surface nanostructure”, where nanostructure is defined as “composition of inter-related constituent parts, in which one or more of those parts is a nanoscale region” and nanoscale is defined as “size range from approximately 1 nm to 100 nm”. Based on the definitions, nanostructured membranes can be defined as membranes having internal or surface nanostructure [2[•]]. The nanostructured membrane can be a dense membrane incorporated with nanomaterials, a porous membrane with nanoscale pores, or a combination of both, as illustrated in Figure 1.

In this review, the recent developments of nanostructured membranes in different applications are covered, including gas separations, reverse osmosis, ultrafiltration, and several other applications including controlled release, antibiotic recovery (e.g., Cephalexin), and nanoporous supports for gas separation. Polymer-based membranes will be emphasized in view of availability, price, and ease of scale-up and commercialization.

Nanostructured Membranes for Gas Separations

Various nanomaterials have been incorporated into polymer matrixes to prepare nanostructured membranes for gas separations, including titanium dioxide (TiO₂), silica (SiO₂), carbon nanotubes, zeolite, and metal organic frameworks (MOF). The selection of the nanomaterial and polymer matrix has been the subject of extensive research recently [3-18]. Titanium dioxide was favored due to its hydrophilicity, chemical and thermal stability, and gas separation properties [3-5]. Up to 10 wt% of fumed TiO₂ nanoparticles (size of 21 nm) was homogeneously dispersed

in polyvinylacetate membranes [6]. Addition of 1 – 10 wt% of TiO_2 improved both the permeability and selectivity of the nanocomposite membranes.

Figure 1. Schematics of nanostructured membranes: (a) Dense membrane incorporated with nanomaterials, i.e., nanoparticles, (b) Porous membrane with nanoscale pores, (c) Dense membrane on a porous membrane with nanoscale pores, and (d) Dense membrane incorporated with nanomaterials, i.e., nanoparticles, on a porous membrane with nanoscale pores.

Silica can enhance the thermal and mechanical stabilities as well as the gas separation property of membranes [7-9]. Xing and Ho [10] incorporated fumed silica nanoparticles (FS) with a size of 7 nm into crosslinked poly(vinyl alcohol)-poly(siloxane) membrane matrixes for high-pressure CO_2/H_2 separation. They obtained the best performance with a CO_2/H_2 selectivity of 87

and a CO₂ permeability of 1296 Barrers (1 Barrer = 10^{-10} cm³ (STP) cm/ (cm² s cmHg) = 3.35×10^{-16} mol m/ (m² s Pa)) at 107°C and 220 psia with 22.3 wt% FS loading in the membrane.

Carbon nanotubes have excellent mechanical and thermal stabilities and potential to minimize the compaction effect in high-pressure gas separation [11,12]. Deng and Hägg [13] reinforced polyvinylamine/polyvinylalcohol blend membrane with 1 wt% of carbon nanotubes (CNTs, 1 – 2 µm in length and 20 – 80 nm in diameter) for CO₂/CH₄ separation. The CNTs were compatible with the blend polymer membrane and enhanced the water swelling, performance, and durability against the compaction effect at elevated pressures up to 15 bar (1.5 MPa). Zhao et al. [14^{••}] utilized both untreated multi-walled carbon nanotubes (MWNTs, 10 – 15 nm in diameter and 0.1 – 10 µm in length) and acid-treated multi-walled carbon nanotubes (AT-MWNTs) as mechanical reinforcing fillers in the crosslinked poly(vinyl alcohol)-poly(siloxane) membrane matrix for high-pressure CO₂/H₂ separation. During the first 18.5 days test at 1.52 MPa and 380.15 K, the membrane had no change of performance with a CO₂ permeability of 836 Barrers and CO₂/H₂ selectivity of 43. The improvement was attributed to the ability of MWNTs to improve the mechanical strength and anti-compaction property of the mixed matrix membranes. The optimum untreated MWNTs loading was 2 wt%, and as the MWNTs increased further, the membrane performance reduced with time due to the poor dispersion of the MWNTs. However, the dispersion improved with AT-MWNTs. The membrane with 4 wt% of AT-MWNTs had a stable membrane performance with a CO₂ permeability of 896 Barrers and a CO₂/H₂ selectivity of 50.9 for at least 11 days.

Graphene oxide has the potential in gas separation application once an ultra-thin (1 – 10 nm) of few layers of graphene is used [15-16]. Shen et al. [17] incorporated laminar structures of

graphene oxide with a thickness of 6 – 15 nm into the polyether block amide (PEBA) matrix and reported a CO₂ permeability of 100 Barrers and a CO₂/N₂ selectivity of 91.

MOFs, which consist of metal ions and organic molecules in three-dimensional structures with high surface area and porosity that can be fine-tuned, have attracted interests from many researchers [18-20]. A dual layer (organic- and inorganic-based) was formed when the zeolitic imidazolate framework (ZIF)-8 with a pore size of 0.34 nm was used as an inorganic filler in the PEBAX-2533 polymer matrix [21]. As the loading of ZIF-8 increased, the inorganic-based layer thickness increased and hence the permeability was increased whereas the selectivity was constant or slightly reduced.

Polymers of intrinsic microporosity (PIMs) have been considered for gas separation application primarily due to its microporosity, which results in a high free volume [22-24]. One type of polymers of intrinsic microporosity (PIMs), PIM-1, has recently been blended with other components such as mesoporous chromium (III) terephthalate MIL-101 [22], polyetherimide [23], and porous aromatic framework PAF-1 [24] in order to improve the specific surface area, gas transport properties, and reduce the porosity loss (physical aging).

Many efforts were made recently to reduce the thickness of the membrane selective layer in order to improve the permeance of gas separation, and some researchers were getting close to the nanoscale range of membrane thickness [25-29]. Nanoporous ultrafiltration membranes were utilized as the supports for very thin selective layers to maintain a good mechanical property. Qiao et al. [25[•]] coated a thin layer of polyvinylamine/piperazine with a thickness as thin as 130 nm on a polysulfone ultrafiltration membrane. The membrane with 220 nm of thickness had a CO₂ permeance of 2.18 μmol/(m² s Pa) and a CO₂/N₂ selectivity of 277 at 22°C and 0.11 MPa. Ho and coworkers [26[•]] developed a novel inorganic/polymer composite membrane, consisting

of a selective amine-containing polymer cover layer / a zeolite nanoparticle layer / a polymer support, for CO₂ capture. Zeolite-Y nanoparticles with around 40 nm of diameter were synthesized with a rapid (1 hour) zeolite growth method [27] and then packed into a layer with a thickness of 250 nm. A selective amine-containing polymer cover layer with a thickness of 200 nm was coated on the zeolite layer. They continuously fabricated a 14" wide of the inorganic/polymer composite membrane and rolled it into a spiral-wound module with a countercurrent configuration. The membrane showed great potential for the post-combustion CO₂ capture from flue gas in coal-fired power plants [28].

Merkel and coworkers [29**] developed a CO₂-selective membrane for H₂ production and CO₂ capture in three stages: laboratory tests (membrane area = 30 cm²), pilot-scale test with real syngas (membrane area = 1 – 4 m²), and membrane demonstration system (membrane area = 20 m²) at the National Carbon Capture Center (NCCC) in Wilsonville, AL. The thin-film composite PolarisTM membranes consisted of around 50 – 200 nm of a CO₂-selective layer on top of around 50 – 200 nm of a gutter layer, which were prepared by dip-coating on a nanoporous ultrafiltration support. The membrane demonstration system fed with 227 kg/h of syngas with around 9% of CO₂ produced a liquid CO₂ product with > 95% of CO₂.

Nanostructured Membranes for Reverse Osmosis

The commercial reverse osmosis membranes are based on a thin-film composite (TFC) of aromatic polyamide on a porous substrate layer prepared via interfacial polymerization, which was invented by Cadotte in 1981 [30]. Therefore, improvements on the state-of-the-art reverse osmosis membrane can be achieved either by improving the polyamide TFC layer or improving

the porous substrate layer. The polyamide TFC layer can be improved by incorporation of additives [31[•]] or incorporation of nanomaterials to form nano-enhanced membranes [32[•]].

Zhao et al. [33,34] incorporated hydrophilic additives during the formation of polyamide membrane by interfacial polymerization on a nanoporous (~7 nm) polysulfone substrate. They concluded that the hydrophilic additive of *o*-aminobenzoic acid-triethylamine (*o*-ABA-TEA) salt gave stable performance of a high water flux of 52.6 gfd (1 gfd = 1 gal/(ft² day) = 4.72 x 10⁻⁷ m³/(m² s)) and a salt rejection of more than 98.8% under testing with brackish water desalination condition of 2000 ppm NaCl solution at 225 psi and 25°C for at least 30 days. The fouling resistance of the membrane was improved by coating a crosslinked polyethylene glycol (PEG-200) layer on top of the polyamide membrane. The membrane exhibited a salt rejection of 98.4% and a very high water flux of 60.4 gfd, which was more than twice of the water flux of the commercial FT-30 membrane. The membrane modified with the crosslinked-PEG had much less water flux reduction due to cationic surfactant (dodecyltrimethylammonium bromide) or organic foulant (tannic acid), which was attributed to the more hydrophilic and smoother surface of the modified membrane.

Zhao and Ho [35^{••}] subsequently tested the high-flux membrane under seawater desalination conditions, both synthetic as well as real seawater from Port Hueneme, CA. The membrane gave a water flux of 44.4 gfd and a salt rejection of 99.41% during the test with a synthetic 3.28 wt% NaCl solution at 800 psi (5.52 MPa) and 25°C. A stable but slightly lower water flux of 41.6 gfd and a salt rejection of 99.4% were obtained during the 30-day test with the real seawater from Port Hueneme, which was attributed to the higher NaCl content of 3.45 wt%. In the presence of sodium alginate (NaAlg), an organic foulant from seaweed, the high-flux membrane with the hydrophilic additive had a considerably less water flux reduction as compared to the basic

membrane without the hydrophilic additive. It was believed that the negatively charged, hydrophilic groups provided by the hydrophilic additive as well as the improved smoothness of membrane surface were the causes of the improved fouling resistance of the high-flux membrane.

For reverse osmosis application, nanomaterials such as zeolites, carbon nanotubes, and graphene oxide are promising since they can be synthesized to have non-tortuous pores on the order of a few nm for the transport of water molecules in the desalination process [36-42]. Fathizadeh et al. [36] incorporated nano-NaX zeolite (40 – 150 nm) during the formation of polyamide membrane via interfacial polymerization. The nano-NaX zeolite increased the water flux by 1.8 times of the neat polyamide membrane without any change in the salt rejection. Pendergast et al. [37] used Linde Type A zeolite to prepare the polyamide membrane via interfacial polymerization on either a polysulfone or zeolite A-polysulfone nanocomposite support.

Advances in the carbon nanotube (CNT) synthesis enable the production of CNTs with a diameter as low as 1.6 nm [38[•]], which makes it useful for the reverse osmosis application. Vertically aligned [VA] and mixed matrix membranes [MMM] containing carbon nanotubes are two types of membranes which have been explored recently [39[•]]. The VA-CNT membranes were prepared by aligning CNTs vertically with supportive fillers between the carbon nanotubes [40]. MMM-CNT membranes were synthesized by incorporating the CNTs into the polymer matrix [41].

Graphene oxide (GO) is a layer of graphite carbon, oxygen, and hydrogen in a thickness around an atom with tunable pore sizes that can be used as molecular sieves [38[•]]. Choi et al. [42] coated multilayers of graphene oxide via layer-by-layer deposition of oppositely charge GO

nanosheets. They demonstrated an improvement on the reduction of salt rejection of the membrane upon exposure to chlorine due to the inert nature of the GO nanosheets.

Considerable efforts were put to develop a new membrane which could outperform the interfacially polymerized aromatic polyamide membranes. Inorganic zeolite membranes were studied including silicalite, ZSM-5, sodalite (SOD), and Linde Type A (LTA) zeolites [32[•]]. Kim et al. [43] synthesized poly(arylene ether sulfone) containing functional zeolite nanoparticles and obtained a water flux of 22.3 gfd and a salt rejection of 98.8%. Akin et al. [44] synthesized the reduced graphene oxide/polyaniline composite dispersed in polysulfone prior to the phase inversion polymerization method. However, more research remains to be done before heading into commercialization of these novel membranes.

Nanostructured Membranes for Ultrafiltration

Ultrafiltration is a membrane-based separation process used in applications such as water treatment and the product separation in food, dairy, textile and chemical industries. Ultrafiltration membranes generally have pores in the nanoscale range of 1 – 100 nm and are prepared by the phase inversion method [45]. The most common way to create the pores in the phase inversion method is by immersion precipitation (also known as nonsolvent induced phase separation), in which a polymer solution cast on a support is immersed in a coagulation bath containing a nonsolvent. During the immersion step, an exchange of solvent and nonsolvent occurs and porous membranes are formed.

One of the recent advances in the preparation of ultrafiltration membranes is the incorporation of inorganic nanoparticles in order to improve the membrane properties such as mechanical strength, structure, hydrophilicity, and surface charge [46-57]. Poly(vinylidene fluoride) (PVDF)

is the most popular polymer used in low-pressure ultrafiltration for water treatment application [46[•]]. Hong and He [47] incorporated ZnO nanoparticles into PVDF and reported that the membrane had a photo-catalysis self-cleaning capability. Jin et al. [48] compared the effects of different fillers (organic additives and nano-TiO₂) on the performance of the PVDF membranes. Yi et al. [49] estimated the fouling stages of Al₂O₃/TiO₂ nanoparticles-modified PVDF membranes in oil/water emulsion separation.

Polysulfone (PSf) is often selected due to its availability commercially, fluid transport properties, ease of processing, and thermal stability [50[•]]. Alhoshan et al. [51] revealed that the PSf membrane containing nano-ZnO had a hydrophilic, smooth, tightly packed surface and a spongy structure with well-interconnected pores. Wu et al. [52] incorporated silica-graphene oxide (SiO₂-GO) nanohybrid into a PSf membrane and increased the water flux up to two times of the PSf membrane. Liu et al. [53] had a breakthrough on the tradeoff between permeability and selectivity of PSf membranes by embedding zeolite 4A, which regulated the morphology and provided nanoscale water flow channels as well as negatively charged membrane surfaces.

Polyethersulfone (PES) is widely used due to its outstanding oxidative and thermal stabilities and mechanical property [54[•]]. Lin et al. [55] embedded tungsten disulfide nanoparticles (nano-WS₂) into a PES membrane and improved the water permeability, solute rejection, and fouling resistance of the PES membrane. Kim et al. [56] compared two methods to incorporate TiO₂ into a PES membrane, i.e., embedding TiO₂ during phase inversion and surface coating by layer-by-layer deposition of TiO₂. Akar et al. [57] investigated the characterization and biofouling properties of the PES membrane containing selenium (Se) and copper (Cu) nanoparticles.

Other polymers (polyacrylonitrile, polyimides, polyamides, and polytetrafluoroethylene) can also be used to synthesize ultrafiltration membranes [58[•]]. The nanoscale range of ultrafiltration

membranes is also attractive for applications outside of ultrafiltration. Researchers attempted to manipulate the pore size and porous structure of the membranes to suit the intended applications [59-67].

Yen et al. [59] varied the polymer concentration in the casting solution during the thermally- and nonsolvent-induced phase inversion steps and reduced the pore size from 90 nm to 55 nm to control the release of lysozyme at a constant rate. This poly(caprolactone) membrane showed potential as a controlled-release drug delivery device for biomedical application. They also investigated the effects of plasma power and treatment time [60] and the effects of graft density and chain length [61] on polyethyleneglycol grafting to prevent biofouling.

Vilt and Ho [62-64] used hollow fiber modules (Module G453 from Membrana) with a pore size of 0.03 μm (30 nm) and a porosity of around 40% as a support of the supported liquid membrane with strip dispersion (SLM-SD) to recover Cephalexin by using the carrier Aliquat 336 (QCI). The mass transfer resistances were analyzed, and the extraction reaction resistance was found dominant (> 90%). In situ removal and recovery of Cephalexin by SLM-SD following the enzymatic synthesis of Cephalexin by using two hollow-fiber modules in series was able to increase the Cephalexin yield from 32% to 42%.

In order to minimize the extraction reaction resistance, Hao et al. [65,66] proposed the supported liquid membranes with feed dispersion (SLM-FD) and organic dispersion (SLM-OD). The SLM-FD was prepared by dispersing the aqueous feed solution in the organic membrane phase, whereas SLM-OD was done by dispersing the organic membrane solution in the aqueous feed phase. The extraction reaction resistance in the SLM-FD as well as SLM-OD was greatly reduced due to a large mass transfer area formed by the dispersions. Moreover, the SLM-OD offered an advantage of the reduced organic membrane solution amount.

Ho and coworkers [67] developed the continuous fabrication of 14-inch wide polyethersulfone (PES) supports with various pore sizes ranging from 40 nm to 90 nm. The membrane with a pore size of 69.5 nm and a porosity of 16.9% was very similar to the commercial PES ultrafiltration membrane (pore size = 72.3 nm, porosity = 15.8%) used in protein purification. Alternatively, the membrane can also be used as a nanoporous support for a very thin selective layer for gas separation application since the nanoporous support will provide a negligible resistance for gas transport.

Concluding Remarks

Remarkable progress has been made during recent years in nanostructured polymer-based membranes for gas separation applications, particularly for CO₂ separations from H₂, N₂ and CH₄. Commercial processes based on the nanostructured membranes may emerge soon as potential technologies in gas separation. Improvement on the commercial nanostructured polyamide membranes through interfacial polymerization for desalination by reverse osmosis has been the subject of intensive research, in addition to the continuous effort to synthesize novel membranes which can outperform the polyamide membranes. The nanoscale porous structures and properties of ultrafiltration membranes can be modified by nanoparticles to broaden the use of such membranes.

Although there are many possibilities of nanostructured polymer-based membranes, a careful evaluation on the limitation of each membrane is required such as material availability, cost, ease of processing, compatibility, scale-up prospect, and safety risks associated with nanomaterials. If an extensive study has been done in the preparation and characterization of novel

nanostructured membranes, then the limitations may be recognized. The future study can then be focused on improving or debottlenecking the current limitations.

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