

# Application of Sustainable Nanocomposites in Membrane Technology



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## 1 Introduction

Nowadays nanocomposite membrane technology is widely used in industrial application. The developments of polymer membrane using new generation materials that broaden the industrial applications of membrane processes entail an elevated level of control over a polymer base and nanoparticles addition in the support layer. Polymeric membrane-based separation processes provide a sustainable separation technique for solid/liquid/gas permeance and selectivity [32–35]. Membrane-based separation is economical and conventional base separation process. Especially the nanocomposite membrane-based separation technology is environment-friendly and economically viable. Development of nanocomposite membrane technology for diverse application is one of the best ways to resolve the current inescapable problems.

Currently, nanocomposite membrane technologies are used in gas separation, for example, functionalized  $\text{TiO}_2$ ,  $\text{SiO}_2$  NPs incorporated thin-film nanocomposite (TFN) membranes are widely used for mixture gas separation to enhance the gas permeance and selectivity [13, 33, 34]. Also same type of nanocomposite membrane materials are used for water purification [21], wastewater treatment [61], dye separation [88] water vapour separation [5, 31, 33, 34] drug separation [91] etc. NPs incorporated membranes are mechanically strong and thermally more stable compared to without NPs incorporated membranes. Generally, two kinds of nanocomposite membranes varieties are available either it is a flat sheet or hollow fiber shape. Addition of inorganic moieties in the polymer matrix is increases the flexibility and ductility of organic polymers. Recent decade researchers found that the commercialization of nanocomposite membrane is easiest way compared with

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another kind of membrane over enhanced flux and selectivity. Khalid et al. suggested that PEG-CNTs nanocomposite PSU membranes are more advanced for wastewater treatment [43]. Nanocomposite membranes also provide motivation to unite the qualities of inorganic nanomaterials and polymeric matrices for exceptional nanofiltration performance [55]. Recently researchers develop the low fouling ultrathin nanocomposite membranes for efficient removal of manganese and lithium [76, 82].

To develop the nanocomposite membrane technology in large scale, early it was the main task of the researcher and now the commercial technology is available in the market. The nanocomposite membranes having mechanical, thermal and swelling properties have developed by using cellulose nanocrystals and PVA [36]. Nanocomposite membrane technology is also applicable for fuel cell applications [7, 84, 86]. Antibacterial mixed matrix nanocomposite membranes fabricated using hybrid nanostructure of silver-coated multi-walled carbon nanotubes by Aani et al. [1]. Using nanocomposite anion exchange membranes, Fernandez-Gonzalez et al. studied the valorization of desalination brines by electrodialysis with bipolar membranes [26]. Within the broad array of commercially existing nanoscale materials,  $\text{TiO}_2$  NPs are gained special interest for water desalination [25, 73]. In membrane distillation perfluorododecyl trichlorosilane (FTCS) was employed to modify the virgin polyvinylidene fluoride electrospun nanofiber membrane (PVDF ENM) [72].  $\text{TiO}_2$  (P25 and ST01) deposited on porous ceramic materials for photocatalytic degradation of organic substances in water, a three-phase catalytic membrane contactor (CMC) was implemented [47, 49].

Structural modification of the polymer membrane materials improves the membrane permeability, permselectivity along with mechanical straight and thermal stability. These properties would play a very significant role in membrane science and technology. Thin film nanocomposite membranes are one of the best examples in membrane science to resolve the various issues related to water [66, 70, 78], energy [80], pharmaceuticals [39], environment [10, 33, 34] etc. Further, incorporation of nanoparticles on the thin layer while polymerization especially graphene oxide (GO) membranes offer a wide range of opportunities. Such materials can be engineered to exhibit the desired for the separation characteristics because of ultimate thinness, flexibility, chemical stability and mechanical strength. Different to glassy polymers with a rigid backbone and a high portion of free volume (PTMSP) or with highly interconnected free volume polymers of intrinsic microporosity, GO materials can achieve high-flux and high-selectivity at the same time.

Nanoparticles incorporation to a polymer matrix control the permeability [60] throughout the subsequent sound effects: (a) they work as molecular sieves and amended the permeability [95], (b) also they interrupt the polymeric structure and increase the permeability [15]. One of the examples for Global warming is the result of increasing atmospheric concentration of greenhouse gases such as carbon dioxide ( $\text{CO}_2$ ), methane ( $\text{CH}_4$ ), nitrous oxides ( $\text{NO}_2$ ), hydrofluorocarbons (HFCs), perfluorocarbon (PFC) and sulfurhexafluoride ( $\text{SF}_6$ ). These gases trap an increasing portion of terrestrial infrared radiation so, it is expected that global temperature will increase between 1.4 and 5.8 °C in 2100 if no policies on climate change are

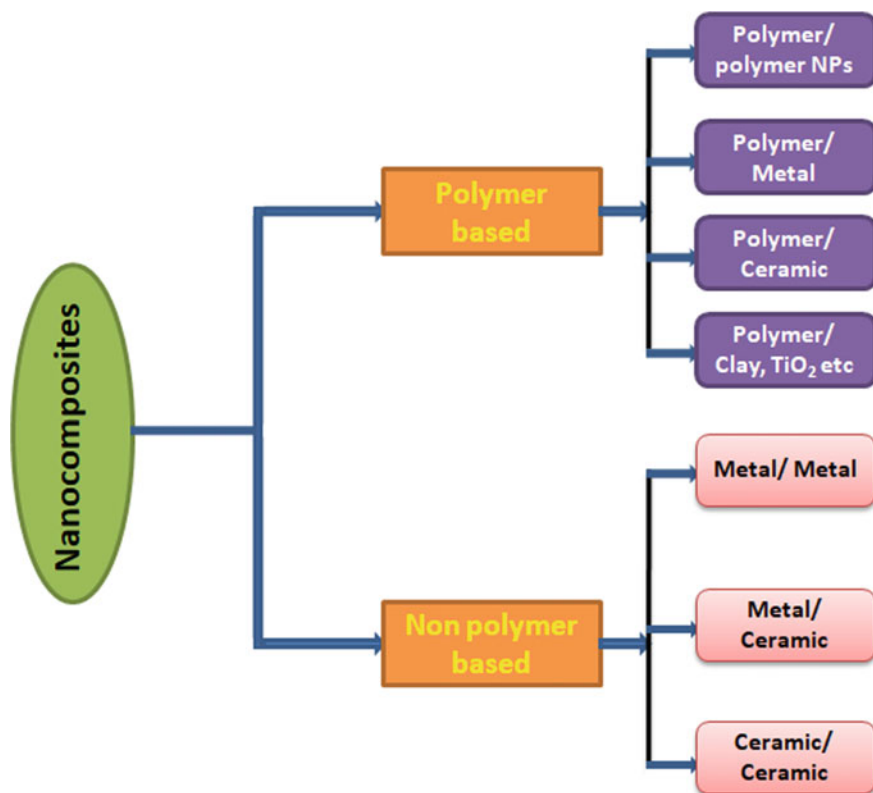
initiated. The temperature variation causes devastating effects in large and diverse areas of the globe such as possible variations in sea levels, changes in ecosystems, biodiversity loss, reduced crop yields and changes in global precipitation patterns, among other. Different types of membrane gas absorption processes will be tested for the removal of GHGs, both solid and in liquid suspension [18, 41]. Target GHGs will be carbon dioxide, nitrous oxide and methane [46]. This elimination is performed by adsorption and/or absorption processes. The experiment will involve separation and kinetic experiments (isotherms) with nanoparticles and membranes under different conditions of concentration, both in dry or in liquid media, bottled in a small volume and operating in discontinuous (microcosm systems) and perfectly airtight. In order to think in future industrial scale implementation, special attention will be focused on the immobilization of the nanoparticles in porous supports or membranes. In this chapter, the weight has been given to nanocomposite membranes preparation and their implementation in diverse applications including gas separation, water desalination, wastewater treatment, water vapour removal, and energy generation.

Nanocomposite materials especially nanocomposite membranes are facilitating speedy improvements in structural and functional materials diagonally all industries and most of the applications. Recently developed a new method of incorporating functional nanoparticles (10–15 nm) in polymer films, which has guided to the manufacture of a new method of thin film nanocomposite (TFN) membranes technology [33]. Super-hydrophilic nanoparticles synthesis and implementation is the first invention of TFN-based membranes. Introduction studies verify that TFN membranes separate the water vapour, with significant energy savings; and it has super-hydrophilic nature. The commercialization or large-scale productions of TFN membranes using prepared nanoparticles are possible without a major change in TFC membrane process and even cost is also not much higher. It will affect only 5–7% higher cost compare with TFC but the results showed the significant effect. Figure 1 represents the types of nanocomposite used in polymer and non-polymer base materials.

## 2 Types of Nanoparticles

### 2.1 *Inorganic Metal Oxide and Hydroxide*

Along with the numerous groups of nanoparticles, inorganic metal oxide and hydroxide have been of extensive attention from both technological and scientific point of view. Compared to the untainted materials the nano size synthesized metal oxide and hydroxides show the superior properties. Nowadays metal oxides and hydroxides are incorporated into other supports, such as polymeric materials for the applications like supercapacitor electrodes [42], polymer composites for aerospace applications [65], etc. Our group have the experience to synthesize SiO<sub>2</sub> NPs having



**Fig. 1** Polymer and non-polymer based nanocomposite

particle size 10 to 15 nm and implemented it successfully in the nanocomposite membrane materials for diverse applications. Also, amorphous hydroxylated Silicon nanoparticles were synthesized in alcohol-based solvents to fabricate nanocomposite membranes have excellent surface hydrophilicity and roughness. After functionalization, nanoparticles showed higher cross-linking density, higher loading capacity, and high membrane performance.

Even though ceramic membranes play very imperative role in water treatment the polymer membrane technology has achieved noteworthy attention for water treatment applications because of advanced characteristics like its high flexibility, broad range of pore sizes and structures, easy developed process, low costs and easy to scale up [43, 61, 97].

## 2.2 Inorganic Nanoparticles to Prepare Polymeric Nanocomposite Membranes

In the polymeric composite membranes mechanical performance, lucidity, and thermal stability still remain the controlling limit for the various applications. Thus, the researchers need to develop strong, transparent and heat-resistant nanocomposite membranes for encouraging realistic outcomes. To develop the nanocomposite membrane, the main innovational target consist of concurrently obtaining high permeability and high selectivity at minimum costs, uniting reactions within the pore structures to avoid membrane fouling with avoiding further downstream unit operations, and rising membrane physical strength [50, 69, 84, 86].

Functional polymer membranes are usually premeditated and optimized with precise applications in researchers mind. Figure 2 represents the variety of nanocomposite membrane materials for diverse applications. The presence of functional groups on the surface of nanoparticles not only provides the hydrophilic nature but also reduced the Van der Waals interactive forces between nanoparticles [8]. Nanocomposite membranes, an innovative class of membranes prepared by coalescing polymeric materials with nanomaterials, are rising as a capable elucidation to resolve the various challenges. Especially several inorganic nanoparticles like zirconium phosphates, heteropolyacids, clays, ionic liquids, metal or metal oxides [4, 37, 67, 74], are of extraordinary attention for developing the composite materials. In the fuel cell application, the inorganic nanoparticles like zirconium phosphates, boron phosphate in the nanocomposite membranes do not only provide the water uptake but also provide an extra proton transport pathway [45].

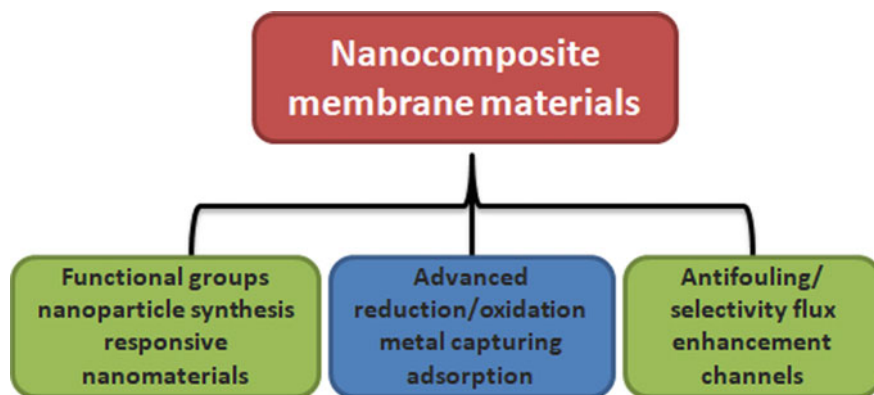


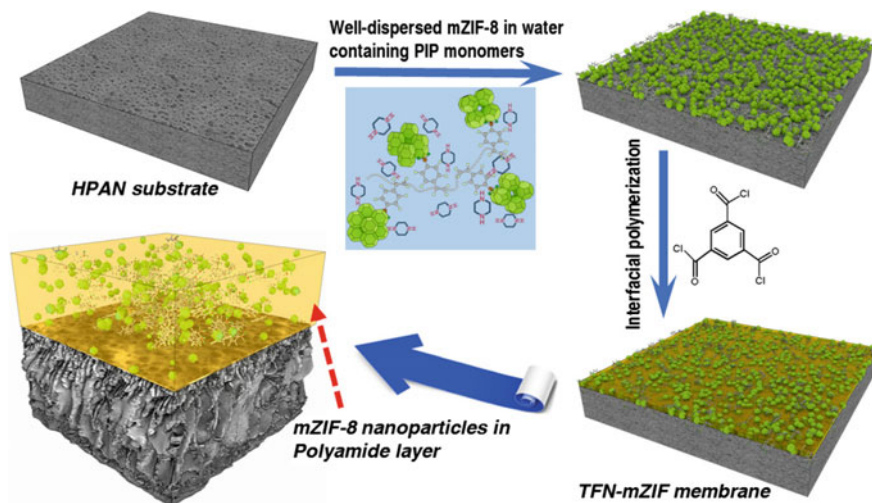
Fig. 2 Diverse nanocomposite membrane materials with various characteristic

### 3 Thin-Film Nanocomposite (TFN)

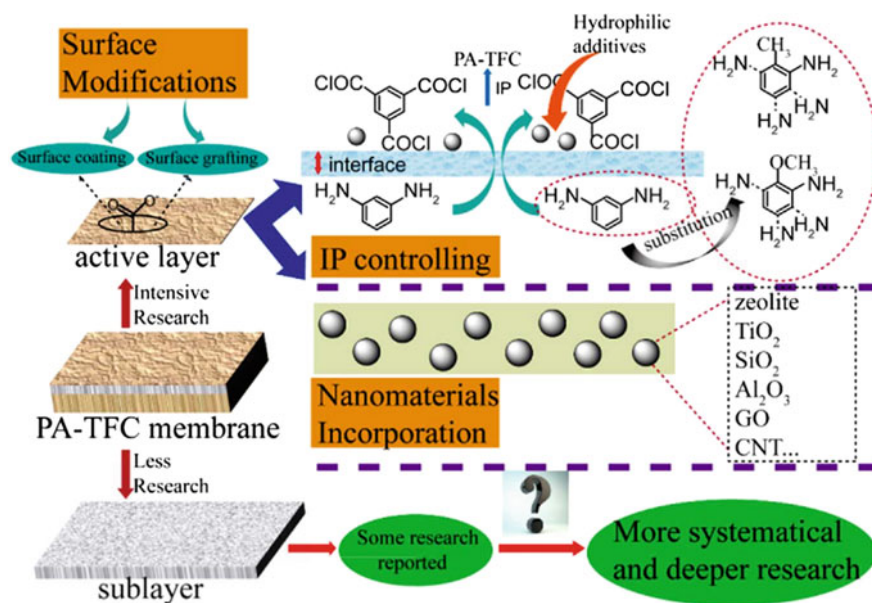
#### 3.1 *Thin-Film Nanocomposite (TFN) Membranes for Water Desalination*

Many efforts have been dedicated to developing the advanced membrane technology to improve the performance of membrane in the form of flux, solute rejection and antifouling properties in the last 3 decades. Year after year research is going to progress and currently, researchers are focusing on nanocomposite membrane to improve the membrane properties. One of the attention was selected by researchers is to prepare the advance thin-film nanocomposite membrane along with support for the high flux, high rejection and antifouling property. Various conditions have been changed while interfacial polymerization (IP) to prepare TFN membranes, changing monomers, monomer concentrations, nanoparticles concentration, nanoparticles size, reaction times, applying chemical modification etc.

Nanomaterials are at present controlling the existing wave of original membrane material development because of the intrinsic explicit physicochemical features that make them apt for water treatment [97]. A number of nanoparticles like silica, graphene, zeolites, carbon nanotubes (both single and multiwalled), silver, metal-organic frameworks (MOFs), silicon and titanium dioxide are the mainly tested nanoparticles in existing and current research. The membranes prepared by using above-mentioned nanoparticles have been shows improved results in the form of permeability, rejection and antifouling properties [2, 24, 102]. Nanoporous silica incorporated membrane shown to reveal a high affinity for water and advanced hydrophilicity of TFN membrane [81]. A  $\text{TiO}_2$  and silver nanoparticles have the main characteristic, is strong antimicrobial property so it is important material to develop the TFN membrane to resolve the biofouling issue [44, 96]. Biofouling is happened due to the formation of biofilm on membrane surface due to the intrinsic hydrophobicity of membrane materials. A metal-organic framework (MOF) is one of the best materials for water purification. Zhe et al. prepared the thin-film nanocomposite (TFN) membrane containing PSS-modified ZIF-8 nanoparticles via interfacial polymerization for the nanofiltration as shown in Fig. 3 [104]. The well TFN membrane process as shown in Figs. 3 and. 4 clearly understood that how the membrane is developed on the substrate via interfacial polymerization [94, 104]. To trounce this shortcoming, a variety of nanocomposite membranes are being modified to convey properties such as anti-fouling, hydrophilicity, self-cleaning, photocatalytic, and photodegradation using the nanoparticles (NPs) incorporated in polymeric membrane matrix or use in the interfacial polymerization process. Somehow still, it challenges the researchers to develop the cheapest nanomaterials to fabricate TFN membranes for commercial use.



**Fig. 3** Preparation process of thin-film nanocomposite (TFN) containing PSS-modified ZIF-8 nanoparticles via interfacial polymerization. Reprinted from Ref. [104], Copyright © 2017 American Chemical Society



**Fig. 4** Surface modification using different NPs to make nanocomposite layer. Reprinted from Ref. [94] Copyright © 2017 with permission from Elsevier

### 3.2 *Thin-Film Nanocomposite (TFN) Membranes for Wastewater Treatment*

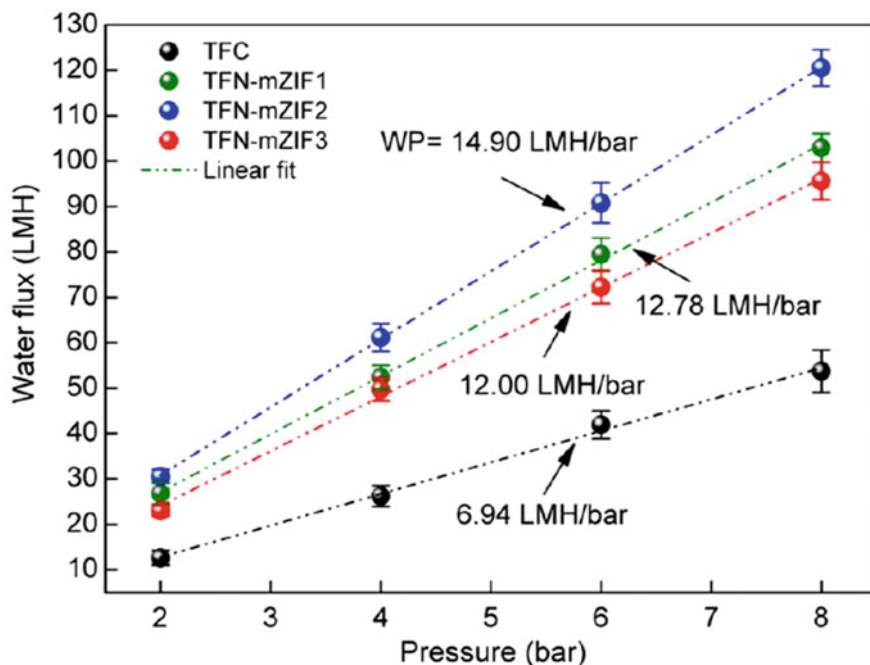
In the reverse osmosis (RO) thin film composite (TFC) membranes are familiar for FO applications [14, 27, 28, 85, 87, 93, 99]. The technique used to make ultrathin polyamide (PA) selective rejection layer on the surface of porous polymer support is interfacial polymerization. Compare with market available commercial membranes (ex. Cellulose membrane) the thin film composite membranes are shown high permeability and also good resistance aligned with biodegradation [20, 103]. There are some disadvantages of TFC membranes while an operation like intrinsic internal concentration polarization (ICP), solute reverse diffusion and fouling has been found. Then researchers think there is need to develop such membranes which will resolve the above issues. So, Jeong et al. studied the concept of fabricating nanocomposite membranes and use it for RO application [38]. Furthermore, Ma et al. also develop the thin-film nanocomposite (TFN) membranes using NaY zeolite nanoparticles incorporation in the active layer while IP [57]. Later on, many research has been done by the researchers using  $\text{TiO}_2$ , silica,  $\text{SiO}_2$ , clay, carbon nanotubes, activated carbon, incorporated TFN membranes for wastewater treatment. The incorporation of NPs is useful for to improved surface hydrophilicity and because of it flux also enhanced drastically. In wastewater treatment researchers use functionalized MOF, CNT and other NPs like  $\text{TiO}_2$  to improve the performance of nanocomposite membranes [56, 68, 104].

Comparative results of permeation through TFC and TFN membranes are shown in Fig. 5 on different operating pressure. Here in the TFN membranes while preparation added a different concentration of MOFs i.e. mZIFs. As a result, the water fluxes were increases sharply while increasing the operating pressure verifying a stable nanofiltration system. Based on the experimental data the water flux increases for TFC membrane  $6.94 \text{ LMH bar}^{-1}$  to  $14.9 \text{ LMH bar}^{-1}$  for the TFN membrane containing 0.10% w/v mZIF nanoparticles [104]. As shown in Fig. 6 Yin et al. prepared a TFN membrane containing GO nanosheets via an interfacial polymerization process. In their study, to prepare thin selective layer, aqueous *m*-phenylenediamine (MPD) and organic trimesoyl chloride (TMC)–GO mixture solutions were used [98]. A small quantity of GO addition is shown excellent results in the form of water flux and rejection as shown in Fig. 7. The GO NPs were added in thin film composite layer while IP to make TFN membranes. Increasing the concentrations of GO NPs the water fluxes were increases drastically as shown in Fig. 7.

### 3.3 *Thin-Film Nanocomposite (TFN) Membranes for Gas Separation*

In the gas separation, nanocomposite proposed an innovative direction to develop polymeric membrane with high performance. In gas separation, nanoporous

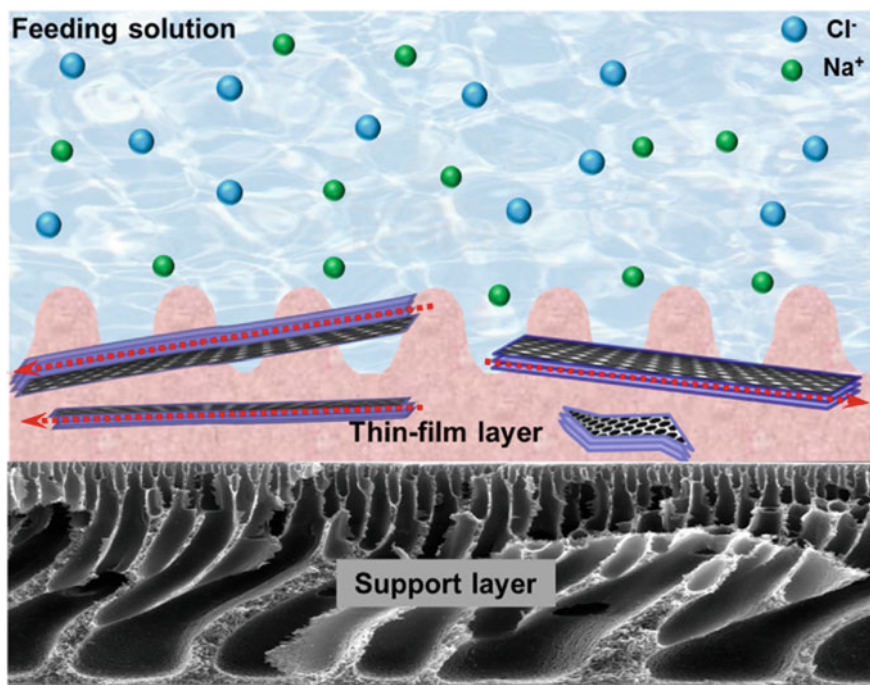




**Fig. 5** Water flux of TFC, TFN-mZIF1, TFN-mZIF2, and TFNmZIF3 membranes. WP: water permeability. (Reprinted from Ref. [104] Copyright © 2017 American Chemical Society)

inorganic materials demonstrate high permeability and high selectivity because of their consistent nanopores. There are several ways to prepare the nano size, dense layer for separation after incorporating diverse NPs into polymeric materials while interfacial polymerization to improve gas permeation performance by troublesome the polymer chain packing [3, 19]. Under optimized conditions, TFN membranes performance is very high compared with TFC membranes in the gas separation due to their hydrophilic, smoother and more negatively charged nature. TFN membranes have the advantage to reduce energy consumption and make simpler operations in gas separation applications [53]. The selective TFN layer necessitates elevated selectivity and high gas permeability to reach proficient separation. As shown in Fig. 8, in mixture gas separation especially  $\text{CO}_2/\text{N}_2$  the porous graphene (PG) nanosheets functionalized TFN shows enhanced  $\text{CO}_2$  permeance and the  $\text{CO}_2/\text{N}_2$  selectively compared to that of the membrane without PG separately. There are lots of literature is available on TFN membrane use in the field of water treatment but from last decades researchers started the application of gas separation using same kinds of membranes.

Figure 9 presents the permeability of  $\text{O}_2$  on a logarithmic scale and the  $\text{O}_2/\text{N}_2$  selectivity after adding inorganic moieties in the polymeric membranes. Wonderful enhancement in the permeability and selectivity had been achieved using diverse polymer materials. Similarly, our previous result also shows using

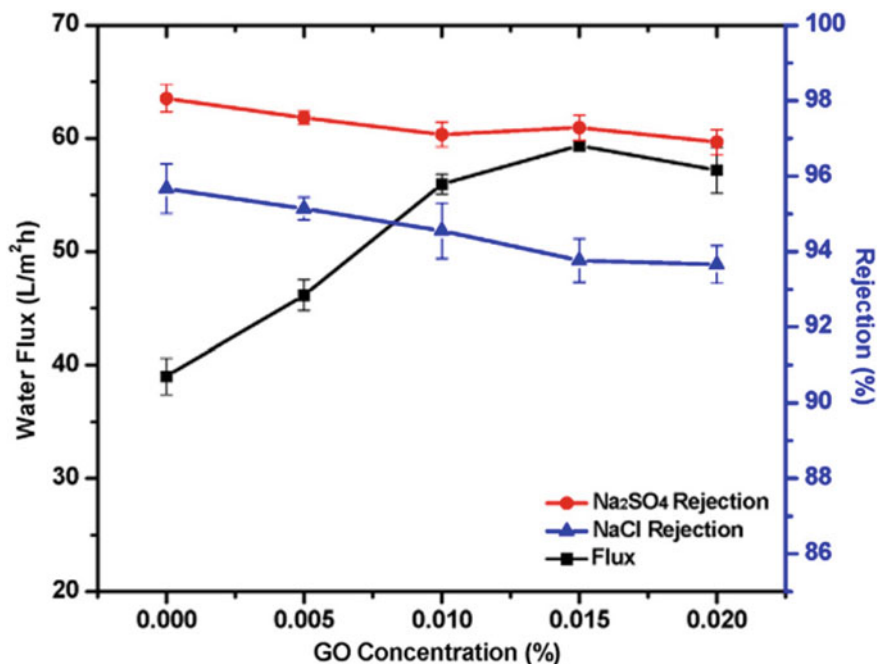


**Fig. 6** Schematic illustration of the hypothesized mechanism of GO TFN membrane. Reprinted from Ref. [98] Copyright © 2016 with permission from Elsevier

PDMS CoSalen mixed matrix membrane achieved the 7.7 ideal gas selectivity and good permeance with defect-free membranes [17]. As seen in literature Ismail et al. reported an MWNTs/polymer thin film nanocomposite membranes are greatly improving the carbon capture capacity from  $N_2$  and  $CH_4$  [89, 90]. Xingwei et al. studies on TFN membranes have focused on using silica NPs for enhanced  $CO_2$  separation from mixture gas separation [92]. The challenge is to develop TFN membranes with high-flux and high-selectivity is an urgent basis for cost-efficient  $CO_2$  capture.

Thus, functional graphene oxide (GO) and/or graphene sheets contain a variety of functional groups, having excellent mechanical strength [51]. GO is a brilliant starting nanomaterial for developing size-selective, uniform and stable TFN membranes [16, 23, 40, 52, 59, 75, 77, 83]. In the TFN membrane, the GO nanoparticles are responsible for enhancing selectivity because selective pores in graphenes are allowed the separation of gas molecules.

Any TFN membranes, the NPs plays a key role in enhancing the separation performance. Most of the cases the functionalized NPs takes part in the interfacial polymerization process, also it is found that as a results chemical functionalization of the NPs pore frame could drastically improve the selectivity of mixture gases especially  $CO_2$  over  $N_2$  [77]. The  $O_2/CO_2$  separation was done by using facilitated

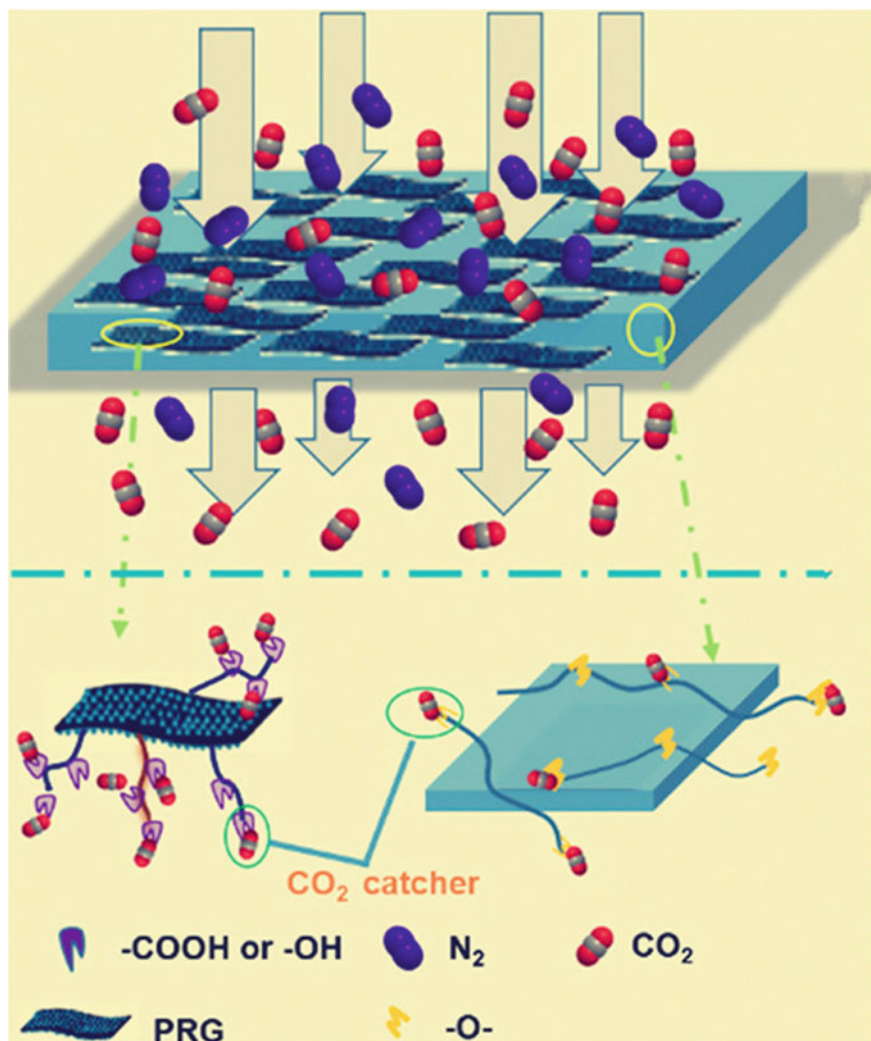


**Fig. 7** Permeate flux and salt rejection of GO TFN membranes. The concentration of the salt solution is 2000 mg/L and the TMP is 300 psi. Reprinted from Ref. [98] Copyright © 2016 with permission from Elsevier

transport hollow fiber membranes. The hollow fiber membrane was coated by using poly(*n*-butyl methacrylate) and cobalt tetraphenylporphyrin complex. The prepared membrane shows 1.5 selectivity of O<sub>2</sub>/CO<sub>2</sub> with a high O<sub>2</sub> permeance of 17 GPU at a pressure of 0.098 bar [16, 52].

### 3.4 Thin-Film Nanocomposite (TFN) Membranes for Fuel Cell Applications

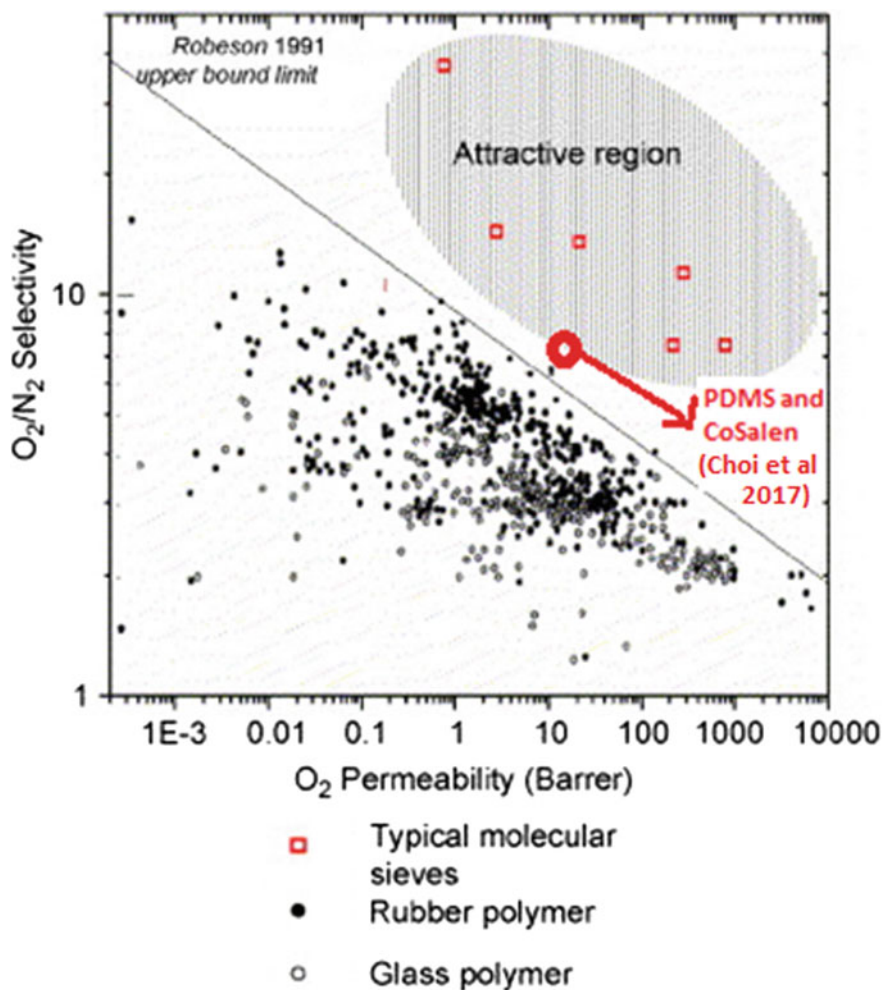
It is well known the fuel cells are a chief technology for the nation's energy portfolio. Fuel cell contribution is a cleaner, more proficient substitute for combustion engines that exploited fossil fuels. Nanocomposite polymer electrolyte membrane (PEM) made up of nanosized inorganic building blocks in the organic polymer by the molecular level of hybridization is pertinent for fuel cell application. The researchers have selected the combined inorganic and organic solid including advance properties like mechanical and thermal stability containing inorganic backbone and specific chemical reactivity, ductility, dielectric, flexibility and processability of the organic polymer to make nanocomposites [83]. During the last ten



**Fig. 8** Mechanism of gas molecules through PG-TFN membranes. Reprinted from Ref. [53] Copyright © 2017 with permission from Elsevier

years, zeolites have attracted a lot of attention and are more and more used in fuel cell applications [27, 28]. There are the criteria for selection of inorganic nanomaterials for fuel cell considering the hygroscopic characteristics, porosity, and pore connectivity, surface area these type of characteristics.

The important thing in the preparation of effective proton conducting nanocomposite membrane for fuel cell application is a covalent bond in between organic moieties and inorganic fillers. One more thing is required to make nanocomposite membrane for a fuel cell is the hydrolytically stable covalent bond between inorganic



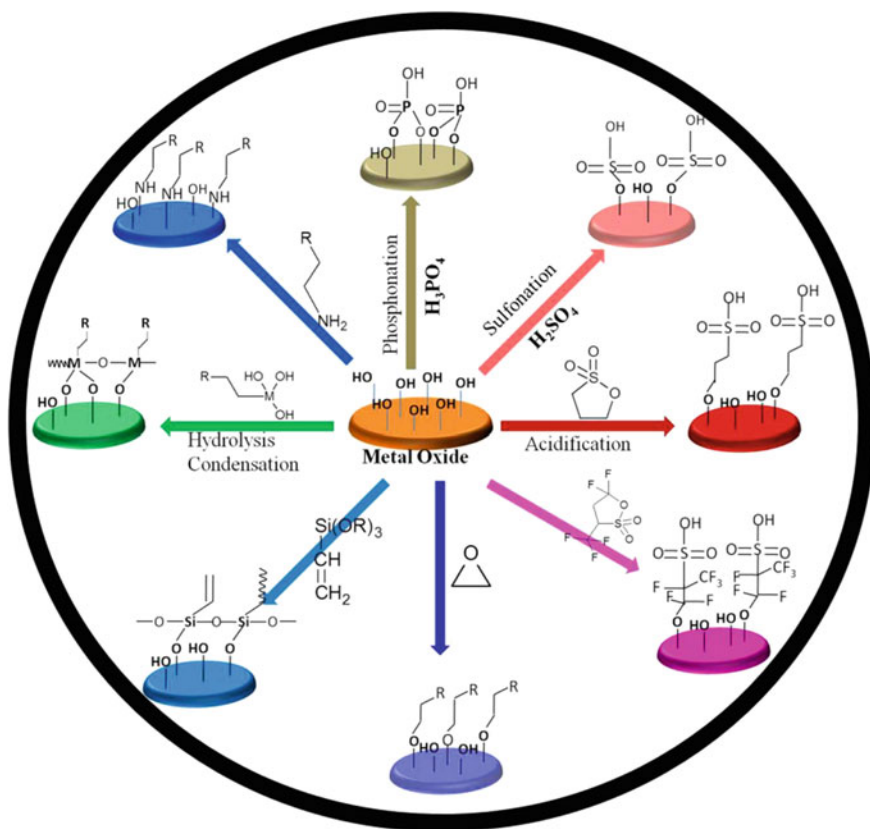
**Fig. 9** Relationship between the  $O_2/N_2$  selectivity and  $O_2$  permeability for polymeric membranes and inorganic membranes (the dots indicate the performance of polymeric materials). Reprinted from Ref. [19] Copyright © 2007 with permission from Elsevier

and organic moieties [62]. There are several ways to modify the organic components for the formation of a stable chemical bond with inorganic components for e.g. silylation (substituted silyl group ( $R_3Si$ ) to a molecule). Reinholdt et al. studied the composite membranes prepared by using synthesized silica nanoparticles and two SPEEK polymers with sulfonation degrees of 69.4 and 85.0% are characterized for their proton conductivity and water uptake properties [71].

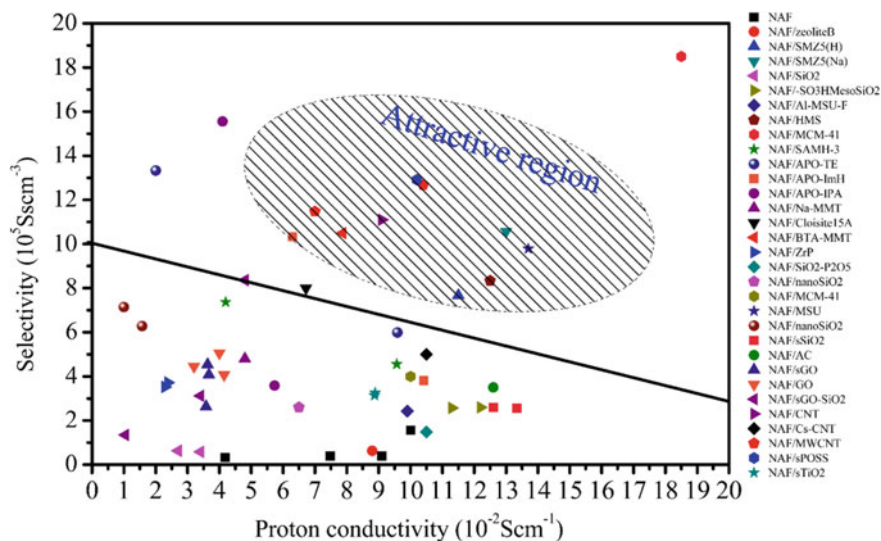
Nafion is one of the key materials for the fuel cell application. Modification of Nafion membrane, the inorganic nanoparticles such as zirconium oxide ( $ZrO_2$ ), silica, and titanium dioxide ( $TiO_2$ ) have been used successfully. Modified

membrane from Nafion/ $\text{ZrO}_2$  is homogeneous and shows high water uptake capacity and high conductivity compare with the unmodified membrane at high temperature [64]. Sulfated zirconia ( $\text{S-ZrO}_2$ ) is also used by the researchers to make the Nafion/ $\text{S-ZrO}_2$  nanocomposite membrane with enhanced properties [22].

In addition, the use of  $\text{S-ZrO}_2$  nanomaterial in Nafion based nanocomposite membranes also enhanced the high-temperature response [63]. Proton conducting mixed matrix membrane (PC-MMM) is the well known an example for fuel cell applications. In PC-MMM the metal oxides (MOs) have been under scrutiny to develop polymer electrolyte membranes (PEMs) because they hold exceptional mechanical and thermal stability, outstanding hygroscopic ability and are in nature abundant [48, 54]. Figure 10 demonstrates the diverse directions used to modified/functionalized MOs for PC-MMM preparation [12]. The different types of MOs form into nanoparticles with a variety of arrangements such as nanohorns, nanorods, nanospheres, and nanotubes, in sort to augment specific surface area to volume



**Fig. 10** Illustration of functionalization strategies used to modify metal oxides (MOs) for PC-MMM. Reprinted from Ref. [12] Copyright © 2016 adapted with permission from Elsevier Ltd

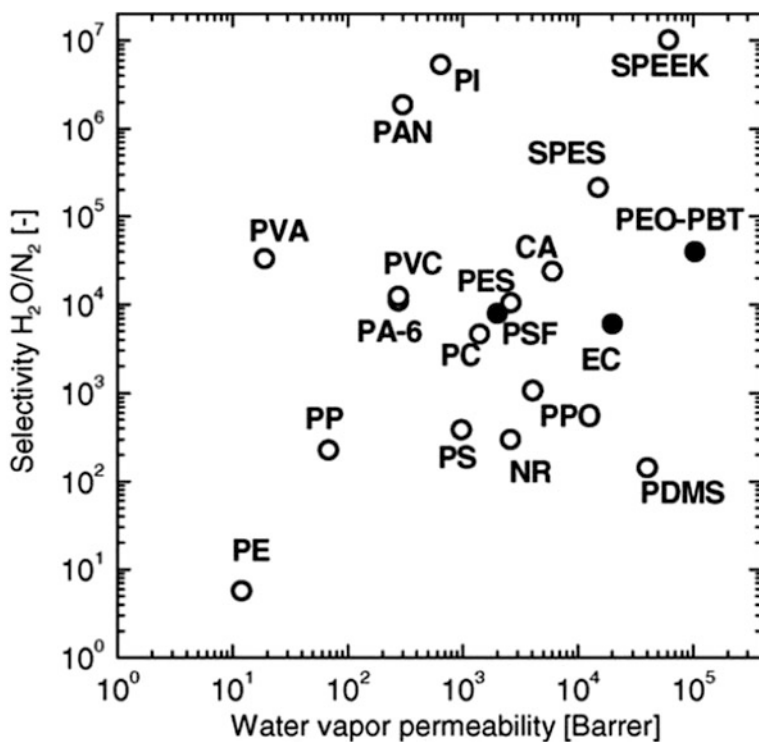


**Fig. 11** Proton conductivity versus methanol crossover of PC-MMM composed with Nafion<sup>®</sup> matrix and inorganic particles at 30 °C and 100% relative humidity (RH). Reprinted from Ref. [12] Copyright © 2016 adapted with permission from Elsevier Ltd

ratio. Figure 11 summarizes the PC-MMM based Nafion<sup>®</sup> matrix and different inorganic fillers proton conductivity and methanol permeability. These types of inorganic fillers added membranes revealed advanced selectivity evaluated to pristine Nafion<sup>®</sup> membranes. The mesoporous fillers i.e. zeolites, aluminosilicate, MesoSiO<sub>2</sub>, CNT that unites the benefit of porous and layered structure, was more successful in dropping the methanol permeability and rising the proton conductivity of the PC-MMM-based Nafion<sup>®</sup> matrix.

### 3.5 Thin-Film Nanocomposite (TFN) Membranes for Flue Gas Dehydration

Removal of the water vapour from the flue gas is a hard task for the researcher. Solid adsorbent materials are well known for water vapour adsorption but yet no low-cost technology is available in the market for high scale utilization. To develop the thin-film nanocomposite membranes, Ingole et al. used different types of NPs with various NPs sizes in a range of 10–100 nm in a polyamide (PA) thin film selective layer via in situ interfacial polymerization on the top of various polymer porous supports like polysulfone, polyethersulfone, polyethylene, polyetherimide etc. [29–31]. Various polymeric membrane studies for the flue gas dehydration had also been done by Metz et al. in details [58] (Fig. 12). Their studies teaches about the

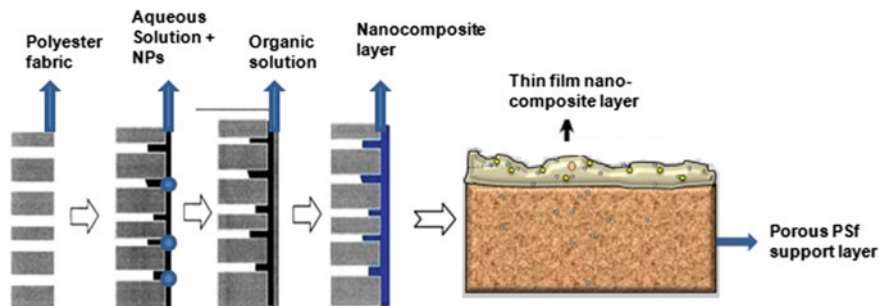


**Fig. 12** Water vapour permeability and water vapour/N<sub>2</sub> selectivity for various polymers at 30 ° C. Reprinted from Ref. [58] Copyright © 2005 Adapted with permission from Elsevier Ltd

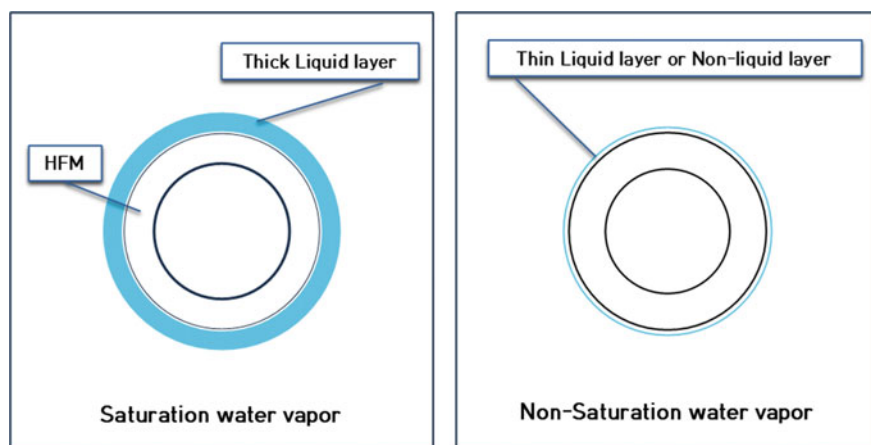
measurement of the permeation properties of highly permeable and highly selective polymers for water vapour/nitrogen gas mixtures, and also they reported the analysis of the mass transport of a highly permeable polymer is complicated by the presence of stagnant boundary layers at feed and permeate side. Sijbesma et al. reported that polymer membrane prepared by PEBAX<sup>®</sup> 1074, a block copolymer, and sulfonated poly(ether ether ketone) (SPEEK) polymers give extremely high separation factors and fluxes for the removal of water vapour from flue gasses [79]. Yun et al. also reported that hydrophilic thin film composite membranes are shown superior performances for flue gas dehydration by water vapour permeation [100, 101].

Furthermore, the flue gas dehydration using polymeric nanocomposite membranes was started by our group in detail. Thin film composite and thin film nanocomposite both types of membranes was targeted to achieve the best result. TFN membranes shows significant performance in the form of permeance and selectivity for flue gas dehydration. For the preparation of TFN membrane, Fig. 13 represented a general procedure for the interfacial polymerization to synthesize the TFN selective barrier layer. TFN membrane is more hydrophilic than TFC membrane so more water vapour has been collected on TFN layer as shown





**Fig. 13** Schematic illustration of the interfacial polymerization to synthesize the TFN selective barrier layer



**Fig. 14** The comparison, surface of the membrane in a saturated water vapour (TFN) with non-saturated water vapour (TFC)

schematically in Fig. 14. Hydrophilicity of both types of membranes was confirmed by contact angle measurement. After adding Si nanoparticles, TFN prepared from *m*-phenylenediamine and trimesoyl chloride (with 0.05% Si NPs) is more hydrophilic than TFC prepared from same monomers without Si NPs. The contact angle of TFC and TFN membranes were found  $55.0^\circ$  and  $37.0^\circ$ , respectively [9, 11].

The water vapour permeation test was conducted at 2 bar of pressure and  $30^\circ\text{C}$  temperature with  $\text{N}_2$  as a carrier gas. The feed gas was fed from the shell side while the permeate side was kept under vacuum. Relative and absolute humidity was measured using the Dew Point meter (HMT 334). At first, the dry gas was passed through the fibers till the steady state of humidity was attained in the membrane. The total flow rate was kept constant at 1000 cc/min. To study the effect of water activity, the wet gas was introduced into the module by using MFC (mass flow controller). The flow rate of wet gas was increased gradually to increase the relative

**Table 1** Operating conditions

Operating conditions	
Feed pressure	2 kgf/cm <sup>2</sup>
Oven temperature	30 °C
Carrier, dilution gas	N <sub>2</sub>
Feed gas flow rate	1000 cc/min

**Table 2** Membrane specifications

Membrane	Fiber strains	I.D. (μm)	O.D. (μm)	Area (cm <sup>2</sup> )
PS <sub>f</sub> TFN membrane	5	1000	1400	47.5

humidity in the feed side while keeping the total flow rate constant. Retentate and permeate flow rates were measured via bubble flow meters. The experimental operating conditions are summarized in Table 1.

The membrane specifications are mentioned in Table 2.

The calculations was done using the below equations.

Water vapour permeance was calculated by first calculating the water vapour flow rates at the feed, retentate and permeate streams by using Eq. (1).

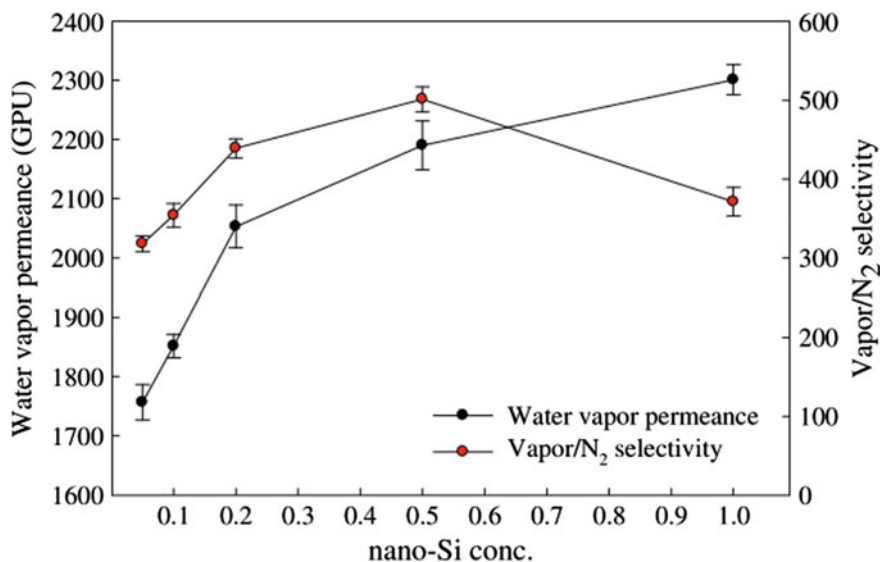
$$Q_{vapour} = \frac{Q_{N_2} \gamma_{H_2O} V_m}{M_{W,H_2O}} \quad (1)$$

where  $Q_{N_2}$  (cm<sup>3</sup>/s) was precised by bubble flow meter following retentate and permeate streams conceded during the iced cold trap.  $\gamma_{H_2O}$  is the absolute humidity (g/m<sup>3</sup>) and  $V_m$  is the volume of 1 mol penetrant at standard temperature and pressure (22.4 L/mol),  $M_{W,H_2O}$  is the molecular weight of water (18 g/mol) and  $Q_{vapour}$  (cm<sup>3</sup>(STP)/s) is the water vapour flow rate at the desired stream.

The permeance of a component  $P_i$  in the mixed gas stream can be premeditated by using Eq. (2).

$$P_i = \frac{Q_P}{\Delta P_i \times A} \quad (2)$$

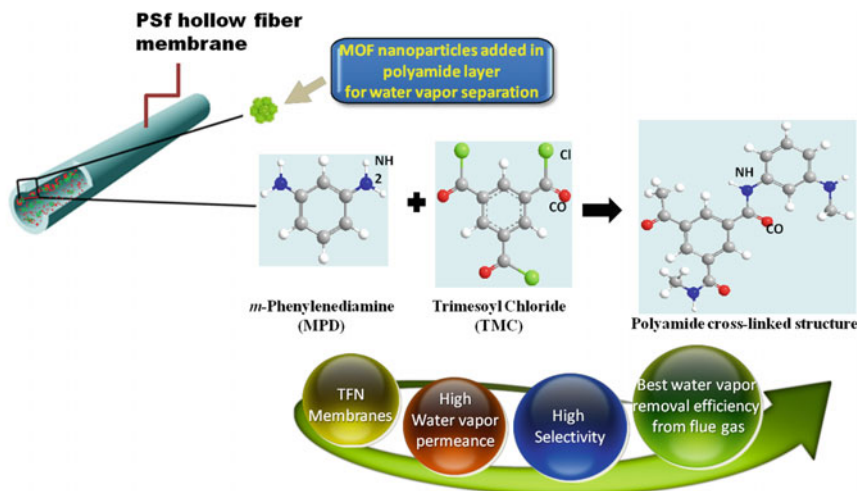
As results are shown in Fig. 15, the water vapour permeance and selectivity both increases until certain Si NPs concentrations but further after specific concentration of Si NPs the permeance become increases but selectivity decreases. The water vapour permeances ascended due to increased surface roughness coupled with lower contact angles contribute to excellent hydrophilic properties of TFN membranes [9, 11]. Due to more hydrophilic nature, the TFN membranes shows good water vapour permeance and selectivity until connections of Si NPS was 0.5% but furthermore, the permeance was increases but selectivity was decreased. The reason for this type of results is the agglomeration of NPs. After 0.5% NPs concentration in



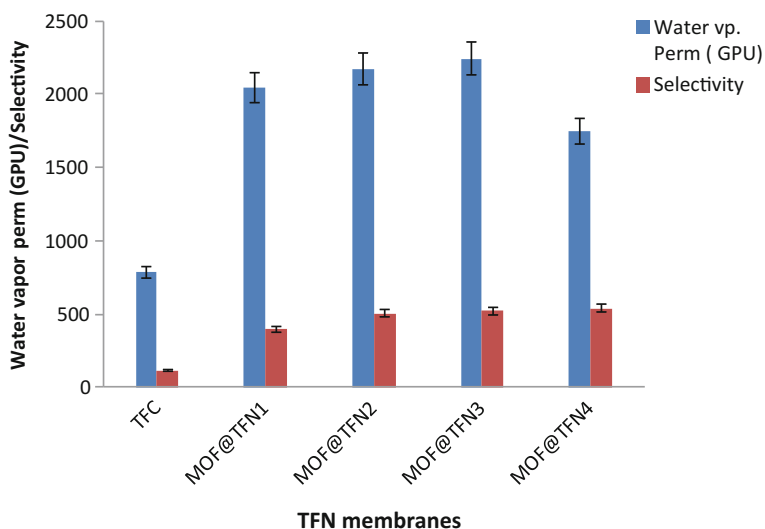
**Fig. 15** Effect on the water vapour permeance and selectivity of TFN membranes at various Si nanoparticles concentration. Experimental conditions: temperature = 30 °C, operating pressure = 3 kgf/cm<sup>2</sup>, feed water vapour activity = 0.7 ~ 0.8, total feed flow rate = 1000 cm<sup>3</sup>/min. Reprinted from Ref. [9, 11] Copyright © 2017 adapted with permission from Elsevier Ltd

monomer solution the NPs agglomeration started and while TFN membrane preparation its shows the disadvantageous towards selectivity because of both N<sub>2</sub> and water vapour permeance increases so as a side effect the selectivity decreases [6, 9, 11].

TFN membranes prepared on the inner surface of the polymeric hollow fiber are extremely terrific materials for water vapour separation from flue gas because of their advanced selectivity. The TFN membranes prepared by using MPD and TMC as monomers along with the incorporation of functionalized MOF (NH<sub>2</sub>-MIL-125(Ti)) shows very interesting results [35]. The TFN selective layer was prepared the inner surface of the hollow fiber membrane. The schematic representations of the TFN membrane preparation on the inner surface of the PSf hollow fiber membranes are shown in Fig. 16. After incorporation of MOF (NH<sub>2</sub>-MIL-125(Ti)) nanoparticles in the TFN layer, the performance of membranes was drastically enhanced. Results as shown in Fig. 17, the concentration of MOF (NH<sub>2</sub>-MIL-125(Ti)) NPs increases from 0.01 to 0.1 w/w% in TFN membranes, the water vapour permeance was enhanced from TFC 785 GPU to TFN 2244 GPU, and the selectivity also jumped from 116 to 542 [35]. Furthermore, after addition of 0.1% NH<sub>2</sub>-MIL-125(Ti) NPs, the permeance is decreased because of agglomeration of nanoparticles in the monomer solution. Because of agglomeration of NH<sub>2</sub>-MIL-125(Ti) particles, the membrane structure become interrupted.



**Fig. 16** Interfacial polymerization reaction between MPD (containing  $\text{NH}_2\text{-MIL-125(Ti)}$  MOF nanoparticles) and TMC to form a cross-linked structure on the inner side of PSf hollow fiber membrane. Reprinted from Ref. [35] Copyright © 2018 adapted with permission from Elsevier Ltd



**Fig. 17** Effect of  $\text{NH}_2\text{-MIL-125(Ti)}$  MOF nanoparticles concentration in TFN membranes on the performance as water vapour permeance and selectivity. Experimental conditions: temperature = 30 °C, operating pressure = 3 kg-f/cm<sup>2</sup>, feed water vapour activity = 0.7–0.8, total feed flow rate = 1200 cm<sup>3</sup>/min. Reprinted from Ref. [35] Copyright © 2018 adapted with permission from Elsevier Ltd

## 4 Conclusions

**Application of sustainable nanocomposites in membrane technology** is the book chapter to bring a wide study of nanocomposite membrane technology. This pioneering book chapter text offers a fluent introduction to the field as well as an inclusive overview of fundamental facets and application area of nanocomposite membrane. Approaching the subject from the materials point of view, this book chapter:

- Discusses the history, synthesis, and characterization of nanocomposite membranes.
- Examines nanocomposite membranes for water desalination, wastewater treatment, gas separation, fuel cell applications, and flue gas dehydration applications.
- Judges processing challenges, including scalability issues and real implementations.

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