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Review

Surface modification methods of organic solvent nanofiltration membranes

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HIGHLIGHTS

- Review recent of progress in the surface modification of OSN membranes.
- Molecular focus on controlling the properties of the selective layer.
- Effects of surface modification on separation performance.
- Critical comparison of the OSN reviewed surface modification techniques.

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ABSTRACT

Organic solvent nanofiltration (OSN) is an emerging technology in which membranes are used for organic solvent separation and purifications. Its fields of applications range from pharmacy, catalyst regeneration, to oil and solvent treatments. A major challenge is to maintain a high stability of these (modified) membranes under different feed conditions. Tailoring the selective layer of OSN membranes is the main approach to develop functionalized membranes which show stable high selectivities and permeabilities. During the past decade, methods such as grafting, light-induced modification, plasma treatment, and polyelectrolyte modification have been intensively studied. This paper reviews the recent progress in this field of surface modification of different types of polymeric and also of ceramic OSN membranes. First, the most crucial surface layer properties that affect the OSN membranes properties are described in detail. Next, different surface modification methods and their effects on membrane selectivity and permeability are reviewed and compared. Finally, a perspective is given on expected future trends in this highly challenging and important field of current research.

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Abbreviations

AEMA	aminoethyl methacrylate
AF	acid fuchsin
AFM	atomic force microscopy
APTES	(3-aminopropyl)triethoxysilane
APTMS	(3-aminopropyl)trimethoxysilane
BTB	bromothymol blue
CA	cellulose acetate
CSA	camphor sulfonic acid
CVD	chemical vapor deposition
DCM	dichloromethane
DEA	diethanolamine
DLC	diamond-like carbon
DMAc	N,N-dimethylacetamide
DMF	N,N-dimethylformamide
DMSO	dimethyl sulfoxide
DR	disperse red 1
EA	ethyl acetate
EtOH	ethanol
GNPs	gold nanoparticles
GO	graphene oxide
H-PAN	hydrolized-polyacrylonitrile
HNSA	6-hydroxy-2-naphthalenesulfonic acid
IPA	*iso*-propyl alcohol
IPD	*iso*-phthaloyl dichloride
ISA	integrally skinned asymmetric
LbL	layer-by-layer
MA	methylacrylate
MEK	methyl ethyl ketone
MeOH	methanol
MMM	mixed matrix membrane
MO	methyl orange
MOF	metal-organic framework
MPD	M-phenylenediamine
MPTES	(3-mercaptopropyl)triethoxysilane
MWCO	molecular weight cut-off
MWNTs	multi-walled carbon nanotubes
NF	nanofiltration
NMP	N-methylpyrrolidinone
OSN	organic solvent nanofiltration
PA	polyamide
PAA	polyacrylic acid
PAN	polyacrylonitrile
PDMS	polydimethylsiloxane
PDDA	poly(diallyldimethylammonium chloride)
PEC	polyelectrolyte complex
PEI	polyethylene imine
PEG	polyethylene glycol
PEM	polyelectrolyte multilayer
PEO	polyethylene oxide
PI	polyimide
PIB	polyisobutylene
PNIPAM	poly(*N*-isopropyl acrylamide)
PPy	polypyrrole
PS	polystyrene
PSf	polysulfone
PSS	poly(sodium styrene sulfonate)
PTMSP	poly[1-(trimethylsilyl)-1-propyne]
RB	Rose Bengal
RO	reverse osmosis
Sa	average roughness
SDS	sodium dodecyl sulphate
SPEEK	sulfonated poly(ether ether ketone)
SPN	segmented polymer network
SRNF	solvent resistant nanofiltration
Sq	root mean square of the roughness data
Sz	difference between the highest peaks and the lowest valleys
TEA	triethylamine
TFC	thin film composite
TFN	thin film nanocomposite
TGA	thermogravimetric analysis
THF	tetrahydrofuran
TMC	trimesoylchloride
TPO	2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide
UF	ultrafiltration

Greek symbol

ε_r	relative dielectric constant

1. Introduction

Nowadays chemical separations are playing crucial roles in processes of the chemical, petrochemical, pharmaceutical and food industries [1]. Membrane-based separation processes have attracted significant attention in industrial applications due to their distinct advantages over traditional separation processes like distillation and extraction. This is primarily due to their better separation performance, the lower size and costs of the equipment used, and a much improved energy efficiency [2–4]. Nanofiltration (NF) membranes with separation properties between those of ultrafiltration (UF) and reverse osmosis (RO) membranes (pore size < 0.5 nm), were first explored in the late 1980's [5,6]. Although NF membranes have been widely applied for water and wastewater treatment processes [7], their application for organic solvent nanofiltration (OSN), sometimes also referred to as solvent-resistant nanofiltration (SRNF) or organophilic NF, is a rather new technology [1]. OSN has a great potential to be employed in a wide range of processes related to, e.g. food [8–10], fine chemical [11–13], pharmaceutical [14–16] and petrochemical industries [17–19] for the treatment of organic solvents. Within the Scopus database a total number of 335 papers in indexed journals was found on keywords related to the topic of OSN membranes as of 2005 (Fig. 1). More than two third of these papers appeared over the last five years, showing the growing interest in OSN membranes.

The compatibility of these membranes under extreme operating conditions like harsh and aggressive media, elevated pH and high temperatures, while maintaining a reasonable long-term separation performance and reproducibility is the main challenge in the further development of OSN membranes. In such membranes,

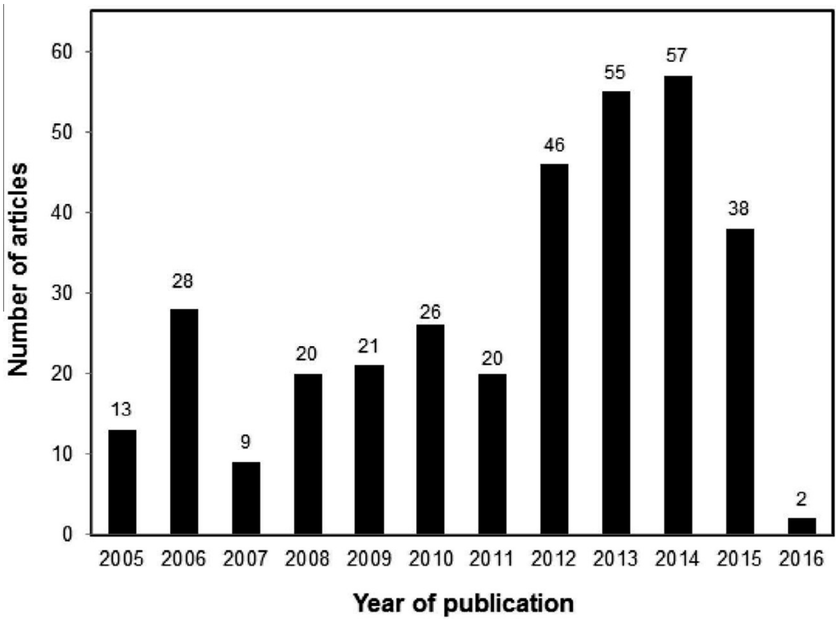

Fig. 1. Record of the number of papers published in indexed journals between 2005 and 2015 containing the keywords "organic solvent nanofiltration" or "solvent resistant nanofiltration" or "organophilic nanofiltration" in the title, abstract or keywords. (Source: Scopus, searched on 19 November, 2015).

solute discrimination occurs in the surface (top) layer at the molecular level. The overall performance is determined by solute/solvent interactions with the membrane top layer [6]. In addition, it is well established that solvent–membrane surface interactions, which can vary with solvent composition, play a key role in the permeation properties of NF membranes [20,21]. Hence, specific modification of the membrane surface becomes important in order to obtain the desired high-performance OSN membranes. In addition, exploring novel and viable approaches to synthesize thermally/chemically stable OSN membranes is another challenging research area. Indeed, during the last decade, several techniques were employed to improve the separation properties of OSN membranes (mainly polymeric membranes) without sacrificing their permeation properties.

Previously published reviews on OSN membranes are devoted to (i) the development of thin film (nano) composite membranes [4], (ii) the application of OSN membranes for molecular level separation [1,6], (iii) the assessment of sustainability of OSN membranes [22], and (iv) the recent advancements in polymeric OSN membranes [2]. In the current review first the concept of OSN membranes will be briefly discussed (Section 2). Then, effects of the key surface properties including surface charge, hydrophilicity/hydrophobicity and surface roughness are discussed (Section 3). After that we review and critically discuss the different methods applied for the surface layer modification of various kinds of OSN membranes at a *molecular level*. This includes the preparation and surface modification of OSN membranes using light-induced procedures, plasma-induced techniques, thin film formation via polymerization, polyelectrolyte modifications, incorporation of nanoparticles and, finally, grafting (Section 4). A schematic overview of all these methods and strategies is presented in Fig. 2.

This review provides valuable insights into the preparation of high-performance OSN membranes as we also included a comparison of the different surface modification methods (Section 5). Finally, a perspective is given on expected future trends (Section 6).

2. OSN concept

OSN is an energy-efficient and sustainable separation process that allows the separation of organic mixtures by simply applying a pressure gradient over the membrane [22]. About one decade ago, Mulder [23] classified membranes based on the pressure required for the separation. According to this classification, a pressure between 5 and 20 bar is applied in NF membranes. However, nowadays, most of the NF membranes are employed at higher pressures up to 40 bar [1].

Both organic (polymeric) and inorganic materials have been widely used for the preparation of the OSN membranes. The mechanical, chemical and thermal stability of these materials are amongst the most important factors having a crucial impact on the final performance of OSN membrane [22]. Solvent stability and swelling resilience of polymer materials significantly affect the performance of OSN membranes. In general, polymers lose their physical integrity in contact with the organic solvent due to their tendency to swell or dissolve [2,24]. However, polymeric OSN membranes must demonstrate continuous long-time operation stability in harsh solvents, while preserving their separation properties. Hence, development of new polymeric materials with superior resistance towards organic solvents such as polyimides [25,26], poly(1-trimethylsilyl-1-propyne) PTMSP [27–29] and polymers with intrinsic microporosity (PIMs) [27,30] has become one of the most interesting research areas in the field of current membrane science and technology. Several overviews of extensively used polymeric materials for the preparation of OSN membrane are presented elsewhere [1,2,6,14].

Tsuru et al. [31,32] prepared the first ceramic OSN membrane from silica–zirconia. Titania, made by a sol–gel method, was also used to fabricate OSN membranes [33]. Utilizing ceramic materials for the preparation of OSN membranes have great potential due to their advantages over polymeric materials, such as a primarily high solvent stability, and their resistance to compaction and swelling. However, the high costs of ceramic membranes and their low organic solvent rejection limit their application in OSN [34]. Hence, surface modification and functionalization techniques have been performed to adjust the surface chemistry (hydrophilicity/hydro phobicity) of ceramic NF membranes and to improve their separation performance.

In addition to the examples above, also hybrid organic/inorganic membranes exist. For example, mixed matrix membranes (MMMs) consist of inorganic fillers dispersed in a polymer matrix

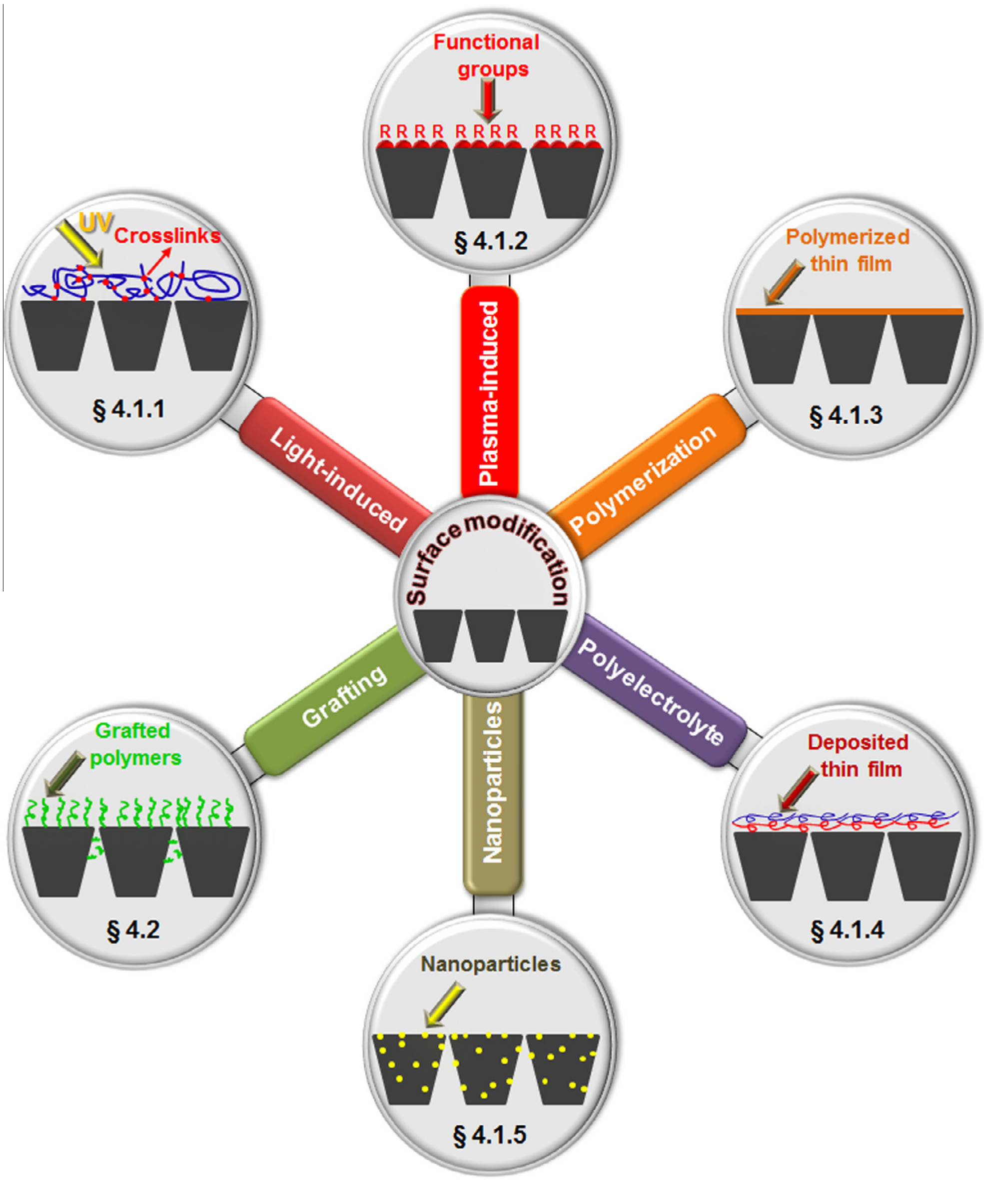

Fig. 2. Schematic overview of the methods discussed for surface modifications of OSN membranes.

and are mainly studied for gas separation purposes [35]. Also, thin film nanocomposite (TFN) membranes with dispersed nanoparticles present in a very thin film (typically 100–500 nm in thickness) on a porous support have received a growing research interest in recent years [36].

3. Surface layer properties influencing the OSN membrane performance

Surface (top layer) properties of membranes such as surface charge, hydrophilicity/hydrophobicity and surface roughness are the most important factors affecting permeation and separation performances of the OSN membranes [1,37]. These characteristics determine the affinity of the membrane selective layer towards the solvent/solute. In order to synthesize high-performance OSN membranes, surface properties must be tuned based on the properties of the solvent and/or solute. To have a better understanding of the mutual interactions between membranes and the solvent/solute, we briefly review the membrane surface properties in the next paragraph with a focus on surface charge (Section 3.1), surface hydrophilicity/hydrophobicity (Section 3.2) and surface roughness (Section 3.3). These different surface properties are summarized schematically in Fig. 3.

3.1. Surface charge

Depending on the interaction between the membrane and the solvent/solute, the membrane surface charge can be an effective feature that influences the membrane performance using charged solutes [38]. Based on the Debye–Hückel theory [39] the thickness of an electrical double layer around an ion is proportional to the square root of the dielectric constant of the surrounding medium. This means that in solvents with high dielectric constants, the charge effects are exerted over a longer distance. For example, in the case of polar solvents such as methanol (MeOH) and *iso*-propyl alcohol (IPA) with dielectric constants (ε_r) of 32.6 and 18.3, respectively, the influence of a charge is more significant than that of apolar solvents such as toluene ($\varepsilon_r = 2.38$) [40,41].

In NF membranes, the sieving effect is the key factor for rejection behavior of uncharged organic molecules, while the separation

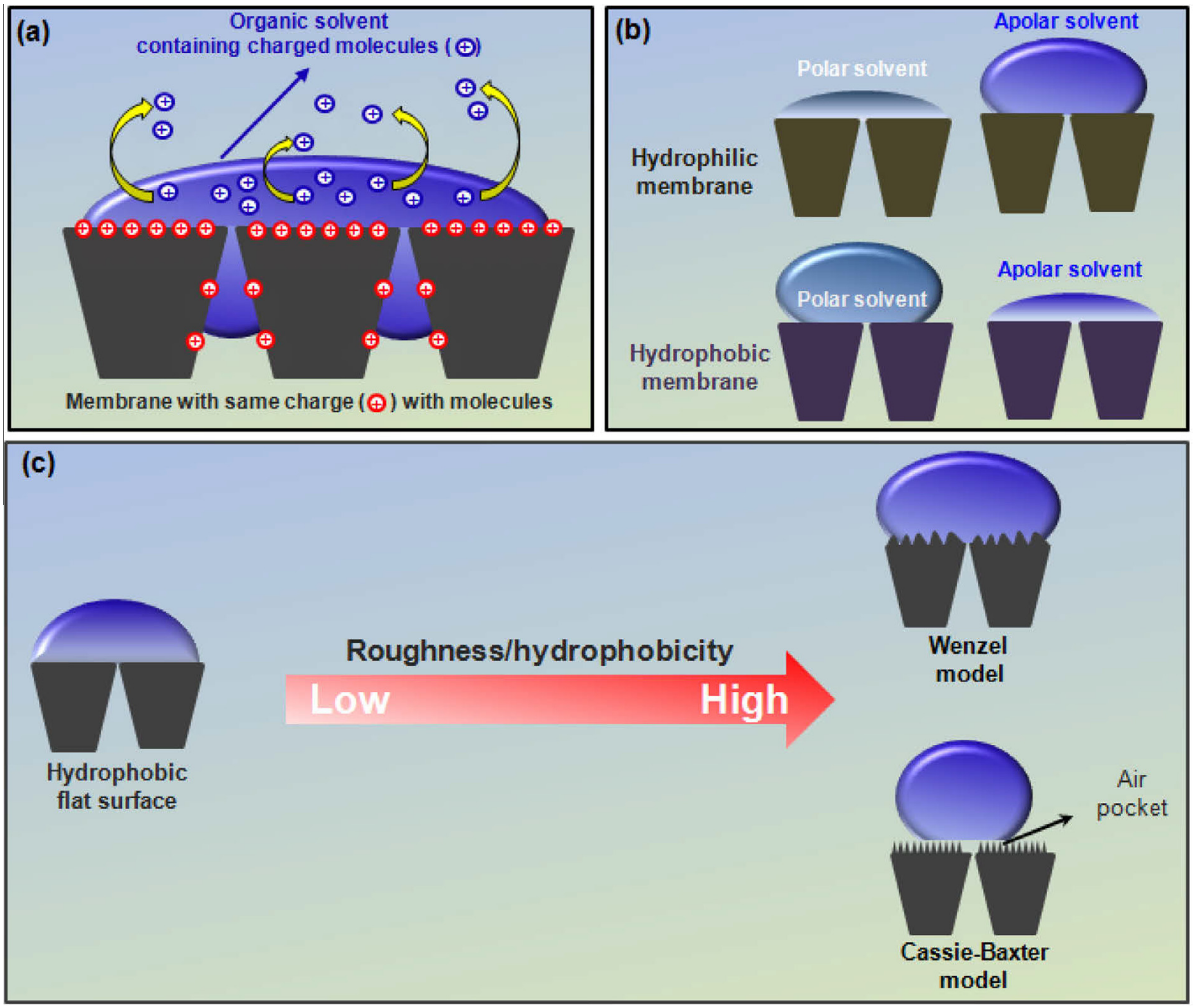

Fig. 3. Surface layer properties influence the performance of OSN membranes: (a) surface charge, (b) hydrophilic/hydrophobic properties and (c) surface roughness.

performance for charged molecules is dominated by charge effects [42]. For example, Ahmadiannamini et al. [43] studied polyelectrolyte multilayer (PEM) membranes with top layers having different types of charge in combination with charged solutes. Donnan exclusion was found to be the main factor in explaining the high retentions for PEM membrane/solute combinations having the same type of charge. On the contrary, they observed a high value of retention for the PEM membranes with positively charged capping layers for separation of negatively charged Rose Bengal (RB) dye molecule in IPA. They concluded that the negatively charged RB adsorbed on the membrane surface and formed an extra layer that neutralizes the positive surface charge and in this way improved the retention of RB from IPA due to the Donnan exclusion. Marchetti et al. [21] explained that the solute-membrane affinity is a function of chemical nature of the molecules, electrostatic (Donnan potential) interactions between the solute and the membrane charge, composition of the solvent mixture and the concentration of salts/ions. Donnan effects were extensively studied in aqueous systems [44] and also the electrostatic interaction has been studied for OSN membranes [38,45,46].

Contradictory findings are reported in literature on the correlation between the membrane rejection and solute charge properties. Bhanushali et al. [45] observed a higher rejection of charged solutes (Orange II and Safranine O) over an electrostatically neutral solute (Solvent Blue 35) in MeOH using hydrophobic MPF-60 membrane and attributed this to the solute/membrane charge effects. In contrast, Zhao and Yuan [38] observed higher rejections of neutral molecules (Soybean daidzin) over charged solutes (Crystal violet and Acid blue 25) in MeOH using a hydrophilic Desal-DK membrane. They concluded that the rejection results strongly depend on the interaction between the type of solvent (polarity), solute (charge) and membrane (hydrophilicity). It is worth noting that, charge effects become a decisive factor in determining the retention of the molecules in NF membranes, when the molecular size of organic molecule is much smaller than the membrane pores [38,47]. Even in this case the surface charge of both the membrane and organic molecule are essential. Van der Bruggen et al. [47] proposed that for a negatively charged membrane, the Donnan exclusion of negatively charged molecules from the membrane increases the rejection, while positively charged molecules might even experience a lower rejection than neutral molecules of similar size. Overall, the solute and membrane charges can increase or decrease the retention because of electrostatic interactions.

It should be highlighted that the mechanism of the surface charge in organic solvents strongly depends on the type of solvent [48]. For instance, acid–base interactions are the main reason for surface charge formation in protic liquids such as alcohols similar to the charge of oxide surfaces in water and involving protons as the potential-determining ion. It was observed that the relative acidity of the liquids and the surface hydroxyl groups are the key factors to define the amount of surface charge in the diluted

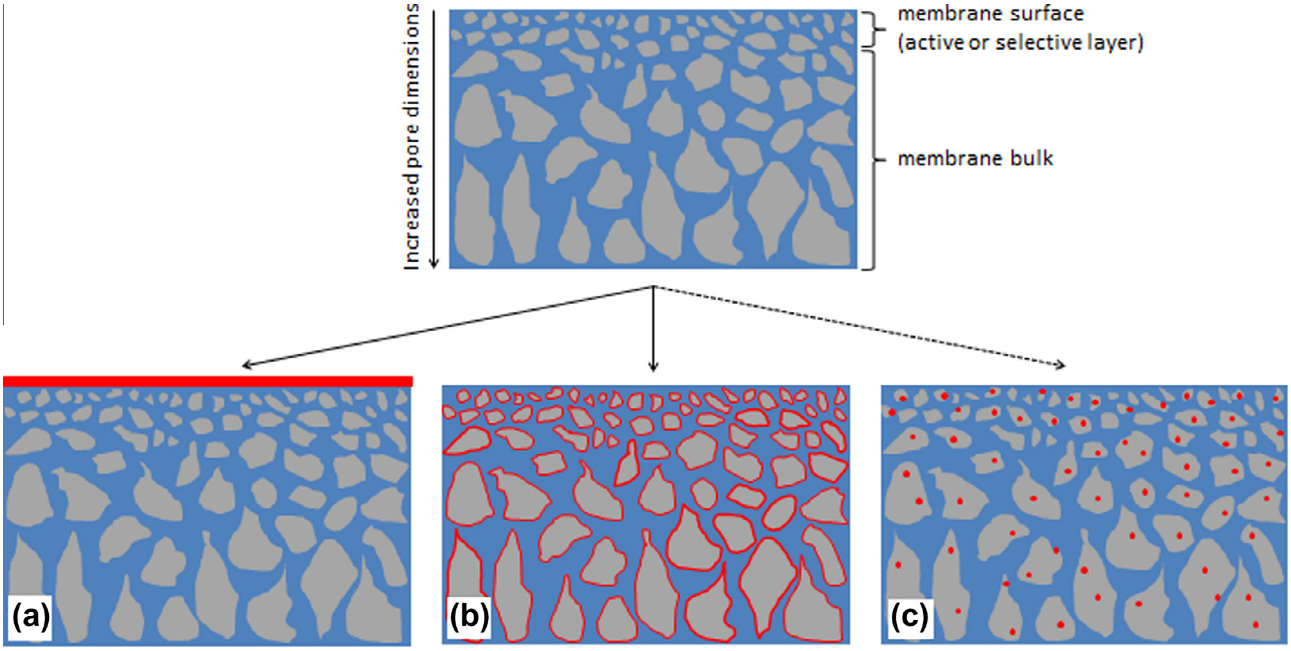

Fig. 4. Schematic of the modification methods applied for OSN membranes: (a) modification of the skin (top) layer, (b) modification of top surface and bulk structure and (c) *in-situ* modification of the surface and bulk structure.

solutions. Otherwise, electron donor–electron acceptor interactions determine the surface charge in dipolar aprotic liquids.

3.2. Surface hydrophilicity/hydrophobicity

The wettability can influence the overall performance of OSN membranes. For example, the combination of the solvent polarity and the hydrophilicity of the membrane determines the permeation properties of alcohols and alkanes through a hydrophilic RO membrane (Osmonics DS11) and a hydrophobic NF membrane (MPF-50) [49]. It has been demonstrated that the permeability of polar solvents in hydrophilic membranes was 8–10 times higher than that of non-polar solvents, whereas in hydrophobic membranes the permeability of non-polar solvents was 2–4 times higher than that of polar solvents.

Zhao and Yuan [38] reported higher rejections of neutral molecules in water than in organic solvents for hydrophilic NF membranes while in the case of hydrophobic membranes the opposite trend was observed. This result matches well with studies of Yang et al. [46] and Geens et al. [50] that report on rejections of charged and neutral molecules being lower in organic solvents than in water for only hydrophilic membranes, but not for hydrophobic membranes. The "hydration/solvation" mechanism was proposed to explain this behavior, which affects the relative solute-membrane versus the solvent–membrane molecular affinity [46]. In highly hydrophobic membranes the interaction with water molecules is very low (*i.e.* no hydration of membrane) and the solvation of the pores of the membrane with MeOH decreases the effective pore size, thus leading to higher rejection in organic solvents than water. However, for hydrophilic membranes the hydration becomes more significant than solvation, resulting smaller effective pore size in water than in organic solvents. In two separate studies, Zhao and Yuan [38] and Yang et al. [46] also reported negligible charge effects during NF of charged solutes in MeOH. These results clearly show that the interaction between the solut e–membrane–solvent is different in aqueous and organic systems.

Over the past 10 years the research group of Van der Bruggen published a number of interesting studies covering the investigation of OSN membrane wetting effects on the separation/permeation properties [50–55]. They observed that apolar solvents with a low surface tension resulted in higher (lower) fluxes by using hydrophobic (hydrophilic) membranes. On the other hand, polar solvents with a high surface tension yielded lower (higher) fluxes by applying hydrophobic (hydrophilic) membranes.

It should be highlighted that there is a strong interaction between the surface tension of the solvent and the hydrophilicity of membranes [49,51–53,55,56]. As a consequence of weaker interactions between the solvent/solute and the surface of hydrophobic membranes, it has been demonstrated that using solvents with a higher surface tension results in higher fluxes through hydrophilic membranes, but lower fluxes through hydrophobic membranes.

In another study, Van Gestel et al. [54] showed that the modification of membranes with higher molecular weight silanes (C8 silane) enhanced n-hexane permeability more significantly as compared to lower molecular weight ones (C1 silane). They attributed this to the formation of more hydrophobic pores with a higher affinity toward n- or cyclohexane by the attachment of longer alkyl chains to the walls of the pores. As an important remark we note that a large variety of surface modification methods using silane chemistry exists [57,58], and that care should be taken on the preparation conditions when one aims for the formation of a true, high-quality monolayer rather than thicker layers with a higher roughness that may be formed due to oligomerization [59].

In summary, the wettability of membranes plays a key role in the separation performance of organic solvents at a molecular level as it strongly influences the solvent–membrane and solute–membrane interactions.

3.3. Surface roughness

Next we discuss the surface roughness, as it is an important structural property of OSN membranes. It is typically measured by AFM and reflected in terms of the average roughness (Sa), the root mean square of the roughness data (Sq) and the mean difference between the highest peaks and the lowest valleys (Sz) [1]. To understand the effects of surface roughness on the wettability of

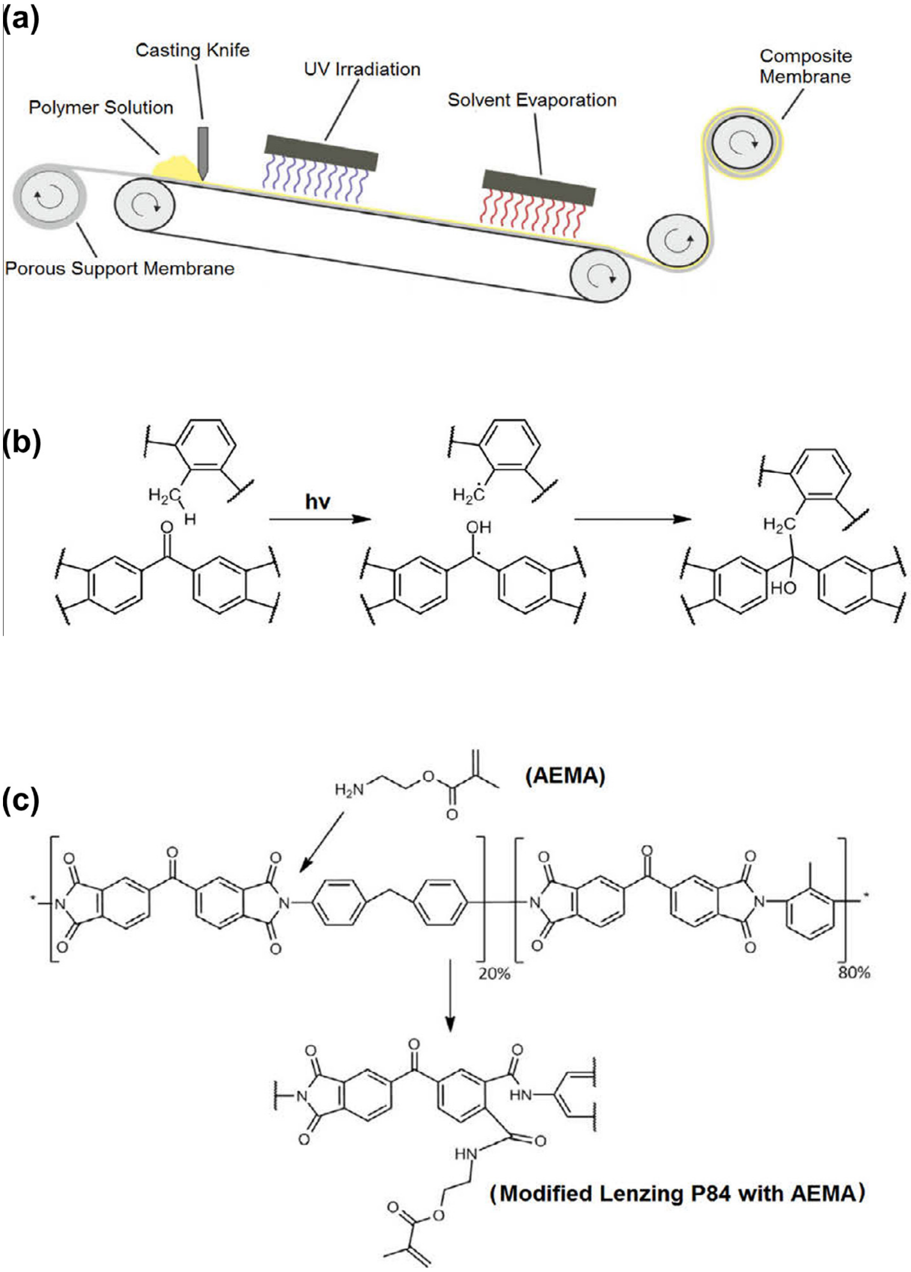

Fig. 5. Schematic of the (a) membrane preparation process, starting with casting a polymer solution onto a porous support membrane, followed by a UV irradiation initiated cross-linking of the polymer, and solvent evaporation leading to a thin-film composite membrane, (b) basic mechanism of the UV-induced cross-linking of a polyimide containing benzophenone groups in the main chain and aliphatic hydrocarbon groups enabling hydrogen abstraction and (c) polymer-analogous modification of the P84® with AEMA (with permission from Elsevier Science Ltd.) [98].

solid surfaces, the famous Wenzel [60] and Cassie–Baxter [61] models have been proposed. According to these models, there are two regimes of wetting of a rough surface: (I) a homogeneous regime with a two-phase solid–liquid interface and (II) a non-homogeneous or composite regime with a three-phase solid–air–liquid interface in which the air pockets are trapped between the solid surface and liquid (Fig. 3c) [62,63]. In Wenzel's model, the liquid completely fills the rough structure of the solid surface and increasing the surface roughness makes hydrophobic surfaces more hydrophobic and hydrophilic surfaces more hydrophilic. The Cassie–Baxter model describes that the liquid drop sits on the top asperities of a dual scale surface structure and air is trapped in the rough structure underneath the liquid, increasing the water contact angle. Work by Peyravi et al. [64] demonstrated that the loading of amine-functionalized TiO_2 into the co-polyamide (PA) thin layer increased the surface roughness as well as the surface hydrophilicity. Furthermore, they concluded that the effect of incorporated TiO_2 nanoparticles on membranes surface roughness was more significant than on surface chemistry. These findings indicate the membrane performance can be controlled by changing the surface roughness. Namvar-Mahboub et al. [65] and Jadav et al. [66] reported similar results by measuring a lower membrane surface roughness upon loading lower amounts of nanoparticles into a polymeric matrix, while higher loadings resulted in an increase due to the agglomeration of nanoparticles.

It is noteworthy to say that the surface roughness scales with the overall surface area and consequently also with the permeation flux. For instance, Sun et al. [67] showed that the addition of triethylamine (TEA) and camphor sulfonic acid (CSA) into the M-phenylenediamine (MPD) solution during an interfacial polymerization reaction enhanced the surface roughness of synthesized PA membranes as well as the surface area, consequently increasing the permeation flux through the membrane. However, it must be noted that, there is always a trade-off relationship between the surface area and the fouling ability of membranes by increasing the surface roughness.

On the one hand, water fluxes increase upon increasing roughness as the effective surface area becomes larger; on the other hand, fluxes may decrease because of increasing fouling. It is well-known that for rougher surfaces the possibility of entrapment of foulants in zones increases by the reverse flow due to the eddy currents occurring behind the peaks. For example, clogging of valleys on the membrane surface was found to result in a significant loss of the permeate flux [68].

In summary, Sections 3.1–3.3 show the importance of the surface membrane properties on the permeation/separation performance of OSN membranes. The surface charge, roughness and wettability affect the solute–solvent–membrane interactions are subsequently influential on the overall separation performance.

4. Surface modification methods of OSN membranes

4.1. Modification of polymeric OSN membranes

Most of the polymeric membranes used in OSN have an asymmetric structure that consists of a porous sublayer which provides the mechanical strength and a dense skin layer that plays the main role in the separation processes [6]. These asymmetric membranes are divided into two major categories, (i) integrally skinned asymmetric (ISA), and (ii) thin film composites (TFC) membranes [69].

ISA membranes are prepared via a phase-inversion method as developed for the first time by Loeb and Sourirajan [70]. This method involves the precipitation of a casting solution by immersion in a coagulation non-solvent bath (in most cases water). Phase-inversion techniques are currently used for the preparation of a wide range of polymeric membranes ranging from microfiltration to gas separation [71–76]. TFC membranes consist of a separating layer on top of a porous substrate. Plasma-induced techniques (Section 4.1.2), thin-film formation via polymerization (Section 4.1.3), polyelectrolyte modifications (Section 4.1.4) and grafting (discussed in Section 4.2) are well-established methods for the preparation of ultrathin dense skin layers on a porous support for OSN applications [22,24].

Modification methods that have been proposed and applied for tuning the characteristics of OSN membranes can be divided into two categories: either only the surface is modified or the surface is modified along with the bulk membrane material (Fig. 4, top for definitions). An example of the last category is chemical cross-linking as an efficient approach to improve the performance of OSN membranes, which does not only improve the (bulk) stability of the membrane, but also may affect the membrane surface properties and is reviewed very recently [1,2,77]. Incorporation of nanoparticles into the polymer matrix is another method that influences both surface and bulk structures simultaneously. In this technique, the modification step (*i.e.* the loading of nanoparticles) takes place during the membrane preparation (*in-situ* modification). It must be noted, however, that often the main target of the addition of nanoparticles into the polymer matrix is to improve the surface properties of membranes. Hence, TFN membranes, composed of a very thin film containing nanoparticles on a porous support are fabricated. Examples of methods that address modification of the surface without changing the bulk membrane structure and properties, include plasma-induced techniques [78] and the addition of a skin (top) layer using polyelectrolytes in combination with membranes having relatively small pore sizes [79]. A schematic showing the different approaches in terms of the surface and bulk modification is presented in Fig. 4.

4.1.1. Radiation/light-induced modification

Among the modification methods used for tuning the membrane surface properties, light irradiation is an effective method due to its simplicity, low operation cost and mild reaction conditions. This method has been recognized as a well-known technique for the preparation of polymeric membranes from precursors, initiating polymerization and cross-linking reactions [80]. Preparation and modification of polymeric NF membranes with high antifouling properties for aqueous feeds is one of the most relevant applications of irradiation techniques [81–84]. Within the context of the operation conditions of OSN, the main applications of

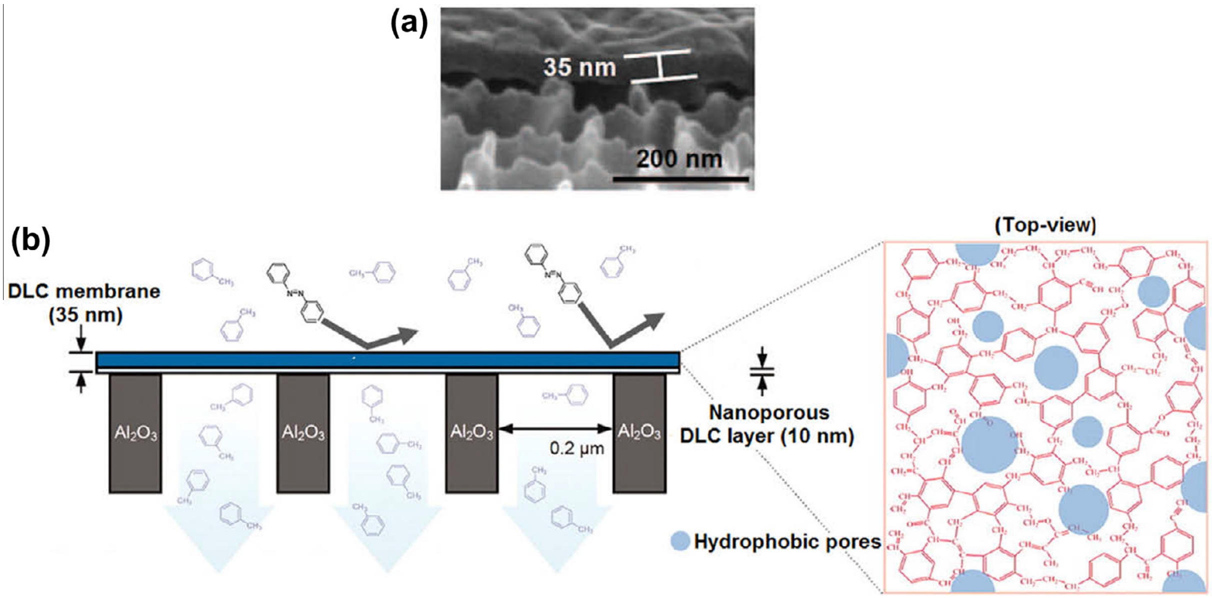

Fig. 6. (a) Cross-sectional SEM image of a 35-nm-thick DLC membrane and (b) schematic presentation of a free-standing DLC membrane formed on submicron pores of a porous alumina support (reproduced with permission from Science Ltd.) [106].

irradiation method are the fabrication and the development of a thin polymeric layer with high stability to improve the membrane performance in organic media. As a first example, electron beam radiation was employed to cross-link polydimethylsiloxane (PDMS) NF membranes and the obtained results indicated that the rejection of 9,10-di-phenylanthracene in xylene was enhanced by increasing the irradiation dose [85]. Membranes with a low irradiation dose showed a higher degree of swelling and a larger transport region within the selective layer and hence diminishing the size-exclusion effect [86]. UV curing was also used to cross-link the methacrylate (MA) functional groups in the preparation of hydrophilic polyethylene oxide–PDMS–polyethylene oxide (PEO–PDMS–PEO) membranes [87].

The Vankelecom group reported a series of studies on the application of irradiation to improve the performance of different types of OSN membranes [88–94]. In more detail, they performed UV irradiation in air at a wavelength of 254 nm to cross-link ordered nanoporous polymer membranes. These membranes were prepared via blending a block copolymer of polystyrene-*b*-poly (ethylene oxide) (PS-*b*-PEO) and poly(acrylic acid) (PAA). Upon application of a simple UV irradiation method the membranes were not only stable to chlorine solutions, but also to a variety of organic solvents [88]. Other work performed by this group, presents the effects of the local heating of cellulose acetate (CA) and gold nanoparticles (GNPs)-filled polyimide (PI) membranes by irradiation with a continues Argon-ion laser beam (514 nm) [89,90]. This novel method resulted in increased permeabilities, obviously due to a lower energy loss by convection in the membrane pores and/or free volume, while the rejection properties did not change (Fig. 5). Incorporated GNPs in the membrane matrix acted as nano heaters and caused localized heating due to the plasmonic heating effect during irradiation.

Li et al. [95] attributed this phenomenon to the fact that local heating lowers the friction between the permeating molecules and the surrounding polymer chains which subsequently increases the flux. However, since rejection is mainly governed by size exclusion, preferential adsorption or electrostatic repulsion at the membrane surface are hardly affected by local heating.

In a similar study by Li et al. [91], silver nanoparticles and LED light were used to cause localized heating, rendering the whole procedure to be more energy efficient, cheaper and less complicated compared to what was discussed above. The permeance of the thus-treated membranes increased and returned to the original value measured without LED light irradiation. This improvement in membrane permeance is due to the heating, rather than to changes in the membrane structure.

Struzynska-Piron et al. [93] employed UV curing after a phase-inversion process to fabricate solvent-stable polysulfone (PSf) or PI membranes. The cross-linked PSf and PI membranes showed good stabilities and good permeation performances in organic solvents such as ethyl acetate (EA) and IPA. For example, cross-linked PSf membranes showed 91% rejection and a permeance of 8.1 L m^{-2} h^{-1} bar^{-1} for RB/EA and 94% rejection and a permeance of 0.2 L m^{-2} h^{-1} bar^{-1} for RB/IPA. Also, UV cross-linked PI membranes showed 96% rejection and a permeance of 1.4 L m^{-2} h^{-1} bar^{-1} for RB/IPA. Another study performed by this group [94] shows that using a combination of acyl phosphine oxide-based

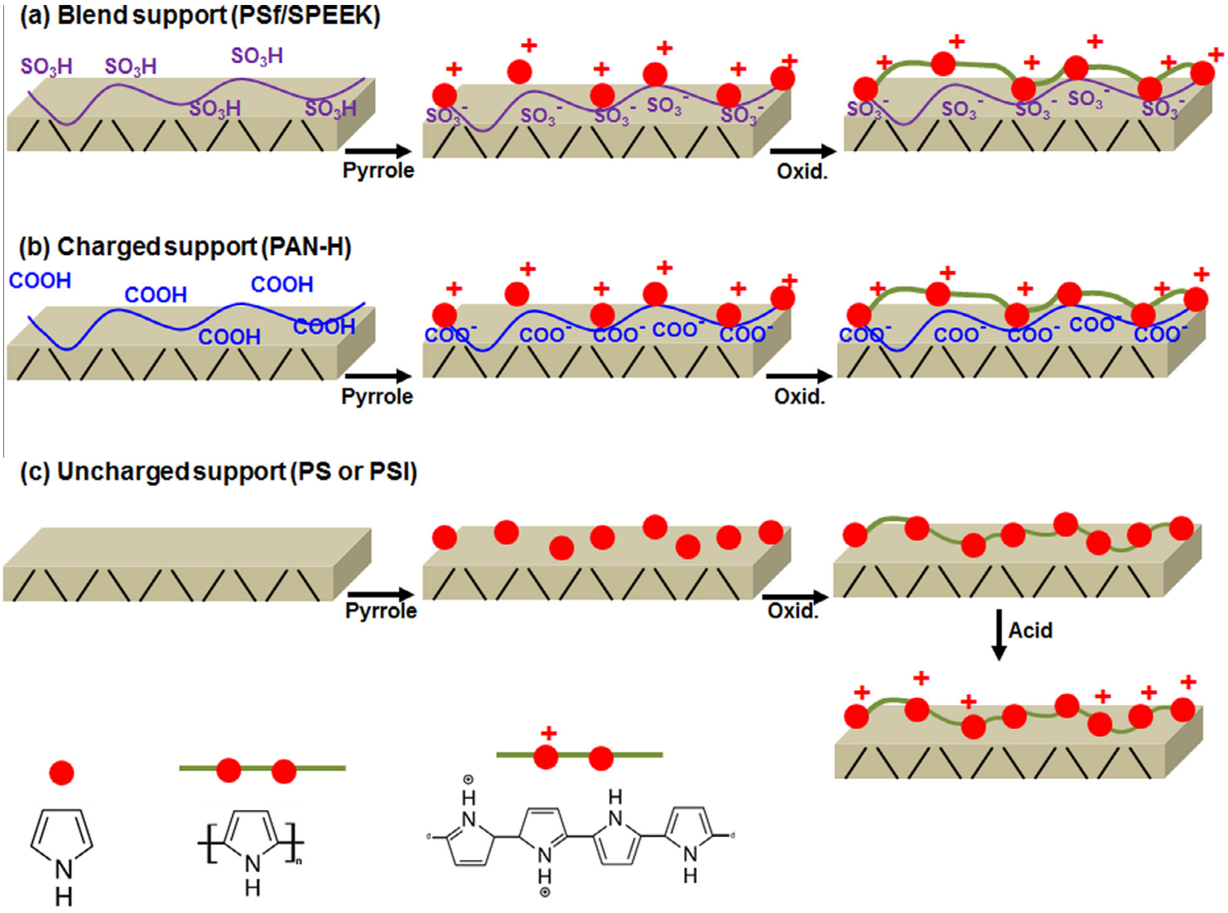

Fig. 7. Preparation of PPy-modified OSN membranes on three different porous supports (reproduced with permission from Elsevier Science Ltd.) [117].

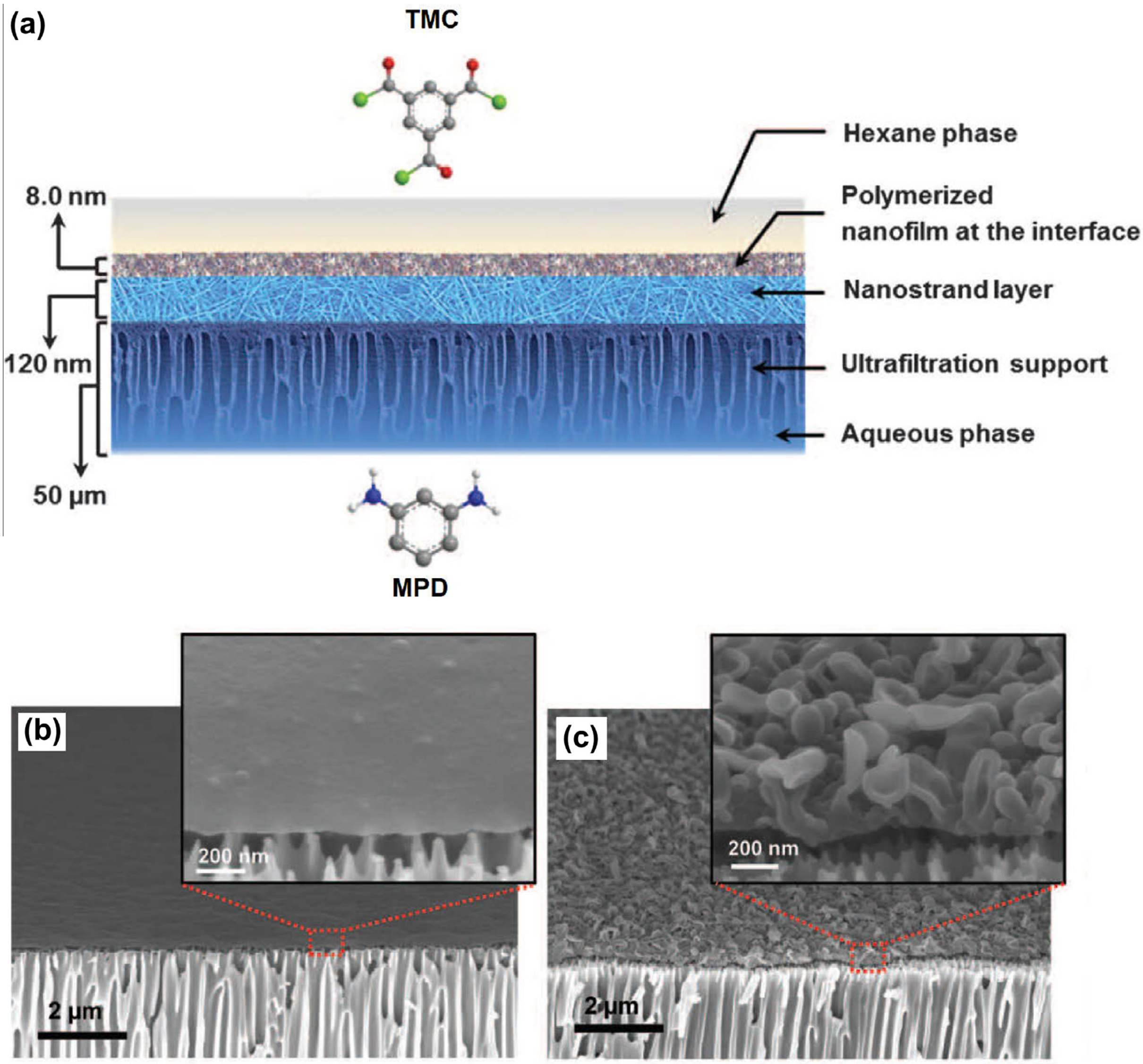

Fig. 8. PA nanofilm prepared via the controlled interfacial polymerization: (a) schematic of the controlled interfacial polymerization process, (b) smooth PA nanofilm on alumina support (0.1% of MPD in a 10-min interfacial reaction) and (c) crumpled PA nanofilm on alumina support (3% of MPD in a 1-min interfacial reaction) (reproduced with permission from Science Ltd.) [118].

photo-initiators with a penta-acrylate cross-linker resulted in PSf UV-cross-linked membranes with a high stability in acetone, n-butyl acetate, EA, toluene and xylene.

UV light approaches were also used to modify PSf membranes prepared with di- to hexa-acrylate cross-linkers and 2,4,6-trimethylbenzoyl-diphenyl-phosphine oxide (TPO) as photo-initiator [92]. UV irradiation improved the cross-linking efficiency and consequently increased the viscosity of the casting solution. As a result the phase inversion mechanism changed from instantaneous to delayed demixing, resulting in a more spongy-like structure without macrovoid formation [96,97].

Recently, Behnke et al. [98] employed UV irradiation to cross-link Lenzing P84® TFC membrane containing a substituted photo-active benzophenone group in its repeating unit (Fig. 5a). Abstraction of hydrogen from a methyl group of a nearby aromatic unit upon the UV irradiation resulted in the formation of two radicals and consequently a new covalent bond by recombination of these radicals (Fig. 5b). The membrane stability in polar aprotic solvents such as DMF is enhanced significantly via the introduction of new reactive side groups by using aminoethyl methacrylate (AEMA) in a reaction with the polymer chain via opening of the imide bond (Fig. 5c).

4.1.2. Plasma-induced techniques

Surface modification of polymeric membranes by low-temperature plasma is one of the interesting methods to change the surface chemistry of membranes whereas their bulk properties remain mainly unchanged [99–101]. This technique is very fast, effective and meets environmental standards for clean technology. A large variety of (macro) molecules can be used to react with the formed free active radicals on the membrane surface. Plasma parameters such as power, pressure and sample deposition and also polymerization conditions such as monomer concentration and grafting time are the most effective parameters to control the grafting density and the chain length [80].

Zhao et al. [102] and Chen et al. [103] employed an Ar-based, low-temperature plasma treatment for styrene grafting on the surface of polyacrylonitrile (PAN) UF membranes to prepare OSN membranes used for the recovery of toluene and methyl ethyl ketone (MEK) from dewaxed oil. Increasing the grafting time leads

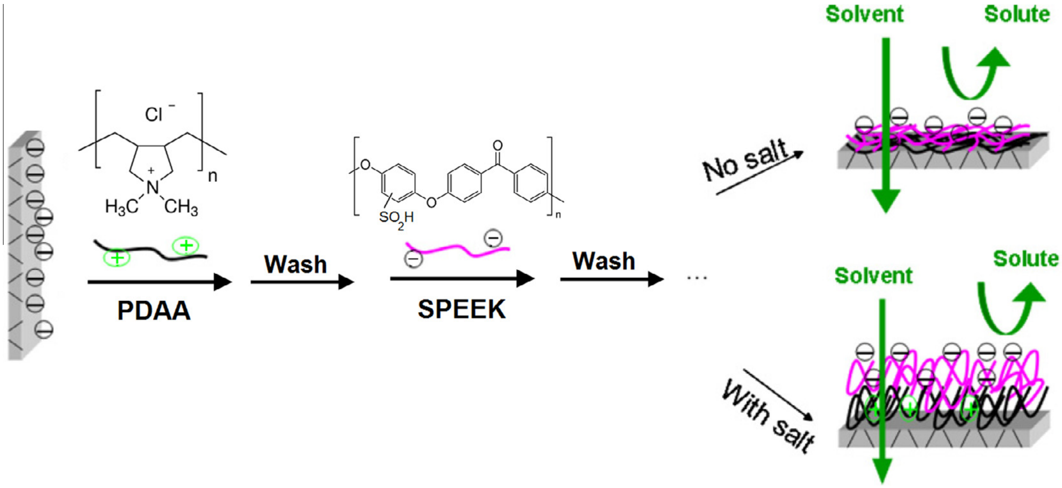

Fig. 9. Schematic of the effects of salt on PE adsorption (reproduced with permission from Elsevier Science Ltd.) [129].

to smaller pore sizes and lower pore densities with a pore size distribution that is significantly more narrow [104]. However, the results revealed that an increase in the membrane hydrophobicity has a larger effect than decreasing the pore size. Hence, the permeation flux increased by increasing the grafting reaction time.

Plasmas based on Ar, Ar–H_2 and Ar–O_2 were employed to treat surfaces of PDMS OSN membranes [105]. The resulting membranes showed higher rejections for dispersed, neutral components compared to charged dyes, while a very high rejection ($\geqslant 95\%$) was obtained with a neat PDMS membrane for charged dyes. The authors explained that plasma treatment decreased the surface hydrophobicity of the PDMS membranes and as a consequence the affinity of the treated membranes toward neutral dyes decreased significantly. The effects of transport asymmetry of the OSN membranes was studied by Volkov et al. [101] for the first time for the PTMSP membranes modified with a plasma treatment using atmospheric air. They found that the permeation properties of the modified PTMSP membranes depended on the membrane orientation with respect to the flow direction. For instance, when the modified surface contacted the feed stream such as MeOH, ethanol (EtOH), propanol and acetone, the permeation fluxes of organic solvents through the membranes were two times lower compared to the unmodified surface. In another work from Karan et al. [106] a plasma-enhanced chemical vapor deposition (CVD) reactor was used to synthesize ultrathin diamond-like carbon (DLC) nanosheet membranes on porous alumina (Fig. 6). Permeation experiments with the DLC nanosheet membranes using a wide range of organic solvents showed higher permeation fluxes (values in the range of UF membranes) with high retention times. They concluded that hydrophobic pores (of 1 nm diameter) in the selective carbon layer deposited on a porous alumina support resulted in an ultrafast viscous permeation of organic solvent through the DLC membranes.

4.1.3. Thin film formation via polymerization

In the early 1980s, pioneering work on interfacial polymerization was performed by Cadotte et al. [107] to prepare TFC aromatic PA membranes. Interfacial polymerization is known as a well-established and useful method to synthesize a dense and active top-layer on a porous support to prepare composite RO and NF membranes [6]. Although interfacial polymerization was mainly used to prepare TFC membranes used in the separation of aqueous feed streams [108], it was developed to synthesize membranes for filtration in organic solvent media as well [2,6]. Application possibilities of this method for the preparation of composite OSN membranes strongly depend on the specific molecular structure of the top-layer and chemical stability of the porous support in organic solvents [6,109]. Generally this method entails the application of an ultra-thin film upon an asymmetric, porous support-layer via an *in-situ* polymerization reaction occurring at the interface between two immiscible solvents containing reactive monomers.

Since thin films play the main role in the separation of organic solvents, it is important to obtain very stable thin films with high separation abilities and permeation properties. Interfacial polymerization of MPD and a blend of trimesoylchloride (TMC) with fluoro-alkyl acyl chloride in the organic phase formed hydrophobic PA membranes with a high stability in DMF [110]. These membranes showed a significantly higher permeation flux without sacrificing rejection for nonpolar solvents, including toluene and EA.

Controlling the rate of the interfacial polymerization reaction and the wettability of the formed thin film by additives are efficient ways to improve the final performance of the prepared membranes [111]. Sodium dodecyl sulfate (SDS) surfactant and TEA/CSA were added to the MPD solution during the IP, resulting in a significant increase of the permeation of MeOH through the TFC OSN membrane [67]. Wettability enhancement of the membrane surface by the addition of SDS improved adsorption of MPD on the substrate [112]. Also, TEA as an acid acceptor increased the reaction rate and formed organic water-soluble salts between its amine group and the sulfonic group of CSA, which leads to an increase of the surface porosity of TFC membranes after interfacial polymerization [113,114].

Jimenez Solomon et al. [115] reported that solvent activation of the TFC membranes after an interfacial polymerization reaction dramatically improved the organic solvent fluxes without compromising rejection. DMF and DMSO have similar Hildebrand solubility parameters to those of the PA top layer (24.8, 26.6 and 23 (MPa)$^{1/2}$, respectively) and can act as a good swelling agents. The swelling and morphology of the thin film PA NF and RO membranes have been studied in great detail by Freger [116], using atomic force microscopy (AFM). The swelling was found to increase along the following series: acidic brine < basic brine < pure water. Enhanced swelling was observed for the (looser) outmost polymer parts. It was concluded that for NF membranes, there was a reasonable correlation between the swelling and permeability properties and the salinity and pH of the feed.

In a closely related method, Li et al. [117] applied *in-situ* polymerization to synthesize a polypyrrole(PPy)-modified top layer on different UF support membranes (Fig. 7). A solution of pyrrole monomer and EtOH was casted on the porous support and polymerized to form a PPy selective layer. The resulting OSN membrane showed high stability in harsh aprotic solvents such as DMF and tetrahydrofuran (THF) with desirable permeation behavior. For instance, the permeance and the rejection of THF/RB mixture were found to be 67.1 L m^{-2} h^{-1} bar^{-1} and 98%, respectively for the membrane prepared on the PAN-H support.

Very recently, the Livingstone group [118] prepared ultrafast permeable PA nanofilms with outstanding rejections to separate negatively charged solutes from MeOH. They controlled the rate of interfacial reaction between MPD and TMC on a sacrificial layer of cadmium hydroxide nanostrands to prepare a sub-10 nm PA film on P84 and alumina support (Fig. 8). The formed nanostrand layers were removed after the PA formation by acid dissolution. They report that the DMF activated PA nanofilm on alumina support, which was prepared with a 1-min interfacial reaction of 3 wt% of MPD in aqueous solution, resulting in an excellent permeance performance with a high rejection. For instance, for the mixtures of MeOH and 6-hydroxy-2-naphthalenesulfonic acid (HNSA) sodium salt, MO, Naphthalene brown and Acid fuchsin (AF), permeance and rejection performances of 52.22, 52.05, 52.00 and 51.84 L m^{-2} h^{-1} bar^{-1} and 98.5%, 98.9%, 99.9% and 99.9% were found, respectively.

In the design of high-performance OSN membranes, the use of segmented polymer networks (SPN) is another approach to prepare a highly-engineered top layer on a porous support. Li et al. [119] employed *in-situ* polymerization to synthesize a multifunctional thin SPN selective layer on PAN porous support. They prepared SPN via free radical copolymerization of the hydrophilic *bis* (acrylate)-terminated PEO as macromolecular cross-linker with different hydrophobic acrylate monomers and Perkadox as the radical initiator. These membranes showed an excellent rejection of RB in organic solvents including IPA (rejection of 99% RB in IPA with a permeance up to 0.4 L m^{-2} h^{-1} bar^{-1}), THF (rejection of 99.3% RB with a permeance up to 1.3 L m^{-2} h^{-1} bar^{-1}) and DMF (rejection of 96% RB with a permeance up to 2.7 L m^{-2} h^{-1} bar^{-1}).

Finally, the interfacial polymerization method is also applied to incorporate nanoparticles, which is reviewed in Section 4.1.5.

4.1.4. Polyelectrolyte modification

Polyelectrolytes are a class of macromolecules with functional groups that either are permanently charged or can be charged under specific pH conditions. Decher and his co-workers pioneered [120–122] the so-called layer-by-layer (LbL) technique for the preparation of multilayer thin films onto a charged surface by the alternating deposition of polycations and polyanions. This surface modification approach has been widely used in various applications, including drug delivery [123], sensors [124,125] and also in membrane separations [79,126]. Polyelectrolyte multilayer (PEM) thin films are considered to be good candidate for OSN applications as well, since thin selective layers have proven to be highly permeable and to some extend selective for charged molecules, while they have excellent stability in common organic solvents [42,126,127].

Li et al. [128] used poly(diallyldimethylammonium chloride) (PDDA) and sulfonated poly(ether ether ketone) (SPEEK) to prepare PEM membranes on hydrolyzed PAN (H-PAN). The resulting membranes were used for the separation of charged aromatic dyes such as RB, crystal violet, methyl orange (MO) and AF. The PEM membranes showed a high chemical stability and high separation performances in aprotic solvents like THF and DMF. In addition, the solvent stability and permeation flux in the presence of salt improved dramatically without sacrificing selectivity [129]. Addition of NaCl to the PE solution used for the PEM membrane formation results in the screening of charges and consequently the intramolecular repulsion of equally charged PE monomers reduces. This resulted in coil-like PE chains with a more loopy (rather than stretched) configuration. Upon adsorption, the thickness and density of membranes were significantly affected. The change in the PE solution resulted in membranes with thicker and looser selective layers (Fig. 9). In a similar study performed by Chen et al. [127], PDDA/SPEEK multilayers were successfully deposited on the H-PAN coated with silicon particles and applied for the filtration of polar aprotic solvents such as THF and DMF. The highest selectivity was found for those systems that have the same charge for the PEM membrane top layer and the solutes. In more detail, a SPEEK-terminated PEM membrane is negatively charged resulting in a Donnan exclusion of a negatively charged solute.

In addition, Ahmadiannamini et al. [130] used PAA as a weak polyanion to prepare PDDA/PAA PEM membranes in different NaCl concentrations and pH conditions. The thickness of the deposited layers decreased as the pH value of PE solutions increased up to 4. At these pH values, less material was required to compensate all charges present on the previously deposited layers due to the increasing in charge density of PAA chains. By further increasing the pH, the thickness increased again because the resulting higher charge density of the PAA chains. These membranes showed good chemical stability and retention in filtration processes of aprotic solvents such as THF. In another study performed by this group, the effects of the H^+-form and the Na^+-form of poly(vinyl sulfate) and poly(sodium styrene sulfonate) PSS as poly anions were investigated on filtration performance of DMF and THF [43]. The membranes prepared with the H^+-form of the polyanions showed higher permeabilities and higher retentions than the ones prepared with the Na^+ salts because of their loopier structures and their higher surface charges.

4.1.5. Incorporation of nanoparticles

The preparation of organic–inorganic composite membranes, called mixed matrix membranes (MMMs), is a promising approach to improve the thermal stability, mechanical strength and solvent resistance of membranes. The main challenge in preparing MMMs is to make a proper connection between the polymer and inorganic phases via covalent bonds, Van der Waals forces or hydrogen bonds to reduce or ideally avoid leaching of nanoparticles during operation. MMMs for OSN application have been prepared in three different ways: (i) dispersing the inorganic filler in the polymer solution [25,89,90,95,131–137], (ii) *in-situ* polymerization, *i.e.* dispersion of nanoparticles in solutions before polymerization [64,65,138–140], and (iii) self-assembling and pre-assembling of nanoparticles, *i.e.* the synthesis of inorganic nanoparticles using precursors during the membrane formation and nanoparticle functionalization before polymerization [141–143]. Table 1 summarizes a selection of the studies in this field.

The use of inorganic materials to enhance the performance of OSN membranes was first proposed at KU Leuven one decade ago by Gevers et al. [131,132] who tested the incorporation of three types of fillers, namely silica, carbon and zeolites into PDMS membranes. They found that the addition of inorganic fillers in the PDMS improved the performance of the membrane for the separation of non-polar solvents by reducing the swelling of the PDMS network. Zeolite-filled (ZSM-5) PDMS showed much stronger anti-swelling properties than PDMS films filled with silica and carbon. This was attributed to an improved dispersion of zeolite in the polymer solution, stronger cross-linking effects. Dobrak-Van Berlo et al. [133] showed that the incorporation of 15 wt% silicalite fillers into the PDMS matrix reduced the swelling significantly and improved the retention for dye/n-propanol systems. Vandezande et al. [25] also confirmed the positive role of silicalite on the reduction of swelling by making asymmetric silicalite-filled PI membranes using the phase inversion technique. The addition of more nano-zeolite suspension to the casting solution changed the

Table 1
Summary of different types of nanoparticles used for the preparation of OSN membranes and the membrane characteristics and performances.

Nanoparticle[a]	Particle size (nm)	Pore size (nm)	Nanoparticle concentration (wt%)	Polymer (selective layer)	Solvent	Permeance (L m^{-2} h–1 bar^{-1})	Solute[a]/MW (g mol^{-1})	Rejection (%)	Ref.
UZM-5	73		0.02	PA	MEK/toluene	0.9	Lube oil	96	[65]
	1000–1500	0.55–0.58	30	PDMS	EA	0.6	Wilkinson catalyst/925	97	[131]
			30		Toluene	0.6		98	
			30		THF	0.9		80	
			30		DCM	0.7		93	
TiO_2	25		0.05	PA	MeOH	24	BTB/624	>90	[64]
							Crystal violet/407	>90	
Au	2			PDMS	IPA	0.04	BTB/624	97	[95]
							MO/324	99	
	2			P84	EtOH	0.2	MO/324	82	[89]
						2.9	BTB/624	58	
	3–5		4	Matrimid 9725	IPA	0.1	RB/1017	98	[161]
						0.1	MO/324	98	
	5		2	CA	EtOH	1.5	BTB/624	82	[90]
Silicalite-1	120	5.4–5.6	1.5	PDMS	IPA	0.3	RB/1017	100	[162]
					THF	1.9	BTB/624	79	
					EA	1.0	BTB/624	100	
					Toluene	0.9	BTB/624	80	
Silicalite-1 hollow spheres	3000–5000		1.5		IPA	1.1	RB/1017	100	
					THF	2.8	BTB/624	78	
					EA	1.5	BTB/624	100	
					Toluene	1.3	BTB/624	98	
PNIPAM	120		5	P84	Acetone	1.3	SO/220	90	[143]
			5		Toluene	0.6		90	
HKUST-1		0.9	20	P84	Acetone	15	SO/1800	90	[135]
$Cu_3(BTC)_2$		0.6	20	PDMS	IPA	0.5	RB/1017	96	[134]
MIL-47		0.85	20			0.5		98	
MIL-53 (Al)		0.85	20			0.5		98	
	60	0.86	0.2	PA	MeOH	1.9	SO/236	99	[139]
ZIF-8	100	0.34	0.2	PA	MeOH	2.1	SO/236	96	[139]
MIL-101		3.4	0.2	PA	MeOH	3.9	SO/236	96	[139]
					THF	11.1		97	
NH2-MIL-53(Al)	133	0.75	0.2		MeOH	1.8		99	
MWNTs	30		0.06	PA	MeOH	6.3	BTB / 624	91	[138]
GO			0.05	PPy	IPA	3.2	RB / 1017	99	[140]
			0.05		EtOH	9.6		99	
			0.05		MeOH	15.3		99	

[a] Abbreviations: PNIPAM: Poly(*N*-isopropyl acrylamide); BTB: Bromothymol blue.

membrane morphology from a finger-like to a sponge-like structure, *i.e.* from elongated macrovoids to spherical microvoids. The latter type of voids were reported to make the membrane more resistant to compaction and swelling.

The incorporation of metal–organic frameworks (MOFs) as a filler for the preparation of OSN membranes was explored by Basu et al. [134]. MOFs are a relatively new class of porous crystalline materials that are composed of metal ions joined by organic ligands, often polycarboxylic acids, via strong coordinative bonds. The nanocomposite membranes prepared by the incorporation of $Cu_3(BTC)_2$, MIL-47, MIL-53(Al) and ZIF-8 into the PDMS matrix showed enhanced permeabilities, but decreased solute rejections compared with the pure PDMS/PI membrane due to a poor adhesion of the MOFs to the PDMS network. Campbell et al. [135] produced MMMs by dispersing pre-formed particles of the MOF HKUST-1 in PI P84 dope solutions. The synthesized MMMs demonstrated both (i) higher rejections of styrene oligomers in the treatment of polystyrene solutions in acetone, and (ii) lower flux decline than those observed for the pure membranes.

TiO_2 nanoparticles have been extensively applied for making MMMs with improved antifouling, hydrophilicity, permselectivity, and photo-catalytic properties. Soroko et al. [136] prepared the first MMMs for OSN applications by dispersing TiO_2 nanoparticles in a PI solution. The formation of macrovoids, which is common in phase inversion membranes, was suppressed by the addition of TiO_2 nanoparticles and finally disappeared at higher loadings (>3 wt%). Compaction resistance of the prepared membranes improved without adversely affecting the flux and rejection in the treatment of styrene oligomer mixtures in EtOH. Li et al. [137] fabricated thermally stable and solvent-resistant TiO_2–PAN hybrid hollow fiber membranes. The thermogravimetric analysis (TGA) results showed high thermal stability of the prepared membranes, which could persist up to 400 °C with a slight weight loss. In order to find the solvent resistance of TiO_2–PAN hybrid fiber membranes, they were exposed to various boiling solvents including N,N-dimethylacetamide (DMAc) and the changes in axial length and weight were measured afterwards. The original PAN membrane was found to dissolve rapidly in most of these solvents, whereas the axial length of the hybrid membranes swelled slightly in the range of 0.8–6.7% and their weight increased from 3.3% to 7.4%.

Novel inorganic fillers like multi-walled carbon nanotubes (MWNTs), MOFs and graphene oxide (GO) have been already utilized for the fabrication of thin film hybrid OSN membranes [138–140]. Roy et al. [138] fabricated interfacial polymerization-generated PA membranes by the dispersion of MWNTs in either the organic phase or the aqueous phase. Raw MWNTs were functionalized with hydrophilic (–COOH) groups or hydrophobic groups (–CONHR) (via microwave treatment) to be dispersed in a polyethylene imine (PEI)-containing aqueous solution and also in an *iso*-phthaloyl dichloride (IPD)-containing organic solution. Their permeation results demonstrated that the MeOH flux of the synthesized membranes is enhanced by an order of magnitude due to nano gaps between the external surfaces of functionalized MWNTs and the polymeric matrix, while the Brilliant blue rejection was at higher value of 91%. A similar permeation behavior was observed for PPy-based OSN membranes embedding GO [140]. In these membranes, pyrrole absorbed onto the GO surface due to the π–π interactions and electrostatic attractions [144,145]. This resulted in polymerization around GO and the formation of thinner selective layers on the surface of the porous PAN-H. Separation experiments revealed that due to the presence of polymer-coated GO in the active layer of the membranes, the permeances of MeOH, EtOH and IPA significantly increased without sacrificing the rejection of RB.

Sorribas et al. [139] conducted the same interfacial polymerization reaction and synthesized TFN membranes containing 50–150 nm size MOF nanoparticles (ZIF-8, MIL-53(Al), NH_2-MIL-53 (Al) and MIL-101(Cr)) on top of cross-linked PI porous supports. They found that organic solvent (MeOH and THF) permeations increased by embedding MOFs into the PA thin layer compared to filler-free membranes without sacrificing styrene oligomers rejections (>90%). Common nanoparticles and zeolites were also utilized for making thin film OSN membranes. Namvar-Mahboub et al. [65] fabricated TFN membranes by the incorporation of amine-functionalized UZM-5 nanoparticles into the PA layer synthesized via an interfacial polymerization of MPD with TMC (Fig. 10). These membranes were studied in a dewaxing solvent recovery process (MEK and toluene from lube oil). The work indicates that the presence of UZM-5 in the PA layer improved both the oil rejection and the permeate flux under an optimal concentration of 0.02% w/v of UZM-5. The increase in the permeate flux upon the addition of UZM-5 was attributed to the pore diameter of UZM-5. In other words, modified UZM-5 with an average pore diameter of 16.8 Å which was loaded at 0.02% w/v into the PA thin film provides a pathway for toluene (6.1 Å) and MEK (5.2 Å) whereas the lube oil macromolecules were rejected. In the higher loading contents of UZM-5, the PA thin layer became less cross-linked with more interface defects and consequently the permeance increased, while the oil rejection declined significantly. Peyravi et al. [64] synthesized TFN membranes by the incorporation of surface-modified TiO_2 nanoparticles into a thin layer of co-PA network fabricated by *in situ* interfacial polymerization reaction. TFN membranes represented higher MeOH flux than filler-free TFC membranes with a slight sacrifice in dye rejection during the NF of a MeOH/dye solution.

Despite outstanding advantages of MMMs, the preparation of these membranes with defect-free hybrid active layer is still challenging. The main problem to be solved is the severe aggregation of the nanoparticles due to their high surface area and their weak compatibility with polymer materials [141]. As a result, often non-selective voids are formed at the interface of the polymer and the inorganic nanoparticles, which typically reduces rejection values significantly. Inspired by the mechanism of mineralization, MMMs can be synthesized by using some functional groups of the polymer as catalyst to generate inorganic nanoparticles via hydrolysis and condensation of inorganic precursors. Applying this technique, inorganic nanoparticles with uniform size distribution can be generated and self-assembled within the polymer matrix. Due to the good compatibility between the polymer and nanoparticles formation of non-selective voids can also be eliminated. For example, Zhang et al. [141] assembled SiO_2 and TiO_2 nanoparticles into the polymer by the hydrolysis of the inorganic precursors, tetraethoxysilane and tetra-n-butyltitanate, respectively, using –NH_2/–NH– groups of PEI. They evaluated the performance of their self-assembled MMMs for OSN applications using n-heptane, toluene, butanone, EA, and IPA as solvents, and polyethylene glycol (PEG) as a solute. It was shown that the presence of nanoparticles improved the solvent resistance of the synthesized membranes (*i.e.* swelling was below 6%). Interestingly, these types of MMMs showed an increase in the solute rejection with a slight decline in solvent flux by increasing the nanoparticle loading, which is not common in hybrid membranes. Siddique et al. [142] followed the same technique and synthesized self-assembled MMMs by using (3-aminopropyl)trimethoxysilane (APTMS) as a cross-linking agent as well as an organo silicone precursor to generate an inorganic network. The SiO_2 network is generated by the hydrolysis and condensation of the methoxysilane moieties in APTMS. The NF of organic solvents such as acetone, DMF and dichloromethane (DCM) showed a reduction in flux after treatment with this organic–inorganic based cross-linker. However, MMMs were improved in terms of rigidity and strength as well as resistance to compaction and swelling. In another study, Siddique et al. [143] fabricated pre-assembled MMMs by incorporating nano-sized polymer particles with methacrylate moieties onto the surface of cross-linked PI UF support membranes. Multiple layers of these nanoparticles (120 nm and 300 nm in diameter) spin-coated on the PI support and the nanoscale interstitial spaces formed between the particles served as permeation channels. In order to prevent the removal of nanoparticles from the surface in the OSN process, they were cross-linked to the support by a photo-initiated, free-radical polymerization using UV light. The

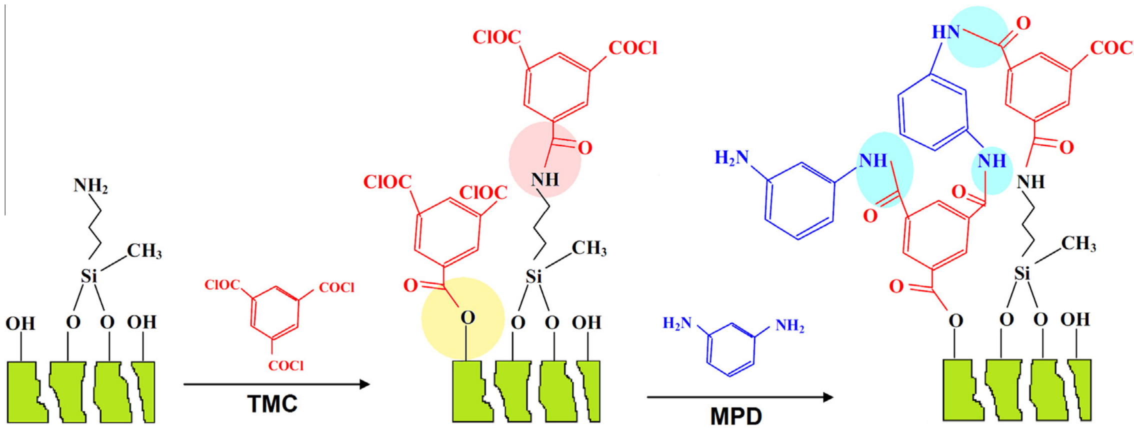

Fig. 10. Schematic of chemical reactions between an amine-functionalized-UZM-5, TMC and MPD during the PA synthesis (reproduced with permission from Elsevier Science Ltd.) [65].

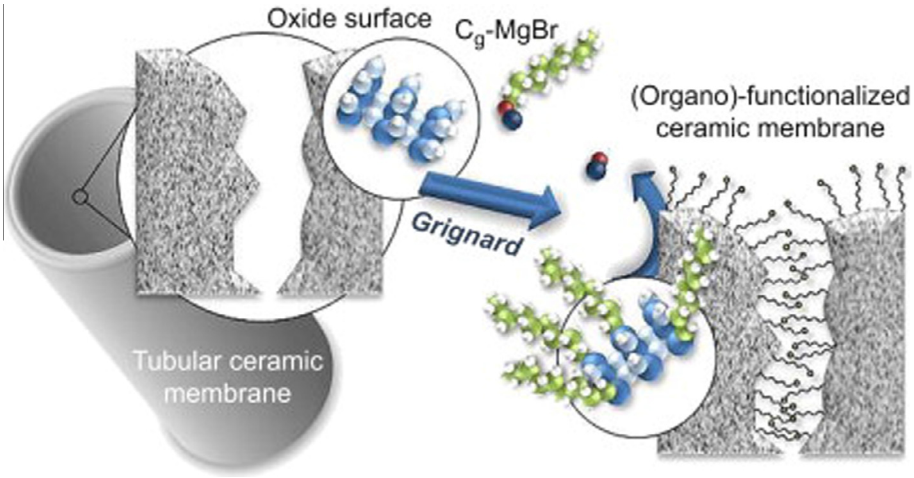

Fig. 11. Schematic representation of the Grignard-grafted ceramic membranes (with permission from Elsevier Science Ltd.) [159].

NF performance of the synthesized membranes was evaluated in solvents such as acetone and toluene. The molecular weight cut-off (MWCO) of the membranes, measured by a styrene oligomer mixture as solute, was in the range of 200 to 1000 g mol^{-1} which depended on the nanoparticle diameter and the thickness of the nanoparticle layer. Membranes coated with nanoparticles showed better rejections and more resistance against compaction compared to commercial polymeric membranes because of their more rigid structure.

4.2. Modification of ceramic OSN membranes

Ceramic membranes show advantageous behavior compared to polymeric membranes under harsh conditions including high pH, high temperature or the exposure to organic solvents. In general, ceramic membranes have an asymmetric structure composed of at least two—in most cases more—different porosity levels including a macroporous support, an active microporous top layer and an intermediate layer with a pore size between that of the support and the active layer [6,146]. The macroporous support provides the mechanical strength for the ceramic membranes. Normally, the sol–gel synthesis method is used to prepare the active top layer of ceramic membranes. Despite these superior characteristics ceramic membranes contain surface hydroxyl groups (OH), hampering the applications in non-aqueous separations due to their hydrophilic nature [147–151]. Pioneering work on using ceramic membranes for OSN has been reported by Tsuru et al. [31,32] While large pore sizes (70 nm in diameter) showed a viscous flow mechanism for MeOH, EtOH and 1-propanol, the permeation mechanism through porous membranes having pore diameters of 1 to 5 nm was found to be different; small molecules showed larger permeabilities than large molecules. Later, this research group successfully applied the sol–gel method to prepare porous silica–zirconia RO membranes [152]. According to their filtration experiments, membranes containing pores of 1 nm in diameter showed high potential for the separation of organic solvents with EtOH flux of up to 3 kg/m^2 h at 30 bar and a MWCO as low as 200 Da.

As was discussed in Section 2, to improve the separation performance of the above-mentioned ceramic OSN membranes, surface chemistry plays an important role. First, the pore sizes can be reduced to nanometer dimensions and, second, the wetting properties can be tuned by the nature of the compounds used in the surface modification. In order to prepare high-performance ceramic membranes for OSN applications, the top layer should be grafted by hydrophobic functional groups, for instance via silylation chemistry [1,147,153,154]. Here we discuss different approaches that cover, silylation, calcination of alkyl-modified colloidal dispersions, a sol–gel based sintering method and Grignard chemistry, showing the diversity of reported strategies.

To render the ceramic membranes with superior hydrophobicity and filtration performance, Dutczak et al. [155] prepared capillary OSN membranes by a combination of the advantages of ceramic supports such as high mechanical, thermal and chemical stability with high separation properties of the PDMS coating layer. It was shown that relatively low PDMS concentrations (<15 w/w% in toluene) are necessary to fabricate very thin (*i.e.* 6–20 μm for 3.75% w/w PDMS) and defect-free PDMS top-layers on the porous support. Composite membranes prepared by a coating of PDMS on the inside of 20 nm pore size α-alumina support showed the best performance. This membrane was stable for over 40 h in toluene with a permeance of 1.6 L m^{-2} h^{-1} bar^{-1} and MWCO of ~500 Da. In another and novel approach, Pinheiro et al. [150] employed PDMS-grafted γ-alumina ceramic membranes in OSN of hexane, toluene and IPA. The authors developed a two step-method to graft PDMS on the surface of ceramic membranes. In this approach (3-aminopropyl)triethoxysilane (APTES) was applied on the surface of a ceramic membrane by either a vapor phase or a solution phase technique in the first step. In the next step, an epoxy-terminated PDMS was grafted onto the APTES layer. PDMS-grafted γ-alumina membranes showed excellent stability in polar and non-polar solvent, whereas the non-polar solvents showed higher permeabilities. In similar work performed by this group [156], monomeso-vinyl terminated PDMS was grafted on the surface of mesoporous γ-alumina membranes using (3-mercap topropyl)triethoxysilane (MPTES) as a linking agent. The results revealed that silylation of the mesoporous γ-alumina substrate by vapor phase deposition provided a more uniform and homogeneous distribution of the products. This was explained by a monolayer silane coverage on the pore walls whereas for solution phase deposition, silane multilayers were formed [153]. The toluene permeability of the membranes was reduced from 5.3 to 2.1 L m^{-2} h^{-1} bar^{-1} upon PDMS grafting. They concluded that the effect of pore size reduction after PDMS grafting was more significant than the effect of the increase of hydrophobicity.

The sol–gel approach is an alternative route to prepare nanometer-sized pores in ceramic membranes. Tsuru [157] et al. employed methylated SiO_2 colloidal sol solutions to prepare organic/inorganic hybrid membranes with nano-size pores (2–4 nm in diameter). In their method, methylated SiO_2

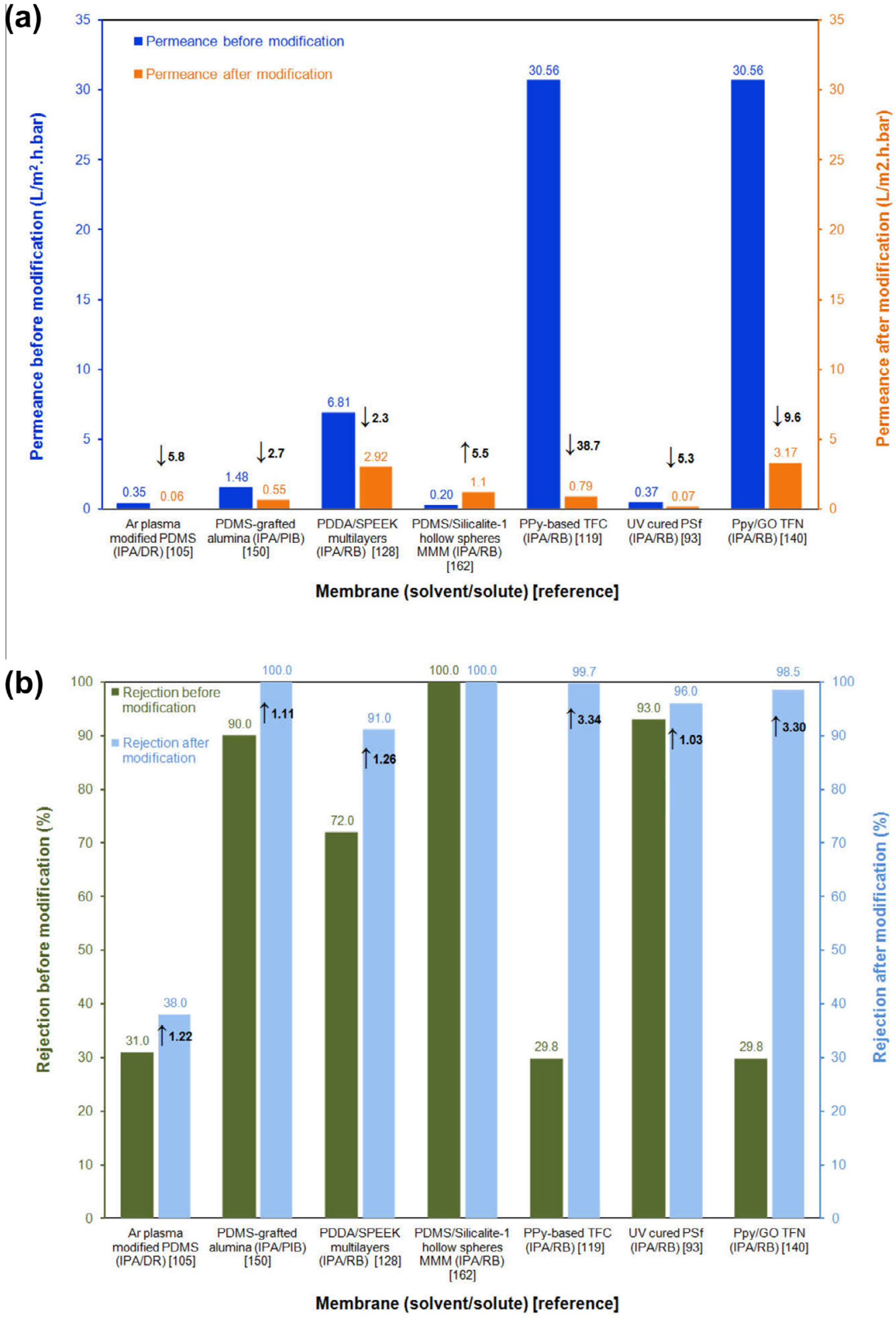

Fig. 12. Comparison of the different modification methods on the (a) permeance and (b) rejection performances of OSN membranes in IPA as a polar solvent.

dispersions coated on porous support and calcinated at 400–600 °C in an inert atmosphere. Permeation experiments with poly olefin oligomers in n–hexane solutions showed an n–hexane permeance of 7.2–27 L m^{-2} h^{-1} bar^{-1} with MWCO of 1000–2000 g/mol.

Also Zeidlet et al. used a sol-based approach to prepare low-MWCO ceramic OSN membranes [158]. They developed hydrophobic NF tubular ceramic membranes with active layers of titanium dioxide/zirconium dioxide with integrated carbon. Diethanolamine (DEA) was added to the sintering sol (titania + zirconia) in order to increase the amount of carbon. DEA acted as a complexation agent preventing the complete hydrolysis and supporting the formation of a polymeric sol. The filtration experiments with a mixture of PS in THF revealed a MWCO ~350 Da, confirming an excellent separation ability of these membranes. Besides the permeation results, permporometry measurements proved the benefits of this new method to change the original pore size of 40.5 nm to the value be small enough to retain the molecules, but big enough to enable solvent permeation.

Very recent work of Rezaei Hosseinabadi et al. [34] covers a Grignard grafting method to functionalize tubular TiO_2 membranes with a series of n-alkyl groups and appropriate organometallic Grignard reagents in order to change membrane affinity to specific solvents and/or solutes (Fig. 11).

The amphiphilic character, reflected by water contact angles in the range of 60–80° of these alkyl-grafted ceramic membranes was explained by the presence of both grafted organic groups and remaining OH groups at the membrane surface. The permeation flux of both polar and non-polar solvents through this type of

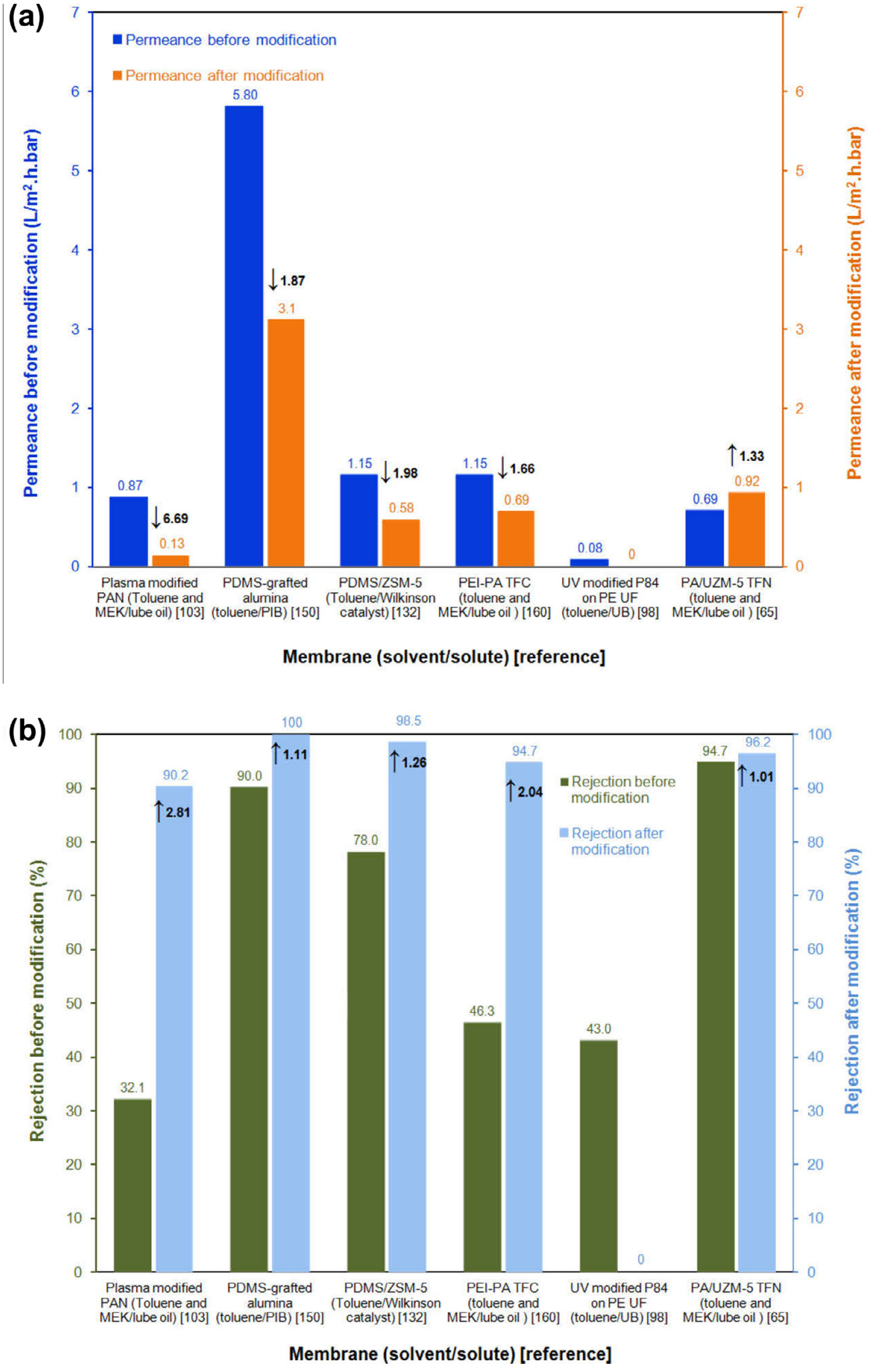

Fig. 13. Comparison of the different modification methods on the (a) permeance and (b) rejection performances of OSN membranes in toluene as an apolar solvent.

partial hydrophobic ceramic NF membranes was obviously high, while the modification did not change the MWCO.

5. Comparison of various modification methods

The development of OSN membranes faces at least two challenges: (1) developing highly stable and selective membranes and (2) forming defect-free skin layers with minimal thickness. As discussed in Section 3, surface layer properties and specific solvent/solute interactions with the (modified) membrane affect the overall performance of OSN membranes. To gain more insight into the effect of the modification techniques, we compare reported results of the permeation/separation performance of OSN membranes in a polar and apolar solvent, respectively: IPA and toluene (Figs. 12 and 13).

As shown in Figs. 12 and 13 there is a trade-off relationship between the permeance and the rejection of the membranes modified with different methods, *i.e.* by improving one of these properties, the other suffers from the modification. Clearly, an ideal modification technique improves both the permeance and the rejection simultaneously or at least improve one of these properties significantly with a minimal sacrifice of the other one. For example, in the case of IPA (Fig. 12), only for the PDMS/silicalite-1 hollow sphere MMM, the IPA permeance increased after modification from 0.2 to 1.1 L m^{-2} h^{-1} bar^{-1} without any changes in the rejection of RB. However, this permeance is still lower than that obtained by polyelectrolyte modified, [128] and TFN membranes [140].

Before discussing the IPA comparison, it must be noted that the data of the unmodified membranes consists of two different series. In the cases of TFC, TFN, PDMS-grafted alumina and PDDA/SPEEK unmodified membranes refer to the porous supports rather than OSN membranes. This explains why the values for the unmodified 'membranes' are relatively low (Fig. 12b). In the other three cases it refers to unmodified OSN membranes.

In terms of the IPA permeance the following two methods are superior over the other listed methods: the PDDA/SPEEK membrane prepared via an LbL polyelectrolyte deposition and the Ppy/GO TFN membrane (Fig. 12a). According to data presented by Li et al. [128], the thin film prepared with 5 bilayers of PDDA/SPEEK have a thickness of 13 nm. This very thin deposited layer provides low resistance against the permeation of organic solvents and, consequently, this modification results in a very high permeance, 2.92 L m^{-2} h^{-1} bar^{-1}, and a good separation factor of about 91%. Also, modified PPy/GO TFN membranes [140] show the highest permeance for IPA (3.17 L m^{-2} h^{-1} bar^{-1}) with a high value of rejection for RB (98.5%) compared to the other modified membranes. It should be noted that due to incorporation of GO into the PPy TFC membrane prepared via IP, the IPA permeance increased significantly from 0.79 to 3.17 L m^{-2} h^{-1} bar^{-1}, while the RB rejection decreased slightly from 99.7% to 98.5%.

Next we discuss the OSN results on toluene in more detail (Fig. 13). For nearly all OSN membranes it is observed that the permeance decreased upon modification. However, the main problem of using OSN membranes in apolar solvents is their rather low stability. Hence, the modification techniques were focused on increasing the chemical stability of the membrane in order to reduce the degree of swelling. It must be realized that for each solvent the modification conditions must be optimized. For example, an unmodified P84 membrane showed a high degree of swelling in toluene and this resulted in a very low rejection of 43% for the separation of UB (Fig. 13) [98]. By optimizing the UV irradiation conditions, the membranes were found to be more stable in different solvents. While upon this irradiation some permeance was observed for DMF, unfortunately no flux with toluene could be measured.

Contrary to the above-discussed, UV-modified membranes, PDMS-grafted alumina membranes showed a very high permeance for toluene (3.1 L m^{-2} h^{-1} bar^{-1}) with a rejection as high as 100% for the separation of polyisobutylene (PIB) from toluene [150]. This excellent performance was attributed to the fine-tuning of surface chemistry and controlling the pore size. This was achieved by the grafting of a thin layer of PDMS on the surface and into the pores of γ-alumina membranes (pore size $\sim$5 nm). According to the OSN experiments on toluene it is evident that the alumina porous membranes provide better permeation results than polymeric PI membranes.

It is worth mentioning that, apart from one specific case of the PA/UZM-5 TFN membrane [65], there is a typical trade-off between permeance and rejection of OSN membranes modified with different techniques for the separation of toluene mixtures. For example, introducing a very thin layer of PA on a PEI-loaded SiO_2 as a support doubles the rejection from 46.3% to 94.7%, while it decreases the permeance from 1.15 to 0.69 L m^{-2} h^{-1} bar^{-1} (*i.e.* a 40% decrease) [160].

As discussed in Section 4.1.5, the addition of 0.02 w/v% of modified UZM-5 to PA not only increased the permeance, but also resulted in a higher rejection. At higher UZM-5 loadings, the rejection decreased and the permeation increased. The enhancement of flux and reduction of rejection by the addition of UZM-5 can be attributed to the changes in the structure of PA and the formation non-selective voids at the interface of polymer and UZM-5.

In summary, the OSN of IPA and toluene solutions suggest that the combination of different modification/preparation techniques are the most promising approaches to obtain improved separation properties. For instance, in order to synthesize nanocomposite OSN membranes, nanoparticles can be self-assembled via a hydrolysis and condensation reaction of inorganic precursors within the polymer matrix at the same time of membrane formation. The incorporation of nanoparticles into the interfacially polymerized selective layer significantly improved the permeance without sacrificing rejection for the OSN of polar solvents. In addition, the incorporation of nanoparticles into the selective layer can be considered as an effective method to increase the stability of membranes and to overcome a trade-off between the permeance and the rejection in the separation of apolar solvents.

6. Conclusions and future trends

In this final section we present general trends in the field of the surface modification of OSN membranes. OSN membranes are a highly promising and new generation of liquid filtration membranes with a high potential to be utilized for different applications such as concentration, purification and solvent exchange processes in organic media. During the past decades, precise tuning of the surface chemistry (selective layer) to the affinity for organic solvents and, in addition, the improvement of membrane stability and lifetime were the primary goals in the field of OSN. New breakthroughs have been attained to make the organic solvent NF membranes more stable and more selective. In this review, we have summarized and discussed the recently reported modification and functionalization techniques applied to optimize the surface layer properties of OSN membranes. In the case of polymeric membranes, major attempts were focused on the improvement of the swelling behavior and a long-time stability, while in ceramic membranes the main target was to obtain well-defined pores using tailored-made molecular chemistry.

The recent efforts in the field of OSN was primarily focused on development of new generation of membranes that can withstand the harsh operating conditions, *i.e.* high temperatures and extreme pH, while preserving both selectivity and permeability at reasonable levels. Therefore, synthesizing a very thin selective layer (at the nanometer scale) on the chemically resistant support should be the main goal of the future research. We consider the recent work of the Livingston group on a sub-10 nm polymer film on different supports to be a breakthrough in this direction [118].

Our review reveals that employing the modification techniques *together*, such as *e.g.* thin film formation and incorporation of nanoparticles, results in membranes with no typical trade-off between the permeance and rejection that exists with the conventional OSN membranes. In this regard, the use of nanoparticles in thin films prepared by the polyelectrolyte LbL technique for polar solvent separation may be a strong candidate. In addition, using porous ceramic membranes as a support for a very thin layer of polymers-loaded nanoparticles is an interesting system for high-performance OSN membranes in apolar solvents.

To conclude, recent improvements in the fabrication of high performance OSN membranes with engineered properties (permeance, rejection and selectivity) will increase the industrial implementation of this type of membranes. Next generations of OSN membranes with a highly stable structure, tunable MWCO and promising permeation properties can be prepared via the optimization of the applied modification techniques.

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