Available online at www.sciencedirect.com

ScienceDirect

Current Opinion in
Chemical Engineering

Recent developments on nanostructured polymer-based membranes

Witopo Salim[1] and WS Winston Ho[1,2]

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 CO_2 separations from H_2, N_2 and CH_4. 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.

Addresses
[1] William G. Lowrie Department of Chemical and Biomolecular Engineering, The Ohio State University, 151 West Woodruff Avenue, Columbus, OH 43210-1350, USA
[2] Department of Materials Science and Engineering, The Ohio State University, 2041 College Road, Columbus, OH 43210-1178, USA

Corresponding author: Ho, WS Winston (ho.192@osu.edu)

Current Opinion in Chemical Engineering 2015, **8**:76–82

This review comes from a themed issue on **Nanotechnology**

Edited by **Hong Yang** and **Hua Chun Zeng**

For a complete overview see the Issue and the Editorial

Available online 31st March 2015

http://dx.doi.org/10.1016/j.coche.2015.03.003

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.

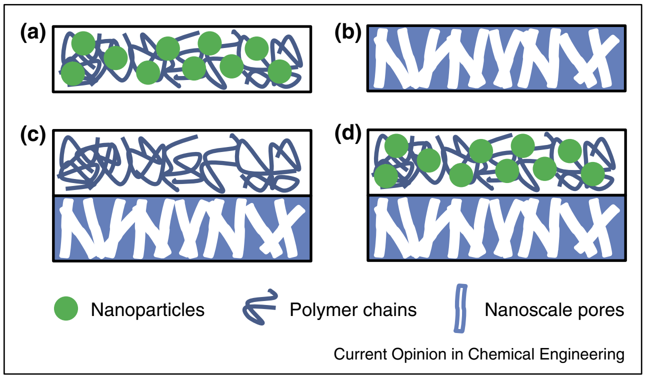
Nanostructured membranes for gas separations

Various nanomaterials have been incorporated into polymer matrixes to prepare nanostructured membranes for gas separations, including titanium dioxide (TiO_2), silica (SiO_2), carbon nanotubes, zeolite, and metal organic frameworks (MOF). The selection of the nanomaterial and polymer matrix has been the subject of extensive research recently [3–13,14••,15–18]. Titanium dioxide was favored due to its hydrophilicity, chemical and thermal stability, and gas separation properties [3–5]. Up to 10 wt% of fumed TiO_2 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.

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 CO_2 permeability of 1296 Barrers (1 Barrer = 10^{-10} cm^3 (STP) cm/(cm^2 s cmHg) = 3.35×10^{-16} mol m/(m^2 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 CO_2/CH_4 separation. The CNTs were compatible with the blend polymer membrane and enhanced the water swelling, performance, and durability against the

Figure 1



Schematics of nanostructured membranes: **(a)** dense membrane incorporated with nanomaterials, that is, nanoparticles, **(b)** porous membrane with nanoscale pores, **(c)** dense membrane on a porous membrane with nanoscale pores, and **(d)** dense membrane incorporated with nanomaterials, that is, nanoparticles, on a porous membrane with nanoscale pores.

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 CO_2/H_2 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 CO_2 permeability of 836 Barrers and CO_2/H_2 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 CO_2 permeability of 896 Barrers and a CO_2/H_2 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 CO_2 permeability of 100 Barrers and a CO_2/N_2 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-based 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•,26•,27,28,29••]. 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 CO_2 permeance of 2.18 μmol/(m^2 s Pa) and a CO_2/N_2 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 CO_2 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 inch 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 CO_2 capture from flue gas in coal-fired power plants [28].

Merkel and coworkers [29••] developed a CO_2-selective membrane for H_2 production and CO_2 capture in three stages: laboratory tests (membrane area = 30 cm^2), pilot-scale test with real syngas (membrane area = 1–4 m^2), and membrane demonstration system (membrane area = 20 m^2) at the National Carbon Capture Center (NCCC) in Wilsonville, AL. The thin-film composite Polaris^{TM} membranes consisted of around 50–200 nm of a CO_2-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/hour of syngas with