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Thinking the future of membranes: Perspectives for advanced and new membrane materials and manufacturing processes

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A B S T R A C T

The state-of-the-art of membrane technology is characterized by a number of mature applications such as sterile filtration, hemodialysis, water purification and gas separation, as well as many more niche applications of successful membrane-based separation and processing of fluid mixtures. The membrane industry is currently employing a portfolio of established materials, mostly standard polymers or inorganic materials (not originally developed for membranes), and easily scalable manufacturing processes such as phase inversion, interfacial polymerization and coating. Innovations in membranes and their manufacturing processes must meet the desired intrinsic properties that determine selectivity and flux, for specific applications. However, tunable and stable performance, as well as sustainability over the entire life cycle of membrane products are becoming increasingly important. Membrane manufacturers are progressively required to share the carbon footprint of their membrane modules with their customers. Environmental awareness among the world's population is a growing phenomenon and finds its reflection in product development and manufacturing processes. In membrane technology one can see initial steps in this direction with the replacement of hazardous solvents, the utilization of renewable materials for membrane production and the reuse of membrane modules. Other examples include increasing the stability of organic membrane polymers and lowering the cost of inorganic membranes. In a long-term perspective, many more developments in materials science will be required for making new, advanced membranes. These include "tools" such as self-assembly or micro- and nano-fabrication, and "building blocks", e.g. tailored block copolymers or 1D, 2D and 3D materials. Such membranes must be fabricated in a simpler manner and be more versatile than existing ones. In this perspective paper, a vision of such LEGO®-like membranes with precisely adjustable properties will be illustrated with, where possible, examples that already demonstrate feasibility. These include the possibility to switch properties using an external stimulus, adapting a membrane's selectivity to a given separation, or providing the ability to assemble, disassemble and reassemble the membrane on a suitable support as scaffold, *in situ*, in place and on-demand. Overall, it is foreseen that the scope of future membrane applications will become much wider, based on improved existing membrane materials and manufacturing processes, as well as the combination of novel, tailor-made "building blocks" and "tools" for the fabrication of next-generation membranes tuned to specific applications.

1. State-of-the-art and motivation for this article

Membrane technology is now well-developed and widely used in numerous industrial processes, such as hemodialysis, wastewater treatment, surface water treatment, desalination, sterile filtration, chloro-alkali electrolysis, food and beverage processing and gas separation processes such as hydrogen separation, nitrogen enrichment and natural gas sweetening. In addition, membrane application in more recently proposed separations, such as specialized biomedical diagnostics and therapy or energy conversion processes (e.g. fuel cells and alternative batteries) has been extensively investigated at lab scale and is being commercialized. Other separations, particularly in the chemical and pharmaceutical industry, are expected to become feasible with the development of novel membranes. In all these processes, the major advantage of membrane technology is the high selectivity, the much lower energy consumption, the possibility of having more compact systems (lower footprint), the potential for replacement of harsher chemical treatments, and the ease of scalability. Each application requires different membrane properties as exemplified in Table 1. In fact, not in all cases is the membrane selectivity already high enough to

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Table 1
State-of-the-art industrial membrane applications with respective membrane barrier type and separation mechanism, as well as important membrane materials and configurations.

Application	Barrier type (pore size[a])	Separation mechanism	Main materials[b]	Preferred configuration[c]
Hemodialysis[d]	UF	size exclusion	PSU	HF
Seawater desalination[e]	RO	size exclusion (solution-diffusion)	PA/PSU, CA	FS (spiral wound) HF
Brackish water desalination	RO	size-exclusion (solution-diffusion)	PA/PSU, CA	FS
	dense charged	ion-exchange	ion-exchange polymers	FS
Microelectronics (ultrapure water)	dense charged mixed ion exchange resin (EDI)	ion exchange and adsorption	ion-exchange polymers mixed anion and cation exchange resin	FS
Water treatment, removal of: colloids, bacteria, viruses, silica, color, micropollutants	MF, UF	size exclusion	PES, PVDF	FS, HF, tubular
	NF		PA/PSU	FS
Sterile filtration	UF, MF	size exclusion	PSU, PVDF, PTFE, PP	FS
Food and beverage processing	MF, UF, NF	mostly size exclusion	PSU, PES, PVDF	FS, HF, tubular
	dense charged	ion-exchange	ion-exchange polymers	FS
Chloro-alkali electrolysis	dense charged	ion-exchange, Donnan exclusion	Nafion®	FS
Gas separation	dense selective layer	solution-diffusion	CA, PSU, PDMS, …	FS (spiral wound, plate and frame), HF
Water electrolysis	dense charged	ion-exchange, Donnan exclusion	Nafion®	FS
Fuel cell	dense charged	ion-exchange, Donnan exclusion	Nafion®	FS
Battery	porous, optionally filled with electrolyte		PP, PE, PTFE, ceramics	FS
Biotech down-stream process	MF, UF, NF	mostly size exclusion	PSU, PVDF	FS
Biomedical diagnostics[d]	mostly porous	often only used as scaffold & for capillary flow of analyte	cellulose derivatives	FS
Biomedical therapy	mostly porous	toxine removal, drug delivery and others	PSU	FS, HF

[a] Pore sizes: MF: > 100 nm; UF: 2–100 nm; NF: 1–2 nm; RO: < 1 nm.
[b] Polysulfone (PSU), polyethersulfone (PES), polypropylene (PP), polyethylene (PE), poly(vinylidene difluoride) (PVDF), poly(tetrafluoro ethylene) (PTFE), cellulose acetate (CA), polyamide (PA), polydimethylsiloxane (PDMS), ion-exchange polymers are typically quaternary ammonium or sulfonic acid functionalized.
[c] FS: flat-sheet; HF: hollow fiber.
[d] Typically single use.
[e] Typical duration of continuous use > 5 years.

outperform alternative separation methods or to provide solutions to very challenging separation problems.

Membrane manufacturing is based on a relatively small number of established materials, many of which were not originally intended for membranes. Currently used industrial fabrication processes have been scaled and optimized for decades, providing cost advantages and low risk but, in a broader perspective, restricting applications to those compatible with currently used materials. Furthermore, these processes were optimized at a time when environmental regulations were not as strict as they are today and concerns over sustainability were far less developed.

Commercial, porous polymeric membranes are primarily manufactured via the phase separation of homopolymer solutions, induced by immersion in a non-solvent, usually water (non-solvent induced phase separation, NIPS) or by a temperature variation (temperature-induced phase separation, TIPS). Spinodal decomposition or nucleation and growth are the mechanisms that lead to pore formation with pore size and uniformity ruled by the incipient segregating polymer-lean domains in solution and the gelation-solidification of the polymer-concentrated phase. The process enables continuous production of membranes with properties controlled by the choice of polymer and additives, their concentration, the type of solvent and non-solvent, and casting conditions. An asymmetric morphology is obtained with a fine porous structure at the surface and a pore gradient of growing diameter in a direction away from the surface. Hollow fiber membranes are produced based on an analogous mechanism, but the polymer dope solution is extruded through a spinneret with a bore fluid injected in the incipient fiber lumen as it is formed before the immersion in the non-solvent bath. NIPS is the main process for the fabrication of microfiltration (MF), ultrafiltration (UF) and gas separation membranes as well as porous supports for composite membranes for reverse osmosis (RO), nanofiltration (NF) and gas separation.

Another method used in the industry for large-scale production of porous membranes is mechanical stretching of pre-extruded semi-crystalline polymer films of polyolefines or PTFE. The resulting membranes are used in MF or as battery separators.

A special method for porous membrane fabrication is track-etching of pre-extruded films of polycarbonate (PC) or poly(ethylene terephthalate) (PET). In this case, the films are exposed to high-energy radiation in a nuclear reactor or to heavy ions in an accelerator and later etched in caustic solutions. Compared to NIPS membranes the track-etched ones have the unique advantage of cylindrical pores with uniform size, which provide a high size-based selectivity. However, they have low pore density. Furthermore, the selective pores in the track-etched membranes go through their whole thickness, while in NIPS membranes the selective layer is much thinner. The overall transport resistance is therefore much higher in the case of track-etched membranes.

The structure of asymmetric NIPS membranes can be controlled to also provide an integral asymmetric membrane with a dense selective layer allowing direct use in RO, NF or gas separation. Today's RO membranes are mostly thin-film composites (TFC) comprised of a polysulfone, NIPS-prepared, asymmetric support membrane over which a thin polyamide layer is formed by interfacial polymerization of organic diamines and carboxylic acid monomers. Most NF membranes in the market are produced by the same process, but typically with different monomers. The very first material used for the production of commercial RO membranes was cellulose acetate. This was the material of choice used by Loeb and Sourirajan when they invented the NIPS process of making asymmetric membranes back in the mid-1960s. TFC membranes typically have higher permeability over CA membranes, while CA membranes have a better, although limited chlorine resistance.

Membranes for electrochemical processes, such as electrodialysis, choro-alkali and water electrolysis or fuel cells, require dense charged membranes. One of the most well-known is the cation-exchange membrane Nafion® (or chemically similar materials with other tradenames), with its high cation conductivity and stability in acid and oxidative environments. Nafion® is produced by extrusion of a precursor, fully fluorinated, organic polymer with sulfonyl acid fluoride functionalization, followed by side group conversion into sulfonic groups by treatment with sodium hydroxide solutions. Classical ion exchange membranes are based on polymers functionalized by quaternary ammonium groups (anion exchange membrane) and sulfonic acid groups (cation exchange membrane). These membranes are applied in electrodialysis processes, like brackish water desalination, wastewater effluent polishing, cheese whey demineralization and fruit juice deacidification.

Finally, ceramic membranes are produced by completely different methods, based on either casting of a particle dispersion or sol-gel process followed, in both cases, by sintering at high temperature. Depending on the target barrier structure, i.e. porous vs. dense, several layers of progressively smaller particle sizes may be necessary. Each new layer requires a sintering step making ceramic membranes with small pore size or even a dense last layer rather expensive.

The motivation for this article is to discuss the future of membrane technology with the focus on membrane materials and fabrication. There is a large variety of work in academia and industry to extend the state-of-the-art as described above. Several recent reviews deal with very relevant aspects of such development, either from the point of view of a special membrane application or process, or with focus on certain classes of materials or fabrication methods (for instance: [1–12]). What is attempted here is somewhat different because we try to identify and critically discuss concrete innovations, trends and visions, which will in the near or later future lead to *significant opportunities for expanding the scope of membrane applications* (i.e., their use in various industries) *and membrane fabrication* (i.e., to a growth of the membrane industry). We begin with a brief discussion of the driving forces for such development (section 2), followed by important trends for making membranes more versatile and sustainable in the frame of already established membrane manufacturing capabilities (section 3). Thereafter, we discuss novel building blocks for membranes (section 4) and advanced tools for membrane fabrication (section 5), before we outline a vision for future modular, versatile and sustainable membrane fabrication schemes (section 6), which utilize materials or concepts covered before.

2. Driving forces for further membrane development

Several global development goals identified and advocated by the United Nations [13] may be considered as general driving forces for developing "supporting fields", such as membrane technology. Obviously, membrane technologies can have a large impact on "clean water and sanitation" (goal 6). And the state-of-the-art (section 1) also indicates that important contributions can be made to the food sector ("zero hunger", goal 2), "good health" (goal 3), "affordable and clean energy" (goal 7), "industry innovation and infrastructure" (goal 9), "responsible consumption and production" (goal 12), "climate action" (goal 13), and overall also to "decent work and economic growth" (goal 8). Having said that, it is also clear that the share of membranes is still small in that global perspective.

More specific and pragmatic motivations for further development of membrane technology should thus be seen from the perspective of current and potential users of membrane technology on the one hand, and the membrane manufacturing industry on the other hand. With view on innovation, the academic sector is important, potentially enabling novel membranes and/or novel membrane processes. While the membrane applications mentioned in Table 1 are already quite well-established, there are many important challenges (see Table 2) to tackle which will require improved or novel membranes (see Table 3).

Notably, membranes can still greatly benefit from improved intrinsic separation properties such as selectivity and permeability (cf. Table 3). There is a natural trade-off between these two properties, most commonly expressed for gas separation membranes as the ideal selectivity versus the membrane material's permeability in the "Robeson Plot" [14]. Similar relationships have been shown for ultrafiltration and reverse osmosis, where there is an overall trend of decreasing permeance with increasing solute rejection [15,16].

New membrane materials and enhanced manufacturing methods must have the potential to push the trade-off curve to higher permeability (or permeance) and selectivity values and possibly provide close to defect-free membranes. Examples of such new materials and methods considered up to date include polymers of intrinsic microporosity [17], metal-organic frameworks [18] or facilitated transport in gas separations [19], desalination membranes incorporating water channels of aquaporins [20], carbon nanotubes [21] or graphene [22], as well as isoporous ultrafiltration membranes fabricated by the self-assembly and non-solvent induced phase separation (SNIPS) [23]. The latter will enable the fractionation of proteins with membranes of very narrow pore size distribution, which can make ultrafiltration compete with low-throughput, multistep bioseparation methods [24]. Inspired by the functionality of biological membranes, the possibilities to expand the selectivity of synthetic filtration membranes are discussed by Sadeghi et al. [25]; in their perspective article they outline approaches for membranes with selectivity for small molecules of same size, potentially enabling the separation of mixtures of isomers including enantiomers. All such innovations will be further discussed in section 4.

Assessment of these new approaches must consider not only small-scale, idealized performance of the membranes, but also the application process where performance will be affected by the actual feed stream properties and process parameters [26]. Surpassing the existing trade-off relationships can render already existing membrane-based processes more economical and make new separations, currently not carried out with membranes, feasible. However, impactful material innovation - with proven excellent performance - must be translatable into a technically feasible and scalable membrane fabrication process.

A further challenge facing already mature membrane applications is the need for sustainable manufacturing processes. Sustainability can be seen in a holistic way, including process scalability, energy saving and economics [27]. However, more important, in the present context, is the use of renewable materials and the minimization of the use and waste of hazardous chemicals. Currently, commercial membrane production utilizes organic solvents for dissolving the polymers used in phase separation or the monomers used for interfacial polymerization. Environmental regulations aim to reduce the use of these solvents and therefore more environmentally benign solvents will be required for membrane fabrication [28]. Studies on replacing conventional solvents with new, potentially less harmful ones are currently being carried out. Taking a step further along this line one may envision membrane fabrication

Table 2
Need for membrane technologies for important applications.

Application	Challenges
Gas and vapor separation	Membranes suited for efficient separation of •olefin vs. paraffin • N_2 vs. CH_4 • CO_2 separation in selected applications (e.g. from N_2 and O_2 in cement industry) • linear vs. branched hydrocarbons • H_2S vs. natural gas
Organic liquid separation	Membranes suited for processing solutions of valuable products in organic solvents (concentration, purification)
Produced Water	Oil/water separation at low fouling and high temperature (90–130 °C)
All	Low energy consumption Zero waste Increased recovery, low fouling and improved cleanability

Table 3
Need for improved or novel membranes and membrane manufacturing technologies.

Membrane type	Challenges
Gas and vapor separation	Membranes with higher selectivity and sufficient permeance Zero defects Higher thermal stability Stability in hydrocarbons and harsh vapors Improved ageing stability
Pervaporation	Higher permeability at high selectivity Chemical resistance
Reverse osmosis	Improved fouling resistance Resistant to cleaning agents in seawater desalination Solvent resistance for use in chemical/petrochemical processes Temperature resistance (90–130 °C) in produced water applications Increased recovery rates
Nano- and ultrafiltration	Zero defects Narrow pore size distribution Solvent and thermal stability for chemical/petrochemical applications Improved ageing stability
Electrodialysis	Lower resistance, higher selectivity, monovalent vs divalent selectivity, reduced fouling properties
Fuel cell	High proton (for cation-exchange membranes) conductivity at low humidity and temperatures above 100 °C; high stability under oxidative conditions (for cation and anion-exchange membranes) with lower cost
Membrane distillation	Prevention of breakthrough Lower cost membranes
Ceramic membranes	More affordable Less brittle Better sealing in modules
All	Higher permeability-to-selectivity ratio, beyond traditional trade-off relationships Robustness of separation properties under real application conditions Scalability, i.e. simple, robust and reproducible fabrication Modularity (tuning separation properties) More sustainable manufacturing (readily available or renewable raw materials, less toxic, green solvents or no solvents) Zero waste in manufacturing (material and solvent recovery) Module and membrane recycling Cost reduction of commodity membrane products

using methods involving just water, or no solvents at all. This will be further discussed in section 3.3.

In addition to improving membranes for existing applications, there is great potential for extending the range of membrane-based processes, for example organic solvent separation (cf. Table 2). Recent years have seen a large number of studies aimed at producing membranes that are stable in organic solvents, as well as other harsh conditions such as extreme pH values and high temperatures. With improved stability, membranes can be employed for new processes in the chemical and petrochemical industry. This will be further discussed in section 3.1.

While the sustainability of membrane fabrication is hampered primarily by the solvents used, there is also the membrane material itself, as well as the materials used for module fabrication. Furthermore, a cradle-to-grave approach is necessary, where not only the membrane process but the fabrication of the membranes and modules, as well as their fate after use should be taken into consideration. Membranes with prolonged lifetime and stable process performance can reduce waste and potentially enable module reuse, while in other applications biodegradable and disposable membrane modules may offer a more sustainable solution. Those aspects will be further discussed in sections 3.2 and 3.4.

Further extending the applicability of membrane separations will likely require completely new approaches in membrane materials and fabrication. Among the key constraints regarding the success and applicability of a novel approach are simplicity and sustainability of the fabrication process, as well as the economical sustainable producibility and availability of the raw materials. Another key point envisioned is the tunability of the fabrication method to produce membranes with desired properties for specific applications. Current membrane fabrication relies on empirical trial-and-error to give a certain set of properties and is still far from predictive fabrication procedures, in advance, for a desired performance. Next-generation membranes should have fabrication methods that facilitate "tailor-made" properties, adapted to or directly integrated in the required separation/application.

3. Making membranes more versatile and sustainable using existing manufacturing platforms

As a first step, the established membrane manufacturing methods and technologies can be evaluated, with an eye towards potential alternatives or improvements guided by the arguments outlined in section 2. In what follows, we show that "evolutionary" improvements in research and development, such as exploring alternative materials and/or solvents used for membrane fabrication, as well as the reuse of membrane modules, are very likely to be applied in industry in the present or near future.

3.1. Highly stable polymeric membranes

While membrane technology has an established and competitive product portfolio in the water sector, there are opportunities and challenges in the chemical, petrochemical or other sectors where process intensification could have a large impact in terms of energy, environment and economics. A hurdle for implementation in these sectors has been the availability of suitable membranes with higher thermal and solvent stability. There is a myth that ceramics would be the only materials able to address the more demanding applications, but their scalability and cost have been prohibitive until now. Although certain high-performance polymers (e.g. high T_g polyimides, poly(ether etherketone)) are commercially used for some membrane applications, the operating window of polymeric membranes could be substantially extended with the wider use of these polymers. In particular, organic solvent nanofiltration is a growing field and should progress even further in the next decades with the advantage of better membranes [29–31].

Membranes based on crosslinked polyimide or polyacrylonitrile/polydimethylsiloxane, commercialized by the companies Evonik and GMT, respectively, are among the few available in the market [32]. Membranes made of cellulose are an alternative for NF application in a wide range of organic solvents (see also section 3.2) [33,34]. Other polymers under investigation for solvent resistant membranes are commercial poly(ether etherketone)s (PEEK) [35], polybenzimidazole [36–38] and lab-synthesized polytriazoles, poly(oxindole biphenylylene) (POXI) and poly(arylene sulfide sulfone) (Fig. 1a) [39–41]. A challenge in this field is the difficulty of dissolving highly stable polymers for membrane manufacturing. PEEK, for instance, is only soluble in strong acids, which are corrosive and difficult to handle in a manufacturing environment. One possibility of avoiding harsh solvents is to functionalize PEEK into a soluble precursor and regenerate it as insoluble material, after the membrane formation [42]. Crosslinking strategies following membrane preparation are however the most applied for the majority of polymers used for solvent-resistant membranes. Besides solvent stability, when crosslinked, an increased thermal resistance can be achieved as well. Using polymers like POXI [41] can provide thermal stability of up to 500 °C. Insolubilization is typically obtained by thermal rearrangement [43], chemical crosslinking or thermal crosslinking [39].

Having a highly chemical and/or thermal resistant membrane by itself is not enough. To be able to successfully apply these membranes in real separation processes, the membrane has to be incorporated into a membrane module. Therefore, the elements making up the module

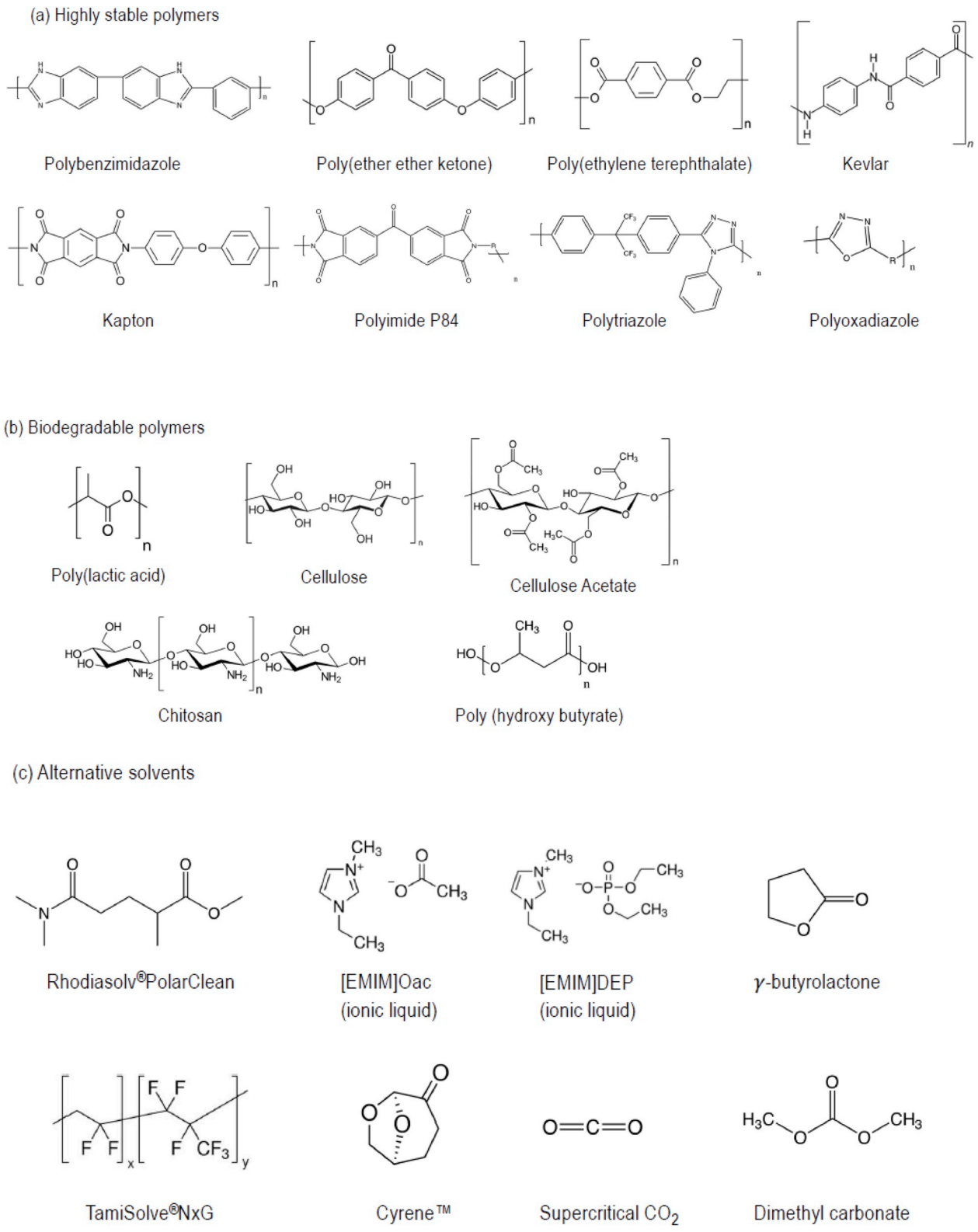

Fig. 1. The structure of polymers, representing (a) high stability or (b) biodegradability. (c) Alternative solvents considered for membrane fabrication by phase separation processes.

require similar chemical and/or thermal resistance as the membrane itself. One should think of housing material, potting or glue materials, spacers, headers, permeate pipes, O-rings, etc. However, discussions or ideas for new module suggestions or improvements of existing module concepts are beyond the scope of this article.

Strict control of selectivity with acceptable permeation, aligned with stability, is a big challenge. Different chemistries for interfacial polymerization and grafting are under investigation, using highly stable porous supports [30,44]. In particular, surface grafting-functionalization of porous inorganic membranes using

reactive copolymers with variable side groups (e.g. maleic acid copolymers) can produce robust membranes for organic solvent nanofiltration [45]. Carbon molecular sieve membranes prepared from polymeric precursors are another approach for combined solvent and temperature resistance [46]. Such and other new approaches will extend membrane technology to applications beyond the already established ones.

3.2. Renewable polymers

While the life time expectancy of most membranes used in water applications, like seawater desalination, surface water filtration and wastewater filtration, is between 5 and 10 years, polymers with natural and faster degradability could be excellent choices for disposable membrane systems used in biomedical and diagnostic applications (cf. Table 1). The first synthetic membranes were based on cellulosic derivatives. The polymer industry had a steep growth in the last 50 years with non-natural materials such as PVDF, PES and PSU taking the lead in applications varying from water filtration, biochemical, food and beverage to hemodialysis. However, the ever-increasing awareness of the environmental impacts incurred by plastic waste provides a strong driver for recycling (cf. section 3.4). And for applications where disposable devices are used in large scale, biodegradable polymers could experience a revival. These polymers can also be promising sustainable alternatives where the filtration conditions are not suitable for biodegradation, such as filtrations in organic solvents.

The introduction of non-harsh solvents for cellulose [47–49], such as ionic liquids, is facilitating the manufacturing of cellulose membranes. Besides cellulose, there is a growing interest in the production of polymers from renewable sources a number of which are already commercially available, e.g. poly(hydroxy butyrate)s and poly(lactic acid) (PLA) (Fig. 1b). In particular, PLA has gained importance in biomedical applications due to its biocompatibility and biodegradability characteristics. Going beyond renewable homopolymers, new strategies are now available for copolymerization and functionalization, which could diversify the properties and possible morphologies of renewable polymers. Copolymers with well-defined blocks of polylactide [50,51] and polypeptides [52] have been synthesized and explored for membrane fabrication. Renewable building blocks for interfacial polymerization, such as tannic acid [53], catechin [54] and cyclodextrin [55], have also been successfully utilized recently.

3.3. Sustainable manufacturing based on alternative solvents

The current membrane manufacturing processes are heavily based on aprotic dipolar organic solvents such as dimethylformamide, N-methylpyrrolidone and dimethylacetamide. These are solvents that have long been on a list of toxic chemicals predestinated to be banned from use in large scale. Environmental concerns and regulations currently under implementation (e.g.: “Registration, Evaluation, Authorization and Restriction of Chemicals”, REACH) [27] aim to reduce solvent emissions and harmful use of toxic solvents. The membrane industry, with decades of optimization in non-solvent or thermal induced phase separations (NIPS and TIPS, respectively) is postponing changes, but alternative solutions will be needed under stricter regulations.

A first step is the switch to established, non-toxic organic solvents such as dimethylsulfoxide (DMSO). It had been shown that by adapting the fabrication conditions for membranes made from PVDF via non-solvent vapor induced phase separation (VIPS), microfiltration membranes with tunable porosity could be obtained in a fast and scalable process [56]. PVDF/DMSO systems in which the phase separation was induced by freezing the solvent led to porous membranes with superior separation performance, compared to PVDF membranes obtained by conventional NIPS processes [57].

Among the sustainable solvents under consideration [27,58,59] are also supercritical CO_2 [60], ionic liquids [48,61], plant-based solvents [62], and emerging commercial synthetic organic solvents, such as methyl-5-(dimethylamino)-2-methyl-5-oxopentanoate (Rhodiasolv® Polar-Clean) [63–65], and the dipolar aprotic TamiSolve® [66] (Fig. 1c). Supercritical CO_2 requires considerable changes in the manufacturing process including the utilization of equipment which is typically used for melt extrusion and very accurate pressure control. However, the other solvents can simply be applied in currently used phase inversion processes.

Beyond the benefit of sustainability, alternative solvents can be seen as an opportunity to improve membrane morphologies and performances. For example, polyethersulfone membranes cast from ionic liquid solutions are sponge-like, more porous, highly permeable with the separation cut-off extended to lower molecular weight (Fig. 2) [61]. Membrane fabrication with ionic liquids has also been demonstrated for other polymers such as cellulose acetate, poly(ether imide sulfone), polybenzimidazole and polyacrylamide [47,67–69]. The different thermodynamic and rheological conditions are believed to alter the mechanism of phase separation and pore formation. Ionic liquids have also been applied for interfacial polymerization [70] in the preparation of thin-film composite membranes. However, ionic liquids are a broad class of chemicals and while their emission of volatile organics is minimal or non-existent the toxicity in water of some ionic liquids is a topic of discussion. Natural, deep eutectic solvents [71,72] share some properties with conventional ionic liquids and are starting to be investigated for membranes.

An elegant and environmentally friendly approach to membrane fabrication was taken by de Vos and his team [73]. They are exploring the possibilities of using water as a solvent and a non-solvent in membrane fabrication by phase inversion. The trick they apply is using polymers that dissolve in water at low or high pH and coagulate them in aqueous solutions with the opposite pH where they are insoluble. Very recently, it was shown that with such a pH switch it is also possible to utilize polyelectrolyte complexation as the cause of phase separation. With this polyelectrolyte complexation-induced aqueous phase separation approach, it was possible to create membranes ranging from microfiltration to nanofiltration, all with promising separation properties.

Finally, the implementation of sustainable manufacturing processes should consider recycling, circular economy and “zero-waste” concepts. One element of such concepts is the use of recyclable supports (or “scaffolds”; cf. section 6) for the actual membrane barrier, as will be further outlined in sections 4.2 to 4.7. Membranes could also be prepared from recycled polymers, such as poly(ethylene terephthalate), used in large amount for other applications [74].

3.4. Module reuse

Membrane technology is often seen as a key to develop sustainable separation processes with lower energy usage, lower CO_2 footprint, recovery of valuable resources from waste streams, or stream fractionation to obtain added value products. However, little or no thought is given in the design phase to the end-of-life management, i.e. the disposal, reuse or recycling of the membrane element at the end of its useful life and the environmental impact it creates. In many membrane plants, the membrane elements constitute the main solid waste. They have a limited lifetime, which depends on the application. RO elements for example usually have a lifetime of 3–7 years and are usually disposed in landfills [75]. Currently, more than 840,000 elements (equivalent to $>$ 14,000 tons) are discharged annually world-wide and this number is growing. An even higher number of installed MF and UF membranes with a life-time of 7–10 years can be found for surface water treatment, wastewater treatment (MBR and tertiary) and seawater pretreatment. For hemodialysis, about 600,000 tons of hazardous waste is produced yearly due to the disposal of dialyzers, a burden which will only further increase in the future [76,77]. In the treatment of natural gas using membranes, elements are regularly replaced (often within one year) due

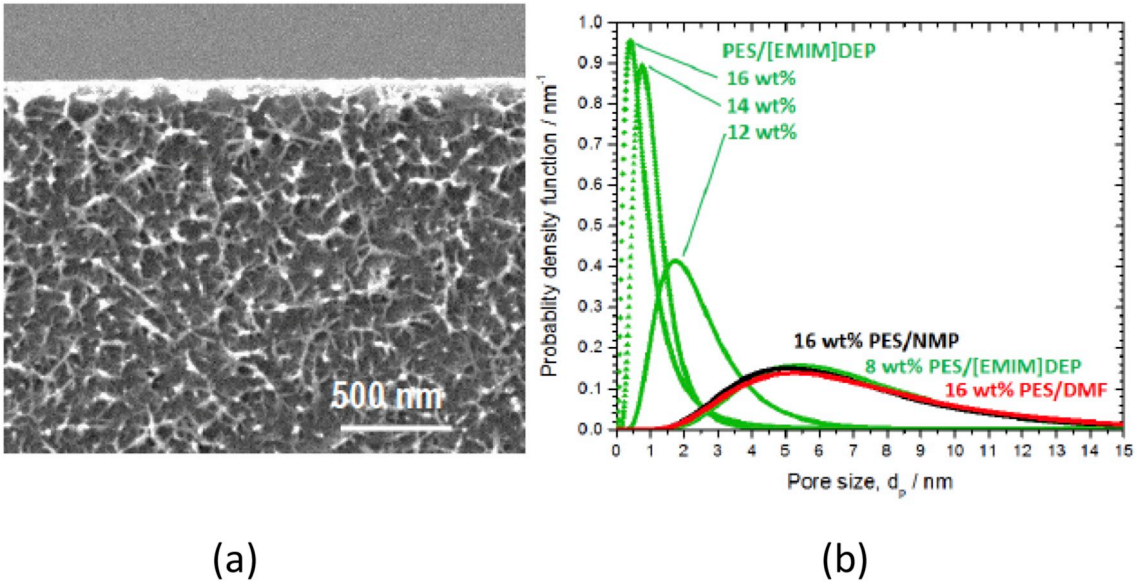

Fig. 2. Polyethersulfone membrane prepared from solutions in the ionic liquid [EMIM]DEP: (a) sponge-like structure; (b) sharp pore size distribution. Reproduced with permission from Ref. [61].

to the harsh conditions, generating also a lot of waste. While the quantity for RO modules discharged annually has been reported in literature (see above), such numbers are not available for gas separation. However, a rough estimate based on the size of its market and assuming prices and weights similar to RO spiral wound elements, the annual waste for gas separation would currently be about 10 times less than for RO.

Proper design concepts that reuse and recycle membrane elements have the potential to tremendously reduce the environmental impact and greatly reduce cost. A method that can help to improve the sustainability of a manufacturing process of a membrane element is to perform a life cycle assessment (LCA). This technique assesses environmental impacts associated with all the stages of a product's life, from raw material through manufacturing, distribution, use, repair and maintenance, and disposal or recycling. For membrane elements, the results of a LCA is often expressed as „Carbon Footprint", where the environmental impact is quantified as equivalent tons of CO_2 emitted. Nowadays, commercial bid documents ask more and more for this kind of information. In the spirit of a circular economy the strategy is to retain most of the value after the use of the product. Ideally, products should be designed and made with the highest possible quality (best performance, anti-fouling, minimal aging or swelling). They should allow repair or maintenance in order to last as long as possible without the need of replacement. Membrane life can typically be extended by operation under mild conditions, like low transmembrane pressures. This allows for filtration processes by gravity on one hand, but requires more membrane surface area on the other hand: a typical choice between OPEX and CAPEX. Proper product monitoring during the lifetime can predict or even prevent failure or breakdown and further reduce unnecessary waste and costs. If the membrane element eventually has to be replaced, its value will decrease following the waste management strategy depicted in Fig. 3 [78].

In the last 10 years, several research groups have begun to investigate approaches to reuse or refurbish RO elements [79–81], which can often be cleaned and reused. Typical measures are inspections of feed spacers, exterior damage, brine seal integrity and external evidence of foulants. After testing at standard conditions and comparing with the manufacturers original data, the module will either be cleaned and reused or refurbished. Recently, companies in the US and Germany have started offering services to reuse or recycle used RO elements [82]. The most common way to refurbish RO elements is to chemically remove the thin polyamide layer by a treatment in NaOCl solutions and transform the RO membrane into an NF, UF or MF membrane [83–86]. Procedures for doing that have already been established and standardized. It was estimated that the replacement of one new 8-inch SW element (with a lifetime of 5 years) by a refurbished RO element (with a lifetime of 2 years) reduced 98.9% of costs and prevents >2600 kg of waste disposed [80,84]. When refurbishing the membrane element is not feasible, the next strategy to follow is assuring easy disassembly, i.e. separating the membranes and potting from its shell or housing. The membranes could potentially be recycled or remanufactured (e.g. after re-dissolving and purifying the materials) for a new application. In spiral-wound modules, spacers, retainers, telescoping devices and other useful components could be reused or recycled as well. The plastic parts used in membrane cartridges could be made from recyclable components. Not only the RO sector, but also the hemodialysis market is taking a closer look at the possibilities of reusing and recycling resources. Besides approaches to reduce the use of fresh water, converting plastic dialysis waste into other products is an avenue being explored [86].

Another approach to reduce environmental impact would be to use

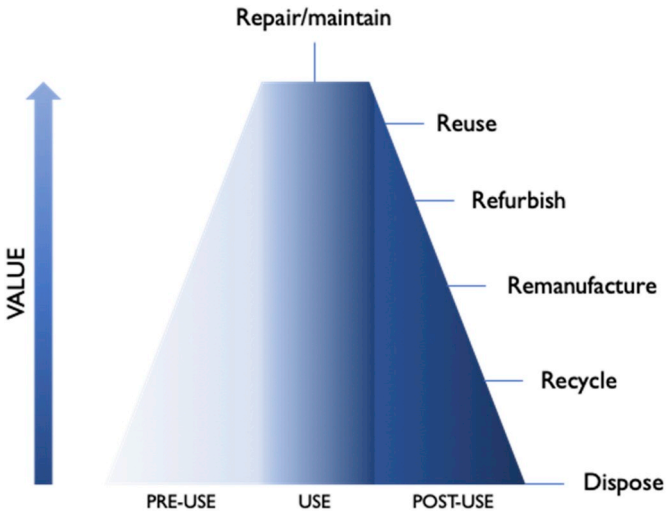

Fig. 3. Waste management strategy to maintain value and minimize waste. Reproduced with permission from Ref. [78].

biodegradable or bio-based polymers to fabricate membranes. Numerous related papers have been published in the last 5–10 years, as separately discussed in section 3.2. Although ceramic membranes cannot compete (yet) with polymeric membranes, they may offer the "ultimate" solution to the waste problem as they are robust, stable and would last a very long time. However, this strongly depends on economically viable production, for example at much lower temperatures (see section 5.3).

Yet another option is the use of established membrane modules as starting point for approaches with the aim to up-grade their separation performance. As will be detailed in section 4.2, this is already done with the "layer-by-layer" method for fabrication of NF membranes based on UF supports. However, this has also been demonstrated via surface grafting functionalization of polyamide TFC membranes in spiral-wound modules under filtration conditions, leveraging concentration polarization to trigger the reaction, and leading to improved boron rejection [87]. Based on the feasibility of the other approaches outlined in sections 4.3-4.7 and 5.1, the potential of up-grading membrane modules by using them as "scaffold" and depositing barrier layers *in situ*, "in place" and "on demand" will be further discussed in section 6.1.

4. Assembling membranes from tailored "building blocks"

Considering the state-of-the-art and on-going efforts to improve the existing membrane manufacturing platforms (cf. section 3), pathways to achieve enhanced separation performance – beyond the commonly observed permeability and selectivity trade-off – must be based on improved (ideally "tailored") membrane materials and/or fabrication methods. On the one hand, the membrane's barrier layer should be well-defined, i.e. comprising a high volume fraction of transport pathways ("channels") of identical size and properties in a robust matrix that ensures stability while, on the other hand, offering as little resistance as possible (e.g., by making the barrier layer as thin as possible).

The alternatives outlined below all consider membrane materials as a set of "building blocks", possessing a particular chemical structure, shape and size as well as the ability to form well-defined arrangements, constructed of either identical or other, complementary, building blocks. The type of achievable arrangement is based on intrinsic properties of the building blocks and, optionally, is guided by external forces. In many cases, principles of self-assembly can be utilized, i.e. a "bottom-up" approach from individual building blocks toward large, ordered aggregates based on multiple non-covalent bonds or micro-phase separation processes. Membrane preparation proceeds from solutions or dispersions of the building blocks and is thus either identical or compatible with existing membrane fabrication methods like film casting or coating. It is very important to note that such approaches can be and are already implemented with both, organic and inorganic „building blocks"; each kind of building block will have a specific set of properties, some crucial for the resulting barrier structures and others important for the mechanical, thermal or chemical stability. A schematic overview of typical resulting barrier layer structures is provided in Fig. 4, with the different cases discussed in the following sub-sections.

4.1. Self-assembly of block copolymers

The traditional NIPS process of membrane preparation using homopolymers produces a relatively broad pore size distribution. High porosity and size uniformity may be achieved by combining NIPS with the self-assembly of block copolymers (SNIPS process) (Fig. 5) [88]. The preparation of asymmetric UF and NF membranes has been demonstrated and optimized mainly using diblock [89,90] and triblock [91] copolymers of polystyrene and poly(4-vinyl pyridine). The high pore density obtained with this method leads to water permeance in the range of 1000–3000 L/m^{2}hbar with molecular weight cut-off around 70 kDa, which is more than an order of magnitude higher than for instance commercial polyethersulfone membranes with similar pore sizes. Beyond the controlled porosity, block copolymer membranes offer a versatile functionality and responsiveness to pH and other stimuli, which can make them function as chemical gates [92,93]. In SNIPS-prepared asymmetric membranes, only the top 500 nm is isoporous. The sublayer has a structure like homopolymer-based phase inversion membranes. Isotropic hierarchical films [94], with 15 nm pores distributed throughout the membrane structure, have recently been reported using copolymers with two hydrophobic blocks.

The main drawbacks or needs for improvement of the SNIPS technology are the following:

(1) The most optimized protocols for SNIPS membranes have been using copolymers with polystyrene (PS) blocks, which are not as stable as other polymeric materials used for membranes, such as PSU or PVDF. Substituting the PS blocks by other chemical compositions could increase the thermal, chemical and mechanical stability. At this moment, the reported membranes are mostly unstable in organic solvents. Crosslinking strategies would be advantageous.
(2) While the isoporosity has been demonstrated for polystyrene-*b*-poly (4-vinylpyridine) and similar copolymers, when using blocks of different chemical composition, the optimization can be arduous.
(3) The cost of block copolymers under consideration for membranes is still high. The mostly used block copolymers for this method are based on styrene and pyridine monomers, and they are not yet commercialized in large scale. Decreasing cost depends on the production scale. Block copolymers like polystyrene-*b*-

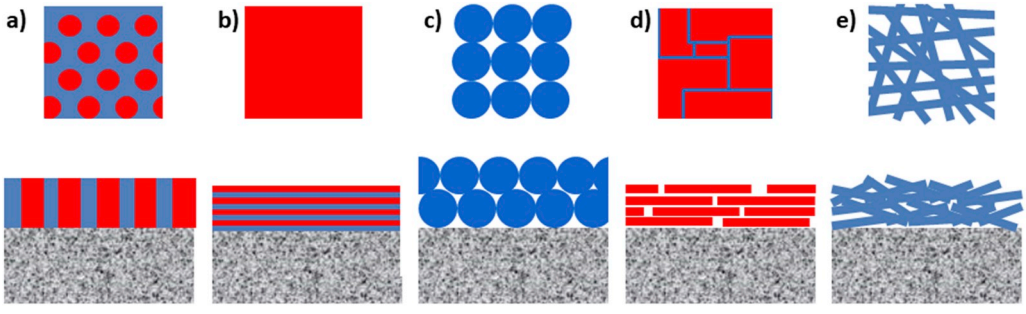

Fig. 4. Schematic visualization of different barrier layer structures, shown here on a porous support membrane, obtained from different „building blocks" (above top view, below cross-section view): (a) microphase-separated block copolymer (in some cases followed by selective etching), (b) layer-by-layer deposited film from two complementary polymers, (c) array of spherical particles („3D materials"), (d) deposited (non-porous or porous) nanosheets („2D materials"), (e) deposited nanofibers („1D materials"); note that ultrathin barrier layers can in principle be obtained by deposition of bilayers ((b)) or monolayers ((c), (d), (e)), but defects may dominate when transferred to large membrane area.

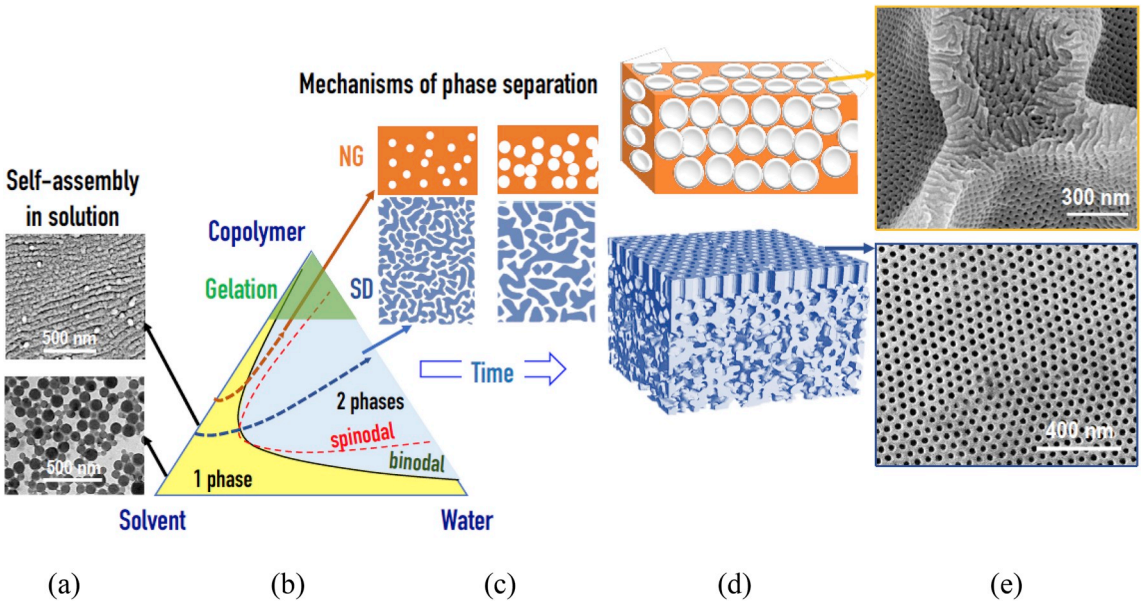

Fig. 5. Block copolymer self-assembly induced by a non-solvent, leading to a porous structure: (a) Self-assembly in diluted (bottom) and semi-diluted (top) homogeneous copolymer solution; (b) ternary phase diagram representing the demixing paths potentially involved in the membrane formation; (c) different mechanisms (nucleation and growth (NG) or spinodal decomposition (SD)); (d) scheme of resulting porous structures and (e) SEM images of selected porous copolymer materials; this has been discussed in detail before, for instance in Refs. [88,94,95].

polybutadiene-*b*-polystyrene are an example of large-scale low-cost products.

(4) Nevertheless, as for classical NIPS homopolymer membranes, so far the regular organic solvents have been used for block copolymer membranes. Exploring fabrication procedures using more sustainable solvents would also be helpful (cf. section 3.3).

A great advantage of membranes prepared by the SNIPS process is that the isoporous structure is obtained in one step and the technology can be transferred to classical continuous membrane fabrication machines. Affordable scaling up is necessary for implementation of these membranes in sectors such as the biotech industry, where multistep separations are applied to reach high purity, valuable products. This is also explored by a start-up company (cf. section 6).

Other methods of membrane preparation based on block copolymers consist of coating, annealing and sacrificing one of the blocks by etching [50] (cf. Fig. 4a). The sacrificial approach has been successfully demonstrated with PLA copolymers. A particularly interesting method promotes the formation, by interfacial polymerization, of thin copolymer layers with etchable PLA domains [96].

Block copolymers can function as anti-fouling additives by mixing with homopolymers such as PVDF, choosing one PVDF-miscible block (e.g. poly(methyl methacrylate)) and a hydrophilic one, such as poly (ethylene oxide) [97]. Earlier, examples of mixing PVDF with PVDF having grafted poly(methacrylic acid) or poly(oxyethylene methacrylate) side chains had been studied by the group of Mayes [98].

The SNIPS and the sacrificial processes require block copolymers as base materials. Nevertheless, nanofiltration membranes with carboxylated 1–3 nm channels can be formed using statistical copolymers with fluorinated and methacrylic acid segments, which are highly immiscible (Fig. 6) [99]. A different approach proposes the preparation of self-healing membranes, starting with affordable styrene-butadiene-styrene block copolymers highly functionalized with H-bond forming groups. The membrane selective layer is then formed by an assembly of nanospheres held together by dynamic H-bond cross-links (Fig. 7) [52]. UF membranes with self-healing properties had previously been reported based on another block copolymer system, as well as making use of reversible multiple non-covalent bonds between copolymer aggregate particles [100]. The structures resulting from *in situ* formed ("dynamic") nanoparticles resemble those obtainable from assembly of pre-synthesized more conventional ("static") particles (cf. section 4.3).

Dense and thin layers formed from block copolymers have been widely demonstrated for gas separation, with one phase forming highly permeable paths and the remaining segments acting as mechanical support [101,102]. In an analogous way, block copolymers can provide ion-conductive pathways, embedded in a non-conductive and more mechanically stable phase, for fuel cell membranes [103–105].

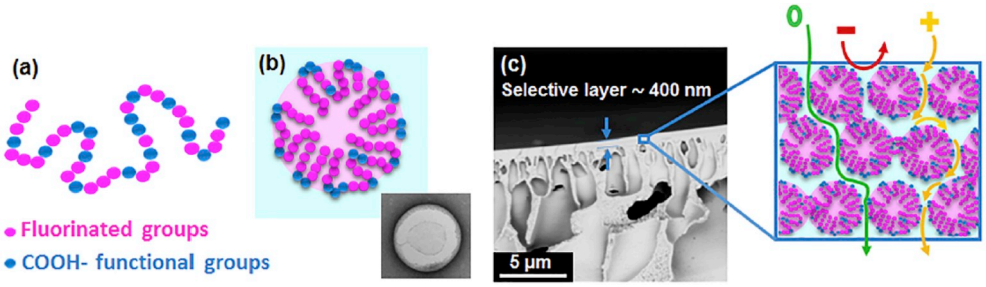

Fig. 6. Membrane formation based on (a) random copolymers with fluorinated and carboxylated repeat units, assembled as (b) micelles in methanol and (c) coated on a porous support, forming ionic nanochannels. Reproduced with permission from Ref. [99].

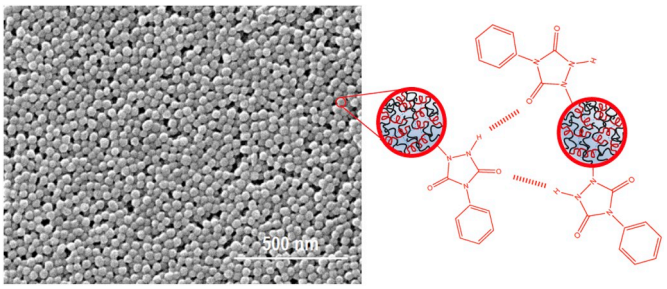

Fig. 7. Self-healing membranes prepared by assembling spherical copolymer particles highly functionalized with H-bonds. Reproduced with permission from Ref. [52].

Copolymers with zwitterionic blocks have been reported to improve the fouling resistance of interfacial polymerized selective layers in TFC membranes [106].

In addition to their application as polymeric membranes, porous block copolymer films are also useful as scaffolds for preparation of inorganic structures [107,108].

As with homopolymers a high copolymer molecular weight improves film-forming properties and provides higher mechanical stability of free-standing membranes. Nevertheless, successful self-assembly and the resulting morphology depend on the homogeneity of the macromolecules, and therefore a low polydispersity of molecular weight is advantageous. The supramolecular assembly of small molecules is known as an excellent toolbox for the design of highly ordered systems (cf. section 4.6). For example, the concept of artificial (water) channels built by using supramolecular assembly is gaining visibility in the membrane technology field. If properly combined with more mechanically stable polymeric systems, this will be a promising strategy for highly selective water and ion transport, mimicking biological systems (cf. sections 4.6 and 4.7), potentially providing successful building block-based membranes in the future. For further details see section 6.

4.2. Layer-by-layer self-assembly

A versatile and easily scalable way to obtain very thin films on substrates is the sequential assembly of linear macromolecules in a layer-by-layer (LbL) fashion. Multivalent binding between the building blocks via complementary coupling groups, while avoiding excess polymer deposition, guarantees that in each step the thickness increases by approximately the diameter of the building block. Thus, the thickness per deposited layer can be as small as 1–2 nm (cf. Fig. 4b). Since the first report on LbL deposition of polyelectrolytes in the early 1990s, the scope of the technology has been largely expanded with respect to the employed building blocks (now also including particles, fibers, or 2D materials), deposition conditions (e.g. immersion vs. spraying) and the resultant materials and functionalities [109]. The preparation of separation membranes via LbL deposition of polyelectrolyte multilayers has been explored for more than two decades and has been reviewed recently [110]. The focus of LbL research has primarily been on NF, showing that with UF membranes as supports, just 5 bilayers can be sufficient for good NF selectivity, with a barrier layer thickness of only 10–20 nm. Using polyelectrolytes as building blocks, the internal multi-bipolar structure leads to high selectivity between bi- and monovalent ions, due to Donnan exclusion. Hence, for optimized LbL-based composite membranes very high transport selectivities, e.g. for earth alkali vs. alkali metal ions or for phosphate versus other anions, can be achieved. It had also been demonstrated that LbL-based NF membranes can be very efficient in removing micropollutants from drinking water [111]. A wide range of polyelectrolytes can be used as building blocks, combined with many preparation parameters. Recently, first steps toward "rational design" of NF membrane properties by linking variations in preparation conditions and separation performance (permeability and selectivity) have been made using artificial neural networks, and additional physical insights into the actual membrane barrier properties have been gained by coupling obtained correlations with a transport model [112].

The scope of polyelectrolyte multilayer composite membranes has also been extended to separation of mixtures in organic solvents by organic solvent nanofiltration or pervaporation (cf. [110]). The following examples are representative of the numerous possibilities for alternative building blocks or procedures within the same overall framework.

In order to establish an alternative for the fabrication of TFC membranes with polymers of intrinsic microporosity (PIMs) as the barrier layer, water soluble PIM building blocks with anionic or cationic groups have been synthesized and successfully used for LbL assembly of NF membranes (Fig. 8). The results demonstrate the feasibility of obtaining competitive NF performance while avoiding the use of organic solvents (cf. section 3.3) and utilizing a method which is less prone to defects (due to the repetitive application of the building blocks); this is considered a "paradigm shift in membrane fabrication from PIMs" [113].

Spray-coating LbL (instead of immersion in the respective solutions; cf. section 5.2), combined with chemical cross-linking within the layer and integration of a neutral amphiphilic copolymer as surface modifier (sprayed in the last step), provides a very efficient alternative fabrication procedure for competitive TFC RO membranes with the additional benefits of higher oxidative stability and less fouling compared to conventional PA TFC membranes [114].

Finally, the integration of laponite nanoplatelets (one type of 2D materials; cf. section 4.4) in the fabrication of PA TFC membranes by molecular layer-by-layer assembly (i.e. step-wise and alternating immersion of the support membrane in the two different reactive monomer solutions producing a polyamide layer [115]) is an example of additional degrees of freedom for tailoring NF properties by appropriate building blocks [116].

For the further implementation of LbL technology, an attractive proposition would be the preparation of composite membranes on support membranes, already within modules. Furthermore, the obtained high-flux NF membranes can be cleaned by back-flushing [117]. The removal of the selective layer and its subsequent re-deposition is another interesting option with respect to long-term application of such NF membranes/modules [118]. Downsides of the LbL approach are that many steps are required for the fabrication, and that in some cases a chemical crosslinking is required to warrant stability, when using the LbL-enabled membranes at high salinities and in the presence of surfactants [119].

Overall, the LbL approach is a proven flexible and versatile toolbox offering a diverse selection of building blocks for alternative fabrication schemes of membranes with dense, microporous or charged barrier layers, and this great opportunity has already been taken up by industry (cf. section 6). Commercial nanofiltration membranes enabled by LbL have specifications, which indicate competitive stability under operation and cleaning conditions. A key feature of the approach is that it is perfectly suited for *in situ*, "in place" and "on demand" fabrication of membranes in pre-fabricated modules used as scaffolds (cf. section 6).

4.3. Assembly of 3D materials

A compact arrangement of rigid particles yields a porous structure in which the size and shape of the interstitial space (pores) depend on those of the utilized particles and their mode of packing. Macro-scale examples are particle beds used for adsorption or filtration. Typically, ceramic membranes are obtained by sintering particles, creating homogeneous porous structures with a narrow pore size distribution. With regularly assembled monodisperse spherical particles it is possible to obtain colloidal crystals, which have occasionally been explored as templates for size-selective MF membranes [108,120]. With microparticles

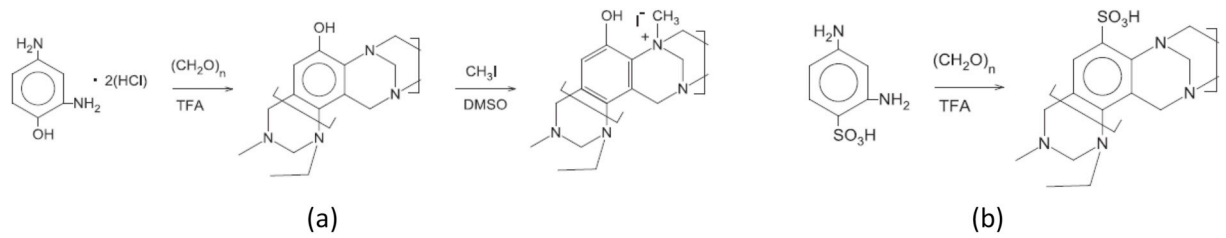

Fig. 8. Synthesis and structure of water-soluble PIM building blocks for LbL fabrication of TFC membranes: Tröger's base derivatives with (a) cationic and (b) anionic groups [113].

(diameter >1 μm), the pore dimension is at best in the upper microfiltration range, and the porosity is rather low (≤40%), so that filter performance is not competitive with existing membranes. However, when smaller, monodisperse particles are used, and the layer thickness deposited on a suitable porous base membrane is minimized (cf. Fig. 4c), it is possible to obtain composite MF or UF membranes with considerably larger permeability at barrier pore sizes comparable to established polymeric or inorganic membranes [121].

At an even smaller scale, the utilization of monodisperse rigid nanoparticles toward very high performance UF membranes has been demonstrated by filtration/deposition of the globular protein ferritin (diameter 12 nm) on a temporary support and chemically cross-linking the layer [122]. After transfer, a composite membrane with a ~60 nm thick selective layer and a 2.2 nm pore size having a very high water permeance of 9000 L/m^{2}hbar had been obtained, due to the presence of well-defined short transport channels formed by the interstitial space between the assembled and cross-linked protein molecules (Fig. 9).

Another interesting concept based on the assembly of even smaller organic building blocks with well-defined spherical shape is based on star polymers having a rigid nonpolar core and short hydrophilic segments at the periphery [123]. NF membranes have been obtained with permeances higher than commercial ones, where the ~10 nm thick active layer was presumably formed by effective percolation of the star polymer molecules. This is possible since these are not rigid particles as in the previous examples. A conceptually analogous approach is using core-shell nanoparticles in combination with adapted annealing post-treatment conditions such that the obtained barrier will not contain void space anymore and consist of two different phases [124]. Hence, the barrier layer comprises a stabilizing matrix phase (the former core) and a transport phase (the former shell), yielding NF membranes. With core-shell polymeric microgel particles it has recently been shown that thin barrier layers, potentially with intrinsic UF properties, can be obtained by filtration/deposition and entanglement of a monolayer of such soft particles (with a hard core) on a porous support membrane [125].

Another possibility is the utilization of the entire internal structure of spherical particles to tune barrier selectivity. This is a pathway for the preparation of ion-exchange or even charge-mosaic membranes [126], either by dispersing ion-exchange microparticles in a solid (polymeric) matrix or by compressing/annealing an array of identical or different (anion-exchange and cation-exchange) particles into a mixed matrix composite membrane. Until now only examples for microparticles as building blocks for such membranes have been reported [126].

There is a large and already proven potential for assembling thin layers of micro- and nanoparticles on supports forming MF and UF membranes utilizing the void space formed between rigid particles. UF and NF membranes may be obtained from rigid/soft core-shell particles or soft (hydrogel) particles followed by a post-treatment, so that either parts or the entire particles can serve as a selective transport phase. Obviously, the approach is also suited for the *in situ*, "in place" and "on demand" fabrication of membranes in pre-fabricated modules used as scaffolds (cf. section 6).

4.4. Assembly of 2D materials

Two-dimensional (2D) materials of atomic thickness are emerging building blocks for high-performance separation membranes that feature unique nanosized pores and/or inter-layer channels [127]. Potentially, these 2D material membranes exhibit extraordinary permeation properties opening a new avenue to ultra-fast and highly-selective membranes for water and gas separation applications. 2D materials can be fabricated as separation membranes in two basic forms:

(1) *nanosheet membrane*, consisting of a monolayer or a few layers of 2D material with intrinsic uniformly sized pores or drilled nanopores for selective permeation;
(2) *laminar membrane*, which is formed by assembling 2D materials into laminates with interlayer galleries used to provide molecular passages.

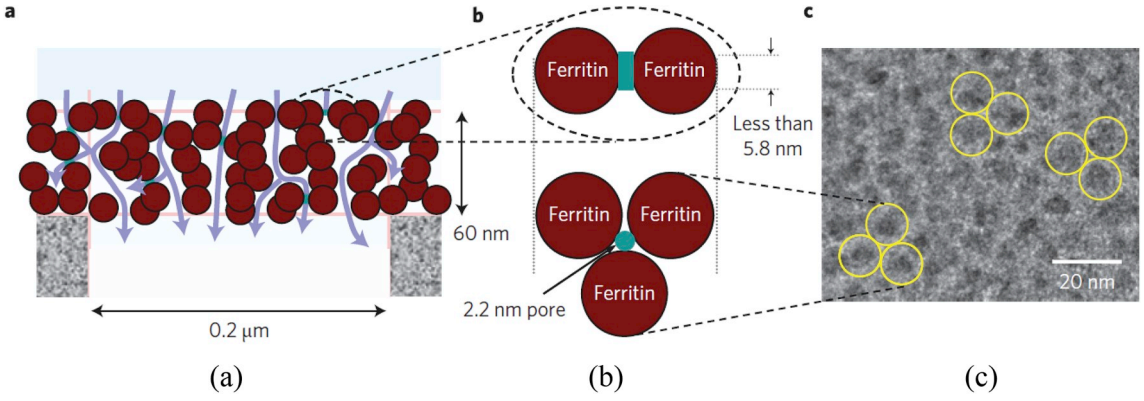

Fig. 9. (a) Schematics of the barrier layer of an ultrafiltration membrane obtained by assembly of rigid monodisperse organic nanoparticles (the protein ferritin; diameter 12 nm) onto a macroporous support and (b) visualization of the experimentally determined barrier pore size to be related to the void spacing between the spherical building blocks; (c) TEM image confirming the regular arrangement of the protein in the layer. Reproduced with permission from Ref. [122].

2D nanosheets with an atomic thickness can be used as ultimate membranes for separation. Membrane pores are provided either by an intrinsic porous structure such as in zeolite [128] and metal-organic framework [129], or by "drilled" pores such as in graphene-like materials [130]. Recent breakthroughs in synthesis [131] or perforation of monolayers [132] promoted the throughput and accuracy of nanosheet membranes for molecular separation. A great challenge remains for nanosheet membranes due to the limited available techniques for exfoliating the high aspect ratio and intact nanoporous monolayers from bulk crystals, and drilling uniform, high-density, large-area, sub-nanosized pores in graphene nanosheets, together with how to scale such atom-thick membranes into applicable separation devices. Recently, Yuan and Duan et al. reported a graphene nanomesh/single-walled carbon nanotube hybrid membrane with excellent mechanical strength, where the high-density sub-nanometer pores in the atomically thin graphene nanomesh showed high water permeance and rejection for salt ions or organic molecules [133].

Alternatively, laminar membranes assembled from 2D materials provide a more practical approach in using 2D materials for separation. Multiple layers of 2D “flakes” create a tortuous pathway for liquids or gases to pass through (cf. Fig. 4d), while the spacing between these layers (interlayer galleries) determine the selective rejection of certain species in the water or certain gas molecules. The beauty of this kind of construction is that the 2D layers can be relatively easy applied by classical casting techniques and from aqueous slurries.

Although laminar membranes have been explored in several other graphene-family 2D atomic crystals and layered oxides, the initial graphene oxide (GO) still remains a focus [134]. A great number of studies demonstrated that the interlayer galleries between GO nanosheets play a vital role in fast and selective transport of water [22,135], ions [136] and gases [137]. Precise control of the interlayer spacing is one of the keys to achieve high-performance GO membranes with a particular challenge in creating sufficient reduction of the interlayer spacing so as to exclude small ions, while maintaining this spacing against swelling of GO membranes when immersed in an aqueous solution. Nair and co-workers proposed a physical confinement approach to control the interlayer spacing and thus achieve accurate and tuneable ion sieving through GO membranes [138]. They stored GO laminates strips under controlled humidity to produce a certain interlayer spacing and then embedded these GO laminates in epoxy to prevent further dimensional change when exposed to water. As a result, the interlayer spacing was reduced from 9.8 to 6.4 Å with relative humidity changing from 100% to 0, and the epoxy mechanically restricted the swelling of the GO laminates on exposure to humidity or liquid water. However, scalable production of such membranes is difficult. Jin and co-workers [139] reported a simple and scalable method to precisely control the interlayer spacing by using the ions themselves. As shown in Fig. 10, cationic control of the interlayer spacing of GO membranes with Angstrom precision was demonstrated using hydrated K^+, Na^+, Ca^{2+}, Li^+ or Mg^{2+} ions to interact with aromatic rings (cation-π interactions) on the GO nanosheet. GO membrane with cation-controlled interlayer spacing was successfully applied for sieving ions from water. Ion permeation tests under forward osmosis conditions indicated that KCl-controlled GO membrane exhibited efficient and stable ion rejection of more than 99% compared to pristine GO membranes meanwhile allowing water permeation with a flux of 0.1–0.36 L/m^{2}h at room temperature. Apparently, other ions could be used to produce a wider range of interlayer spacing of GO membranes that can be applied for gas purification, solvent dehydration, lithium-based batteries and supercapacitors. A high water permeance, alongside enhanced rejection of divalent ions was achieved with a surface-charged GO membrane [140].

Structural stability is another critical issue for 2D material-assembled laminar membranes. For instance, the oxygen-containing groups in GO lead to undesirable redispersion of GO laminates in water, resulting in poor stability of GO membranes for aqueous separation, especially under cross-flow conditions. Chemical crosslinking or reduction of GO could stabilize the membrane structure, but may also decrease the water permeance. A promising approach to achieve both high separation efficiency and stability could be nanoparticles grown, *in situ*, on GO nanosheets, enlarging the nanochannels while preserving selectivity, and enhancing the structural stability of GO laminates in water and under high feed pressure via the chemical bonding between the nanoparticles and GO [141].

Fabrication of an ultra-thin separation layer extended the application spectrum of GO membranes from water separation to gas separation and organic solvent nanofiltration. Efficient water desalination via pressure-driven filtration remains a challenge for 2D-material membranes, demanding a robust membrane structure with permanent sub-nanosized

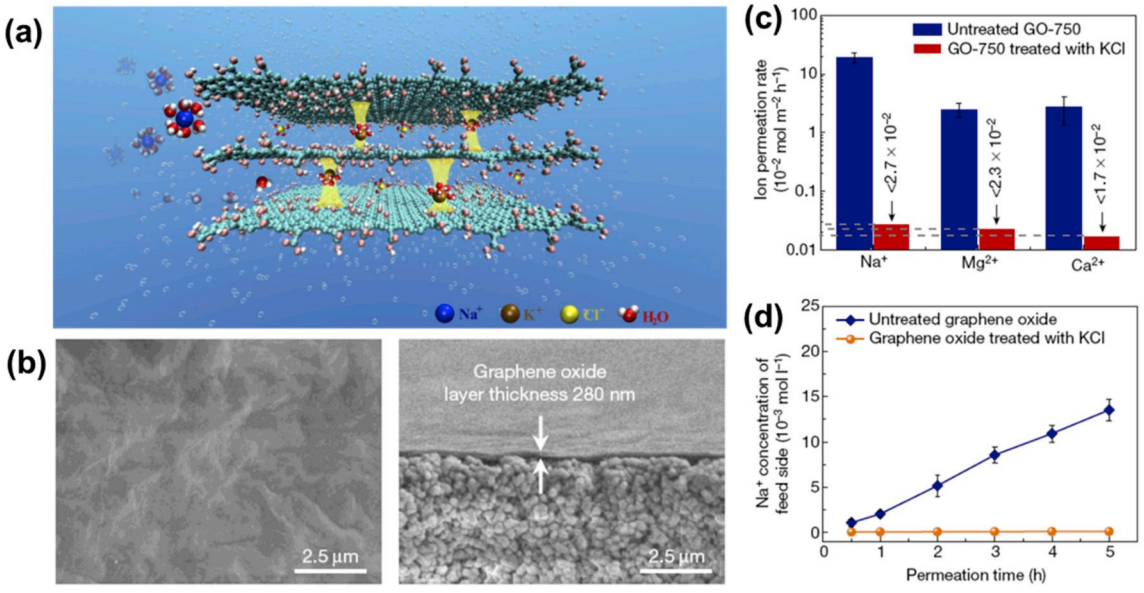

Fig. 10. (a) A schematic of how K^+ ions in a GO membrane determine and fix the interlayer spacing such that other cations are rejected while pure water can penetrate; (b) surface SEM image and cross-sectional SEM image of an Al_2O_3-supported GO membrane; (c) Na^+, Ca^{2+} and Mg^{2+} permeation rates of untreated and KCl-treated GO membranes, dashed lines indicate the detection limits of the different cations; (d) Na^+ permeation rates of untreated and KCl-treated GO membrane with a thickness of about 280 nm. Reproduced with permission from Ref. [139].

channels. Recent start-up companies have already identified commercial opportunities in this area (cf. section 6).

Insights from GO membranes might pave the way to a new family of high-performance separation membranes derived from other two-dimensional materials such as MXene [142,143], MoS_2 [144], as well as nanoporous metal-organic framework (MOF) [122] nanosheets. Future directions may focus on:

(1) precise control of interlayer spacing and *in situ* synthesis of an ultra-thin and defect-free membrane layer;
(2) achieving structural stability while retaining the high performance;
(3) updating theoretical models to accurately describe the confined transport through 2D-material membranes, accompanied by in-depth characterization of transport passages.

Significant effort should be applied to develop robust membranes with stable performance under realistic operating conditions. More research is also required to address specific requirements of exciting, yet challenging applications such as water desalination and olefin/paraffin separation.

4.5. Assembly of 1D materials

Fiber-based materials - organic or inorganic, woven or non-woven - are well established for liquid and gas filtration. With decreasing fiber diameter, the dimension of the void space is also reduced; hence nanofibers are an attractive option for creating filter selectivity in the UF range or even below. Electro-spinning of polymers from their melt or solution is extensively explored and used for that purpose (for a review see Ref. [145]), and will not be discussed here. Instead, the focus is placed on relatively "short" fibers, where the aspect ratio is small enough so that they can be used as (nanoparticulate) building blocks (cf. Fig. 4e). In the past decade, many examples have been reported for nanofibers from different materials; representative examples will be covered below.

Carbon nanotubes. Driven by the large interest in carbon nanotubes (CNT), these materials have also been used to form porous layers by deposition on permanent or temporary supports. In the latter case, "buckypaper" CNT membranes have been obtained which are very robust irrespective of their small thickness, so that high permeances compared to conventional filtration membranes can be achieved with identical selectivity; more details about the diverse types and characteristics of CNT-based membranes can be found in a recent review [146].

Metal hydroxide nanostrands. Various metal hydroxides form, under special conditions, ultrathin nanostrands, with diameter ~2 nm and length of a few μm [147]. Due to their positive surface charge metal hydroxide nanostrands readily form electrostatic composites with oppositely charged molecules. Their assembly leads to ultrathin nanocomposite sheets of variable composition which can show excellent UF performance. Alternatively, such nanostrands have been used as sacrificial layers during fabrication of ultrathin, porous free-standing membranes (see, for example, Fig. 9).

Biopolymers. "Nanocellulose", i.e. fibers of crystalline cellulose with diameters of 5–100 nm and lengths of a few μm, is commercially available. Dispersions of such material have been used to prepare "nanopaper" membranes obtained by filtration deposition on a support and mechanical compression; the resulting membranes had promising separation performance in organic solvent nanofiltration [148]. Ultra-fine cellulose nanofibers at very narrow size distribution (4–11 nm) have been prepared by a special dissolution/dispersion procedure, followed by filtration/deposition onto a macroporous support [149]. The UF cut-off was a function of the thickness of the layer, i.e. > 90% rejection for a 12 nm protein with 24 nm thickness; > 90% rejection for 5 nm gold nanoparticles with 45 nm thickness; water permeances for these membranes were between 22.000 and 3.600 L/m^{2}hbar. In another work [150], silk nanofibrils were prepared and used in an analogous way to obtain composite UF membranes. As shown in Fig. 11, the pore size distribution was also a function of membrane thickness, and the relationship between rejection and water permeance was superior to the state-of-the-art, including examples for other 3D, 2D or 1D nanomaterials covered above or in sections 4.3 or 4.4. Subsequent work by the same group [151] expanded the membrane fabrication to two steps, i.e. i) silk nanofibril self-assembly into a three-dimensional network, ii) biomineralization with hydroxyapatite, leading to a high flux multilayer membrane with combined adsorptive properties for a wide range of water contaminants. The mixed-dimensional assembly of 2D COF nanosheets (cf. section 4.4) and 1D cellulose nanofibers lead to membranes with barrier layer having pore sizes of 0.45–1.0 nm; the scaffold function of the cellulose nanofibers was discussed to lead to a more precise molecular sieving ability and higher membrane stability [133].

Overall, it is clear that thin layers of nanofibers have great potential to obtain ultra- and nanofiltration membranes, where the void space is used as a filter medium; tunable separation performance depends on properties of the building blocks, especially fiber diameter and polydispersity as well as quantity, quality and packing density of the deposited building blocks. The compatibility of the approach with an *in situ*, "in place" and "on demand" fabrication of membranes in prefabricated modules (cf. section 6) can be envisioned.

4.6. Utilization of low molecular weight building blocks and their self-assembly

The field of supramolecular chemistry covers the formation of ordered large-scale, possibly hierarchical structures, by multiple weak non-covalent bonds of small molecules. The assembly can take place in solution or at interfaces with or without larger entities acting as a "template". This is a very dynamic research field and "membranes" have been envisioned from early on (e.g.: [152]). The formation of artificial water or ion channels from small functional molecules, mimicking the core function of biological membrane proteins, is a very active field of research [153]. A prominent example for a first break-through was the supramolecular assembly of ureido imidazole compounds as water-channel analogue [154]. However, the concrete demonstration of the feasibility of the concept for an actual membrane-based mass separation process has seldom been reported (for a recent example see section 4.7).

In general, three different approaches using small molecules can be distinguished, based on their self-assembly into:

(1) fibers (1D), sheets (2D) or particles (3D) of well-defined shape, size and functional groups to connect with each other; the resulting objects can build a membrane barrier during or after their formation, where the *interstitial space is used as a porous sieving medium*;
(2) microphase-segregated non-porous films;
(3) ordered (liquid-crystalline) *super-structures that contain well-defined, Angstrom-scale pores* and can either form a membrane directly, as film, or after further alignment or fixation.

Case 1 has analogies to the examples shown in Fig. 4, but because the building blocks are held together by weak non-covalent interactions, their disassembly is possible under mild conditions compared to, for example, covalently cross-linked polymeric particles or semi-crystalline cellulose nanofibers. Compared to other 1D, 2D or 3D materials from conventional organic polymers, which result from various established shaping processes the disassembly and reassembly to the same shape and size are in principle possible for supramolecular materials. If needed stabilization of the self-assembled structures by covalent bonds is of course also possible, for example by a molecular design which includes reactive groups at appropriate positions. Intermediate cases are so-called dynamic polymers ("dynamers"), where self-assembly and

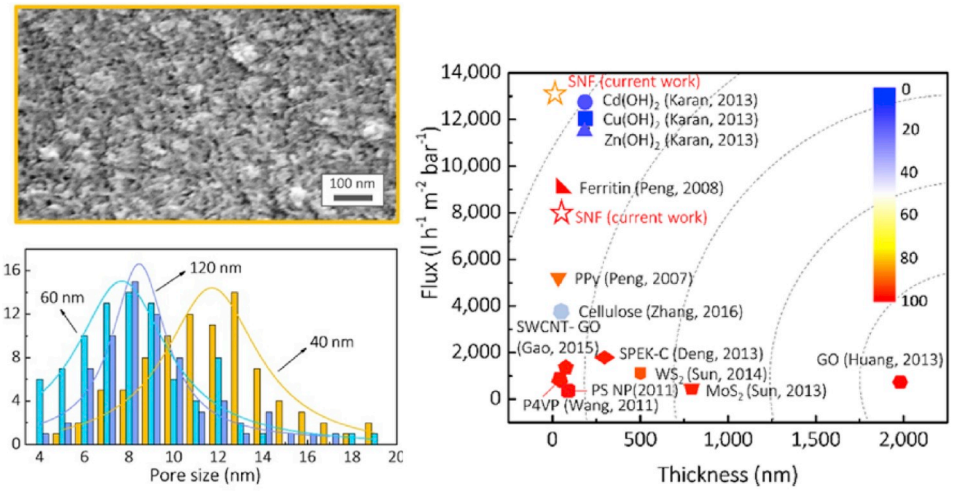

Fig. 11. SEM image of the barrier layer of an UF membrane prepared by filtration-deposition of silk nanofibrils (SNF) on a macroporous support; pore size distribution as function of the nanofibril layer thickness; and comparison with membranes obtained by assembly of other 3D, 2D or 1D nanomaterials (color scale refers to cytochrom C rejection; „ferritin "is from Ref. [122]; „$Cd(OH)_2$, Cu(OH) and $Zn(OH)_2$" are from Ref. [147], „cellulose" is from Ref. [149]. Reproduced with permission from Ref. [150]. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

reversible covalent bonds are utilized. The following examples illustrate the potential of the different cases to fabricate novel membranes.

An entirely non-covalent water-based membrane has been obtained by self-assembly of amphiphilic molecules into supramolecular fibers followed by deposition of the three-dimensional fiber aggregates on a porous support (cf. "case 1." above). The obtained membrane had sharp molecular weight cut off at about 150 kDa (8 nm) and could be disassembled, purified, reassembled and reused, with the same separation performance (Fig. 12) [155].

The combination of systematically varied oligomeric building blocks capable of undergoing supramolecular self-assembly and reversible formation of covalent bonds was successfully used to obtain gas separation membranes with tunable separation properties (cf. "case 2." above). This was explained by the formation of an ordered microsegregated morphology with "size-addressable" soft diffusion domains and dense hard domains [156].

Certain lyotropic liquid crystalline (LLC) morphologies can provide a regular, relatively dense pattern of transport pathways in a matrix; with suitable amphiphilic building blocks a regular array of connected water-filled domains in a polymer matrix can be obtained (cf. "case 3." above). The groups of Gin and Noble have made large and systematic progress in that direction [157]. One approach used a special amphiphilic gemini monomer, featuring two imidazolium groups, which are each alkylated with a C18 chain, having two conjugated double bonds at their end and which are connected by a an aliphatic C6 linker. By *in situ* crosslinking polymerization, a bicontinuous cubic phase (Q_I) was then turned into a molecular size-selective water filtration membrane with an effective pore size of about 0.75 nm. Adapted processing methods enabled production of larger areas of thin-film composite membranes with competitive separation performance [158]. A similar approach using wedge-shaped liquid crystal-forming molecules, featuring one cationic head group and double bonds for cross-linking in the side groups

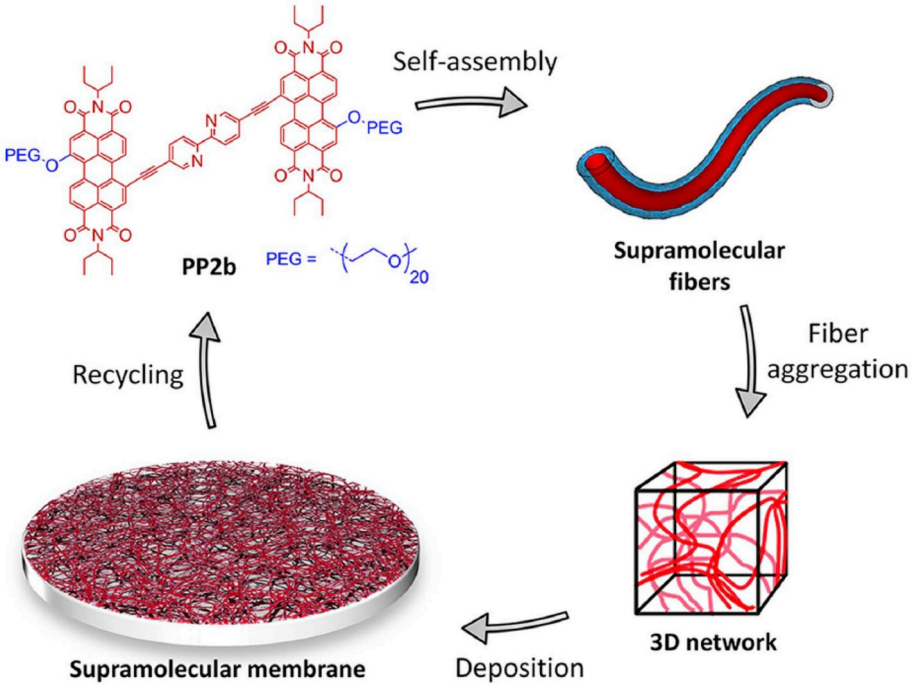

Fig. 12. Membrane formation by the molecular supramolecular assembly of amphiphilic building blocks with preferred aggregation sites into fibers which can be deposited on a porous support and utilized as an ultrafiltration membrane for aqueous solutions and subsequently be recycled by changing the solvent. Reproduced with permission from Ref. [155].

extending from the core had also been reported. The competitive separation performance of the obtained thin-film composite membrane could also be described based on a well-ordered array of sub-nm water channels with significant salt rejection and a pronounced ion-selectivity (Fig. 13) [159]. Nevertheless, the scale-up of such LLC-based membranes will be a challenge, because the synthesis of the building blocks with relatively complex structure requires multiple steps. They include careful purification and establishing processing conditions to obtain thin films with the desired long-range order and to preserve this order upon fixation by cross-linking, which is not straightforward.

In two other examples metal ions were utilized to form well-defined nanoporous assemblies as thin barrier layers in high performance membranes. With phytic acid, a natural strong electron donor, as multifunctional building block the combination with metal ion-based electron acceptors in aqueous solution yielded metal-organophosphate membranes which were evaluated in NF [160]. Metal-induced ordered microporous polymers, a new class of porous polymers, were obtained by co-assembling amine-bearing polymers, small organic linkers and divalent metal ions and yielded size-selective membranes with very promising gas separation performance [161].

Overall, the versatility and potential of self-assembly of low molecular weight compounds for actual membrane-based mass separation has already been demonstrated in a few cases. The integration and stabilization of barrier structures seem to be crucial, especially when precise separations in the Angstrom scale are targeted. This is possible by cross-linking, but also by combination with self-assembling block copolymers (cf. sections 4.1 and 4.7).

4.7. *Integrating different materials and concepts for hierarchical assembly of different building blocks*

Each of the previous sub-sections focused on a special type of membrane material (building block) along with the appropriate fabrication methods. Many more opportunities exist for combinations of materials and methods. Of particular interest are those which can lead to synergies due to a tailored overall membrane structure. An excellent and inspiring new example for integrating different building blocks and different concepts for their assembly has been reported by Kumar and coworkers [162]. Combining low molecular weight synthetic molecules designed as artificial water channels with amphiphilic block copolymers via self-assembly, leads to crystalline nanosheets with a proper arrangement of the nanopores in an almost impermeable matrix (i.e. 2D porous nanosheets). The subsequent layer-by-layer assembly of the nanosheets with polyethyleneimine on a porous support yields a thin-film composite membrane with precisely designed Angstrom-scale pore size and excellent separation performance (molecular weight cut-off 500 Da and water permeance 65 L/m^{2}hbar; Fig. 14). This and similar works demonstrate the feasibility of multi-scale LEGO®-like membrane systems as will be discussed in section 6.

5. Advanced "tools" to extend the existing membrane manufacturing platforms

5.1. *Dynamic membranes (material deposition during filtration on a support)*

A well-known and proven concept in filtration is utilizing the "cake layer", which is formed on a porous filter medium during the filtration process. This is a means to improve separation efficiency because smaller particles can be retained within the porous cake formed by bigger particles. The system's performance is variable under dead-end filtration as deposition is continuous. Under cross-flow filtration it is possible to reach a steady-state with respect to particle deposition to and removal from the filter cake, so that a dynamic filter with (almost) constant properties is formed. The analogous concept can also be applied to membrane filtration in order to separate smaller (colloidal) particles with sizes down to a few nanometers. This so-called "dynamic membrane" approach, where a filter cake on a conventional woven or mesh filter is utilized has been identified as an opportunity to membrane bioreactor systems which rely on MF or UF membranes as the actual selective barrier (for a review see Ref. [163]). For the same reason hollow fiber membranes based on a membrane coating on a hollow braid are "self-healing" in MBR applications when the coating layer gets damaged. The cake layer will quickly build up in that highly permeable section and creates a selective repair. Hence, particle fouling can be turned from a problem into a solution.

It is also known that analogous effects occur for even smaller particles or solutes. The presence of organic fouling layers, which are composed of organic macromolecules can have a pronounced effect on selectivity in UF, NF or RO. Usually, this unintended phenomenon is considered a problem, but it could also be intentionally utilized if the interplay of the material forming a "dynamic membrane" and the process conditions are known in detail and could thus be used to enhance selectivity (and overall separation performance).

Therefore, it is worthwhile to reconsider the established concept of a "dynamic membrane", and to explore its potential in a much broader context. In fact, there are already examples that "building blocks" for membranes are assembled under defined filtration conditions on a

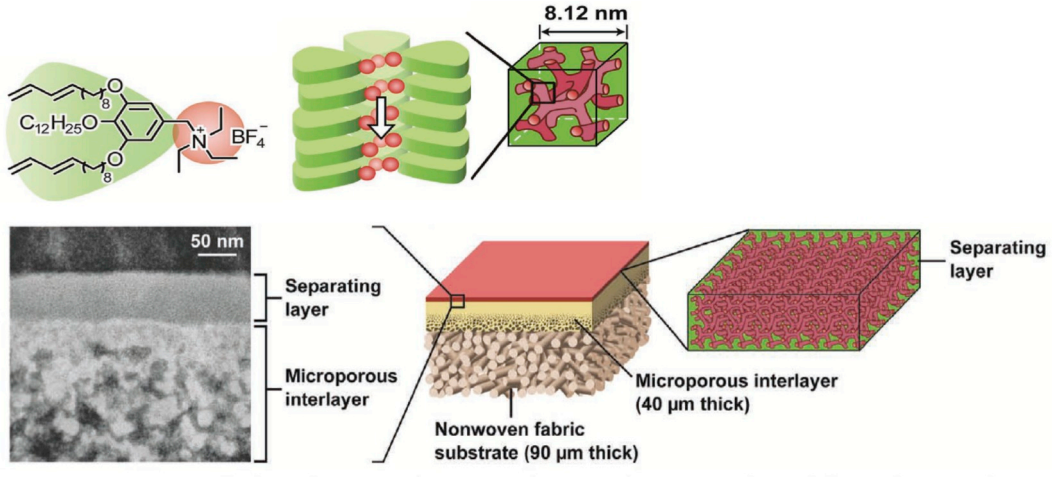

Fig. 13. Molecular self-assembly of wedge-shaped amphiphilic molecules into a liquid crystalline layer with ionic nanochannels toward a thin-film composite membrane for nanofiltration. Reproduced with permission from Ref. [159].

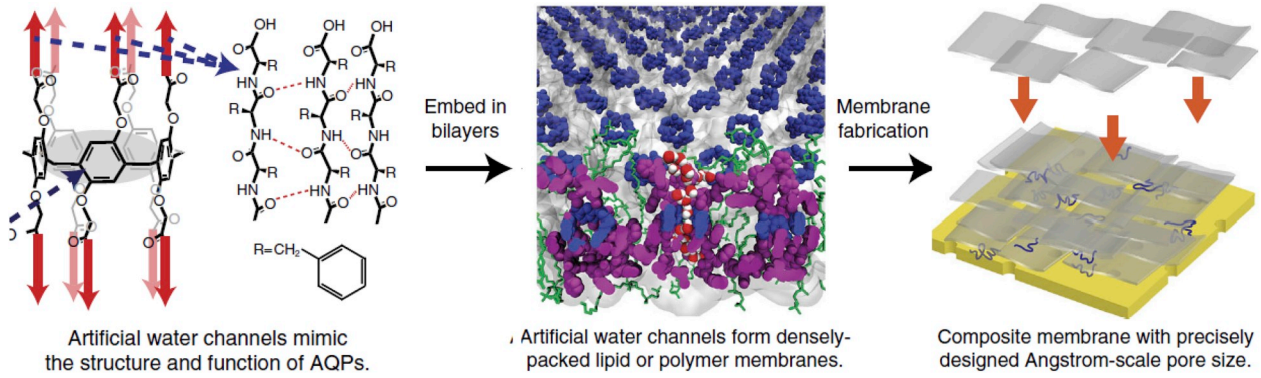

Fig. 14. Artificial water channel formation based on pillar[5]arene assembly and step-wise integration into a thin-film composite format for demonstration of mass separation capability. Reproduced with permission from Ref. [162].

support membrane in order to obtain a tailored selectivity governed by the thus formed barrier layer (see examples for filtration-driven assembly of 3D, 2D or 1D materials in section 4). Most notable is the LbL assembly of nanofiltration membranes where their formation by infiltration into a module with a support membrane and also their removal after loss of function and reapplication of a new membrane in the same module had already been demonstrated (see section 4.2).

5.2. Deposition of material from gas or plasma phase

Almost all industrially established processes for membrane fabrication are based on processing the membrane materials (mostly organic polymers, but also precursors of inorganic oxides or various kinds of solid particles) from solutions or liquid dispersions. Also, the formation of "dynamic membranes" (cf. section 5.1) is exclusively connected to liquid separation processes.

Spray coating is based on the utilization of aerosols to apply films on substrates. Solutions of polymers or dispersions of nanoparticles are typically used, with compositions similar to "inks" used for printing (i.e. spatially controlled deposition instead of a uniform coating; see section 5.4). The aerosols can be formed by different principles, mostly by mechanical (nozzle spray) or electrical means (electro spray). In "thermal spraying", the fluid material to be deposited is either obtained by heating or chemical activation (e.g. plasma, see below). Film formation proceeds by deposition, optionally evaporation of volatile components, fusion and adhesion of material onto the substrate to be coated. It is noted that spray coating can also be applied in a layer-by-layer fashion, where it has been successfully used to facilitate the preparation of functional coatings or separation layers of membranes, which originally would have been prepared by sequential dip coating (in a large excess of the polymer solutions; cf. section 4.2).

The utilization of spray coating to prepare UF membranes on a porous support has been investigated with dispersions of nanocellulose, a relevant 1D material (cf. section 4.5). The resulting membrane's separation performance was superior (higher flux at same rejection) compared to the analogous, conventionally prepared membrane (knife casting) [164]. Some other examples will be described in section 5.4.

Plasma deposition or *chemical vapor deposition (CVD)* processes have successfully evolved, over the last decades, to proven technologies for application of thin films from all kinds of materials (metal, ceramics, carbon, organic materials) on a wide range of substrates. The large diversity of material combinations and process conditions will not be covered here. For reasons of simplicity deposition from "plasma" or "chemical vapor" may be distinguished by the state of matter (plasma vs. gas phase as carrier of deposited material or its precursor) and the used pressure (conditions for both plasma and CVD, depending on the involved chemistry and target film properties can range from deep vacuum to ambient pressure). However, precursors for the actual CVD-based coating can be prepared by producing an aerosol or by activation with plasma. An interesting extension of one step CVD procedures for films with uniform composition and thickness tuned by deposition time is atomic layer deposition (ALD); here the sequential exposure to two different precursors with complementary reactivity leads to step-wise growth with sub-nanometer precision due to the self-limiting character and a wide range of accessible well-defined chemical structures. In contrast to spray coating technologies, where material is usually deposited without chemical conversion in CVD and ALD processes the material is formed by more or less well-defined *in situ* chemical reactions during plasma deposition. Hence, compared to spray coating it is in principle easier to obtain ultra-thin layers (in the low nm range) at high precision.

The deposition of the membrane material from the gas (or plasma) phase is *a priori* a solvent-less or solvent-free alternative to other coating processes and it can be designed to reduce or avoid waste, leading to a high "atom efficiency" and a potentially "green", sustainable character. On the other hand, such processes are (in principle) perfectly suited for fabrication of (ultra)thin layers, either as barrier layer in a composite membrane or as functional coating on all kinds of membranes. Overviews on the utilization of plasma or CVD processes for advanced or functional separation membranes can be found in recent reviews [165, 166]. Here, the diversity and potential will briefly be discussed with focus on a few approaches of particular interest, illustrated by selected examples.

Microporous silica barrier layers in inorganic thin-film composite membranes for gas separation can be fabricated via CVD and impressive progress has been made in recent decades [167]. The extension to NF and other processes is also feasible. An interesting aspect is that in case of silica the formation of the actual separation layer can be achieved at ambient temperature without any need for thermal post-treatment. This may indicate options for making preparation of ceramic membrane less costly. Nevertheless, the fabrication of macroporous ceramic membranes and ceramic interlayers, employed as/in the support, still requires the typical high temperature sintering conditions.

Carbon-based barrier layers are also highly attractive for advanced gas and liquid separations with numerous notable efforts devoted to the development of single-nm thin barrier layers with tailored porosity. An example which shows the impressive potential for pushing the limits according to the state-of-the-art is the preparation of a very robust microporous diamond-like carbon layer and its utilization in a composite membrane for organic solvent nanofiltration. Using a plasma-enhanced CVD with acetylene as precursor, 35 nm thin films were obtained which after transfer to a porous support via removal of a sacrificial layer from cadmium hydroxide nanostrands (cf. section 4.5) yielded exceptionally high permeance for organic solvent. Values up to three orders higher than those for commercially available membranes with the same effective pore size were reported [168] (Fig. 15); for

example for an UF membrane with complete rejection of 5 nm gold particles hexane flux was 2910 L/m^{2}hm at 0.8 bar, or for a NF membrane with 94% rejection of azobenzene (0.69 nm) ethanol flux was 67 L/m^{2}h at 0.8 bar. This work has inspired recent research on membranes with microporous carbon- or polymer-based barrier layer using other fabrication routes such as carbonization of microporous polymers [46] or interfacial polymerization [169].

The preferred route to high-quality monolayer graphene, considered the ultimate barrier material (cf. section 4.4), is by CVD on a metal foil as substrate. Recently, it has been demonstrated that a scalable process is possible producing membranes comprising an atomically thin graphene layer on a polymer support. The established roll-to-roll CVD and polymer support casting at a speed of 5 cm/min enables the fabrication of membranes with size-selective transport (based on intrinsic defects of the graphene) comparable to membranes prepared by conventional (lab-scale) methods [170]. Such technology could, for example, be combined with the fabrication of monolayer graphene/polymer composite UF membranes where swift heavy ion irradiation is used to create size-selective pores in the graphene layer and ion tracks in the polymer support; the latter can then be used to (track-)etch transport pores in the support so that the resistance for mass transport is in the ultrathin graphene layer [171].

Organic polymer-based barrier layers in thin-film composite membranes can also be realized by gas phase processes. This is, for example, demonstrated by the step-wise synthesis of polyimide on nanoporous alumina via ALD [172], or by the synthesis of tailored polyzwitterionic acrylate-based polymer layers via initiated chemical vapor deposition on commercial PA TFC membranes [173].

It is of interest that CVD-based coatings have already been used successfully to seal defects in ceramic membranes for gas separation [174]. Finally, as expected for technologies which are suited for surface "finishing" for all kinds of substrates plasma- and CVD-based processes have been extensively used for membrane post-modification in order to change the wetting properties on demand or to impart other functions such as antibacterial or catalytic properties [166]. However, spray coating is increasingly considered an easier alternative to plasma- or CVD-based processes.

5.3. Affordable ceramics

Ceramics with higher chemical stability and organic solvent resistance compared to organic polymers are widely studied and used for membranes [175,176]. The conventional ceramic fabrication is normally carried out by a multiple-step process including ceramic powder synthesis and membrane sintering. Depending on the final pore size a ceramic membrane typically consists of multiple layers, starting with a coarse support structure followed by subsequent layers comprised of smaller particle sizes to generate layers with smaller pores. UF membranes can have up to 2–4 layers, while NF and gas separation membrane can have even more layers. After the application of a new layer the membrane has to go through a sintering process first before the next layer can be applied. High temperatures (usually >1000 °C) are necessary to obtain ceramics with desired physical and (electro-) chemical properties such as crystallinity, strength, density, electrical conductivity and thermal conductivity, which will further impact on the performance of ceramic membranes in terms of permeability, selectivity and lifetime. In water filtration ceramic membranes are typically restricted to MF with pore size of 0.1 μm and consist of 2–3 layers to keep cost to an acceptable level. Materials of choice are Al_2O_3 or SiC. Production cost today is still too high (approximately 10x) for these membranes to compete with polymeric membranes despite the benefit of a higher operational flux (typically up to 2x).

The complexity and unsustainability of ceramic fabrication could be prominent in ceramics made of multicomponent metal oxides with more than two metal elements. For example, perovskite ceramic membrane exhibiting high oxygen ionic and electronic conductivities are widely used for oxygen separation and catalytic membrane reactor [177–179]. The perovskite oxides are usually quaternary or quinary compounds, e.g. AA'BB'O_{3-d} (A′, A: La, Ce, Sr Ba; B, B': Fe, Co, Mo, Zr, Al, Nb), such as $Ba_{0.5}Sr_{10.5}Co_{0.2}Fe_{0.8}O_{3-d}$ or $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-d}$. To fabricate

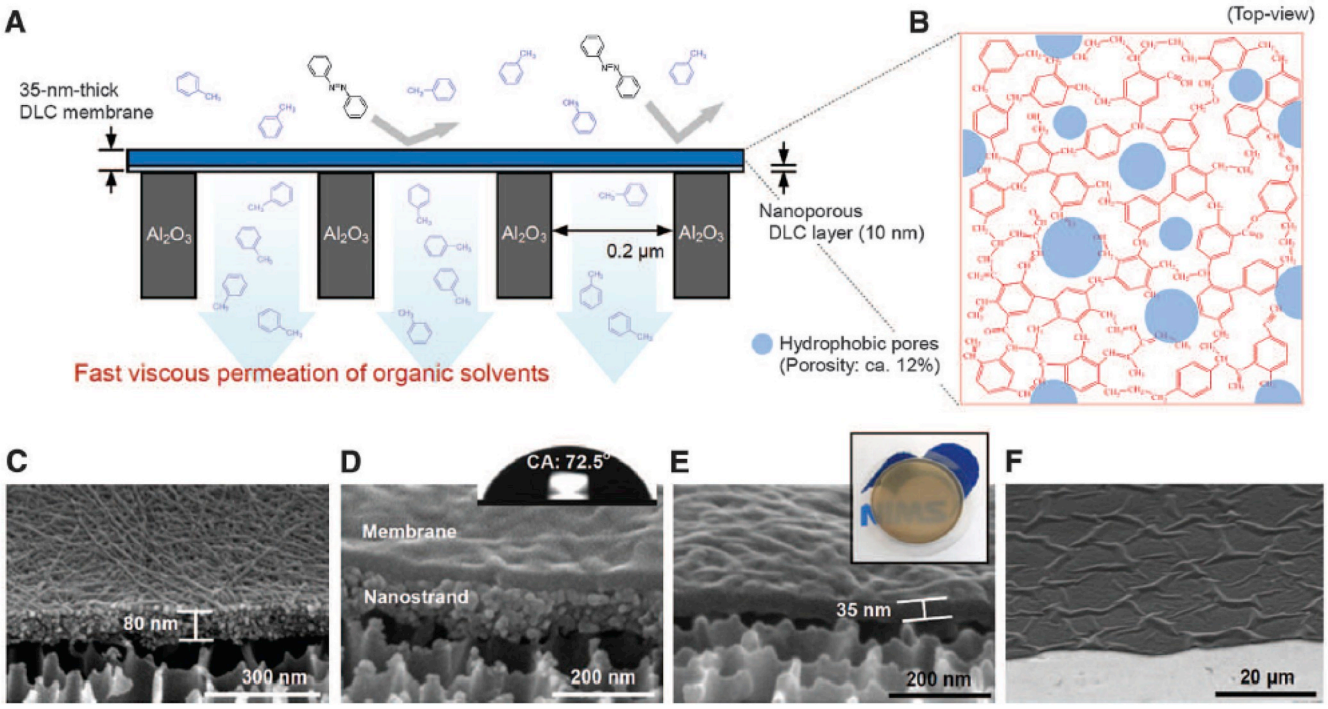

Fig. 15. Ultrafast organic solvent nanofiltration membrane prepared by plasma-enhanced CVD of diamond-like carbon layer on sacrificial nanostrand layer and subsequent transfer onto a porous support; A, B: schematic visualization of resulting membrane; C to F: SEM images of top layers after the different fabrication steps. Reproduced with permission from Ref. [168].

perovskite ceramic membranes, perovskite powder will be firstly synthetized at high temperature (usually >900 °C) via complicated solid-state reactions or wet-chemistry routes and a subsequent high temperature sintering (usually >1200 °C) is carried out to obtain a dense ceramic body [180,181] (Fig. 16a). Ceramic manufacturing process could be economical and sustainable if one could reduce the number of steps in the processing. For instance, introducing raw chemicals (e.g. oxides or carbonates rather than as-prepared perovskite oxides) into the membrane fabrication (e.g. hollow fiber membrane fabrication via phase inversion [182–184]), the perovskite ceramic membranes are obtained via only a single thermal processing step where *in situ* synthesis and sintering are taking place [185] (Fig. 16b); this one step thermal processing method saves much time and energy (≈50%), opening exciting sustainable and low cost manufacturing possibilities for ceramic membranes.

Another major challenge to obtain affordable ceramic membranes is that high sintering temperature and high energy input in most circumstances are necessary for ceramic densification. Emerged sintering techniques such as cold sintering process have demonstrated that sintering can also take place at significantly lower temperatures [186–188]. Membranes made of binary compounds, such as ZrO_2, ZnO, Al_2O_3 etc., can be sintered at mild temperature (<300 °C) [187,189]. However, great challenges remain in dense perovskite ceramic membrane fabrication as its complex chemistries (e.g. deficiency, crystal structure, conductivities, ionic diffusions) need to be carefully controlled [190]. These new approaches can be extended to composite ceramic membranes (e.g. dual-phase membrane and molten salt membrane) and material systems with strict requirements on temperature (e.g. bioceramics and bioglasses).

5.4. Micro- and nanofabrication

5.4.1. Shaping membranes toward tailored surface patterns

Advances in micro- and nanofabrication enable the precise tailoring of polymer *surface topography*. This has recently also been explored for separation membranes, so that established barrier properties can be combined with different shapes (for a recent review see Ref. [191]). Via (re)shaping, different kinds of patterns or corrugations can be applied to the normally (rather) smooth surfaces of conventional membranes; a schematic visualization of two approaches for flat-sheet membranes is provided in Fig. 17. While phase separation micromolding (PSμM) has been explored for patterns in the μm-range, thermal embossing micromolding has also successfully been used to fabricate patterns in the range of 100 nm. The scale-up to continuous fabrication with PSμM is very complicated. However, shaping by a post-treatment with thermal embossing micromolding, via plastic deformation of the membrane polymer below the glass transition temperature, seems to be possible in a roll-to-roll process [192]. For capillary membranes, corrugations with dimensions in the range of a few tens of micrometers on the outer or inner surface, parallel to the capillary axis, have been realized by using modified spinnerets with the complementary shape [193]. Recently, by using a modified 3D-printed rotating spinneret (see below), corrugations

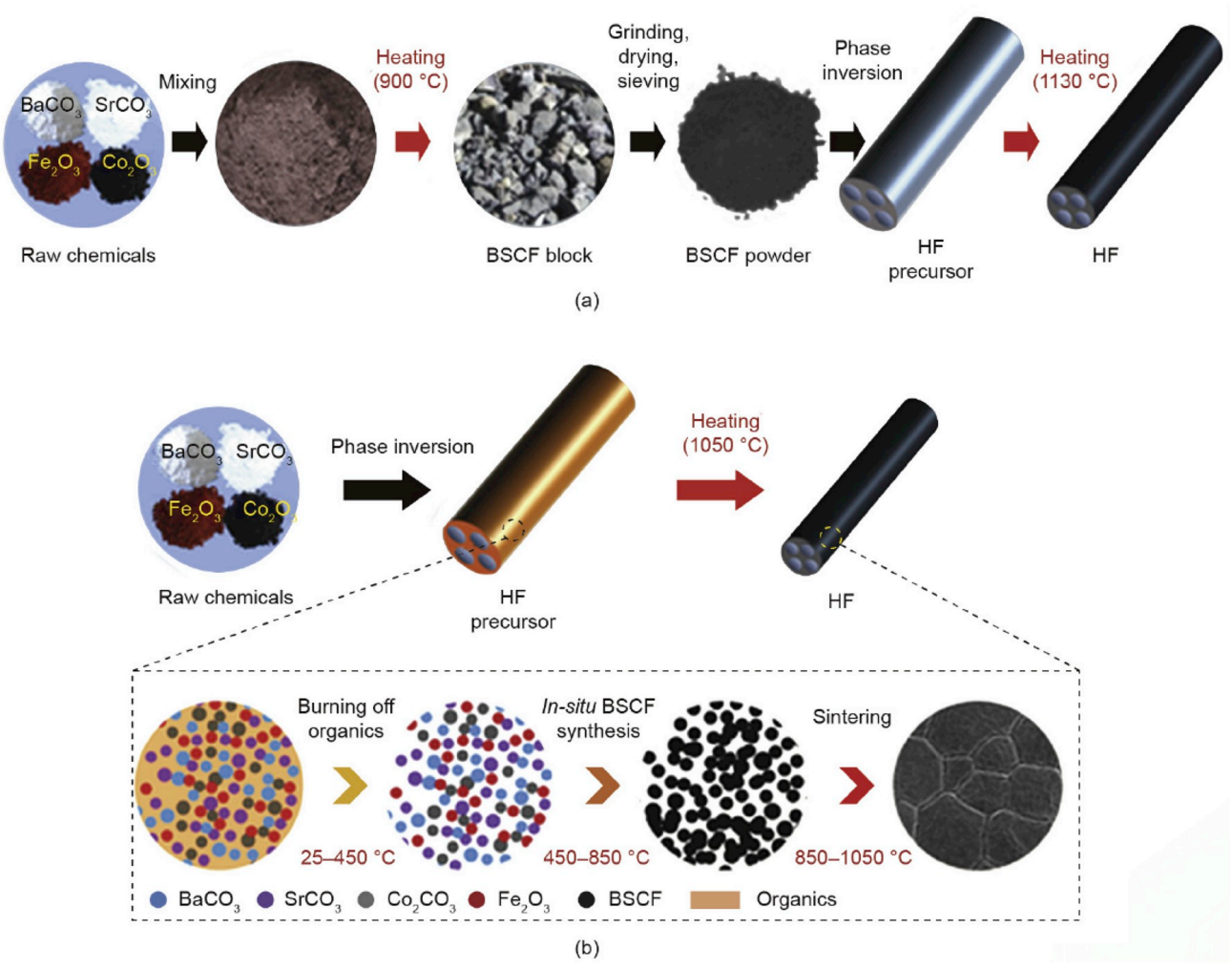

Fig. 16. A schematic overview of perovskite HF membrane fabrication approaches. (a) Conventional approach with two-step thermal processing; (b) one-step thermal-processing approach. Reproduced with permission from Ref. [185].

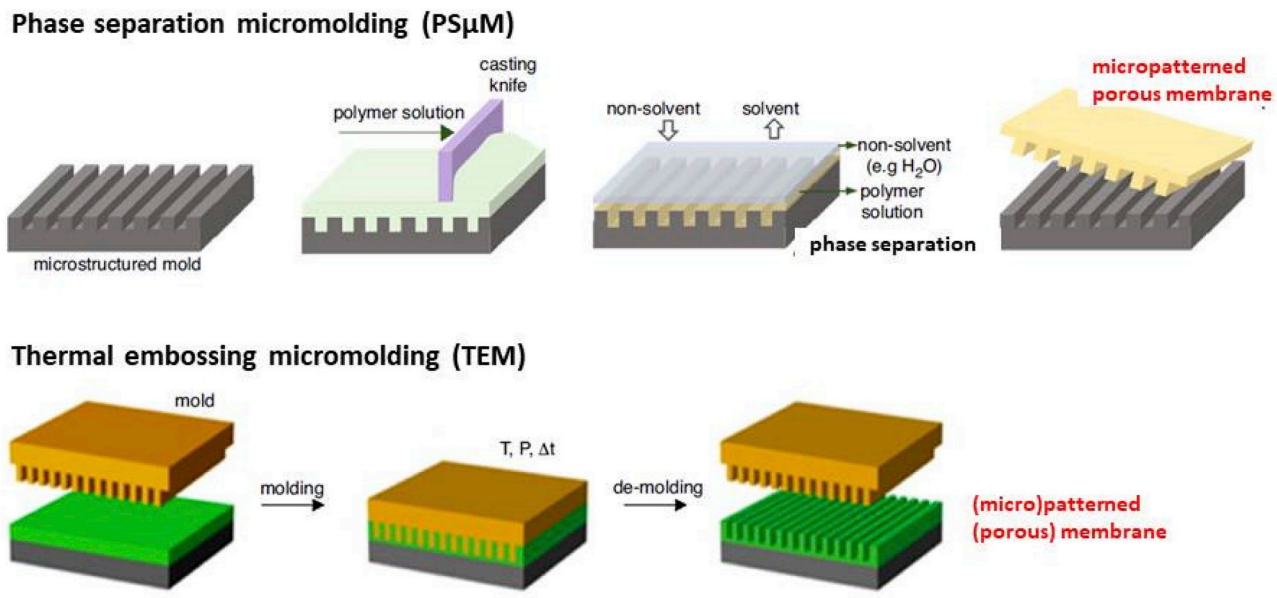

Fig. 17. Surface patterning techniques suited for preparation of porous polymer-based membranes. Reproduced in modified form with permission from Ref. [191].

with a twist along the capillary axis have been realized as well [194]. Attractive potential benefits of the patterned surfaces in terms of membrane separation performance are related to:

- higher flux at same driving force because of increased active surface area, and
- modified hydrodynamics at the membrane surface leading to lower concentration polarization [195] and reduced fouling [196].

From the initial work in that area it is already clear that the full potential of such 3D structured membranes can only be utilized if the design and fabrication of the patterns is well adapted to the module design and process conditions.

5.4.2. Toward fabrication of entire membranes

Another objective for micro- and nanofabrication would be to create the actual barrier structure by fabrication methods different from the established (cf. section 1) or emerging ones (cf. sections 4 and 5.2), which are shaping by casting or coating as well as reshaping (thermal embossing micromolding, see above). In principle, such "unconventional" alternatives can be classified into subtractive or additive approaches.

As an example for subtractive manufacturing, *microlithography* has been established to prepare microsieves from silicon nitride or ceramics about two decades ago [197]. Thin membranes with very *well-defined pores with predefined shape and porosity* have been realized and demonstrated superior filtration performance compared to conventional membranes with identical pore size. This development is limited to the microfiltration range (smallest accessible pore size ~100 nm). The creation of much smaller pores to enable UF or even NF is very challenging. On top of that, cost and scalability of known subtractive methods are currently prohibitive for large membrane areas. Nevertheless, the creation of smaller pores is technically feasible; examples for "ultimate" MF and UF membranes have been prepared by using focused ion beam in order to "drill" well-defined pores (for the different membranes between 1 μm and 50 nm) in monolayer graphene suspended on a support [198] (cf. section 4.4). Utilizing self-assembled block copolymers to enhance, augment and advance the performance of lithographic processes is an alternative to obtain well-defined arrays of small uniform pores [199].

Conventional printing can also be used to create patterns on membranes, with addressable differences in surface topography or membrane chemistry. To data, only a few case studies on ink-jet printing used for creation of patterned membranes have been reported. A very interesting example is the preparation of a charged mosaic membrane by creating a pattern ("mosaic") of micron-sized anionic and cationic domains via printing/pore filling of a porous support membrane [200]. Such membranes are very attractive because of their very special selectivity for salts and it is impossible to obtain such membrane architecture by standard membrane fabrication methods.

Additive manufacturing (also known as *3D printing*) is a very rapidly developing technology for the direct fabrication of objects of (essentially) any shape. Nowadays, there is a range of different methods using different principles and materials thus enabling different degrees of freedom in particular with respect to resolution and shape fidelity. The perspectives and the preliminary state-of-the-art with respect to membrane technology had been reviewed recently [201]. It is emphasized that additive manufacturing is a different membrane fabrication method which complements conventional techniques, so that membranes of different shapes, types, and designs could be obtained, potentially more precisely designed, fabricated and controlled than using the more traditional fabrication methods available today. In principle, both the micro- and macro-structure of the membrane and the module could be designed and fabricated in one machine and one (sequential) process. This will lead to radically novel options for combined and integrated design in order to improve membrane-based separations at the materials and process architecture levels [201]. An additional advantage compared to standard phase separation of polymer solutions is that several versions of 3D printing require much less or even no solvents.

However, the most important conclusion with respect to the current status is that *3D printing of entire membranes*, mimicking their established high-performance counterparts, is still impossible for almost all membrane applications. Exceptions in the near future may be thick isotropic macroporous membranes for coarse microfiltration or non-porous ion-exchange membranes. The main reasons are limitations in resolution (at best in the low μm-range) and the limited choice of materials.

Nevertheless, there is already very important progress with respect to *3D printing of different parts of membranes and membrane systems*. The most relevant cases are:

- tools for fabrication of membranes with otherwise not accessible shapes, e.g. the 3D printed spinneret for fabrication of twisted membranes [194];
- methods to obtain an entirely functional membrane with a shape which is not accessible by conventional manufacturing, e.g. a thick gas exchange membrane from silicone, cast in a mold ("tool") which has been produced by 3D printing rapid prototyping [202];
- 3D printed modules and spacers with special shapes (for a review on that topic see Ref. [203]; for a first example of commercialization cf. section 6);
- porous support for membranes, e.g. a 3D printed coarse porous support providing the otherwise conventional ultrafiltration membrane with a special undulated surface topography, which has a beneficial effect because of reduced fouling [204].

There is also a very interesting recent paper on "3D printed" polyamide membranes for desalination [205]. However, only the barrier layer, not the entire membrane, had been printed (this is analogous to Ref. [203]) and the printing was not truly 3D. The electrospray-enabled layer-by-layer fabrication of a polyamide thin-film composite membrane, by sequentially spraying the aqueous diamine and the organic acid chloride solutions, leads to similar chemical structure and barrier properties, but much lower surface roughness compared to conventional interfacial polymerization. Essentially, this is a different implementation of the molecular LbL preparation previously shown to lead to similar results, i.e. much smoother surface at same barrier properties [112] (cf. section 4.2). However, as already discussed in section 5.2, solvent-less spray coating has clear benefits with respect to improved sustainability of the fabrication process. A significant reduction in materials consumed compared to traditional TFC processes results at the same time in less waste production.

It is interesting to note that one can already find industrially produced high-flux UF membranes made by solvent-free "3D printing". The actual fabrication of these membranes is based on spinning a PVDF nanofiber non-woven and subsequently compressing it into the final filter structure (cf. section 6).

Overall, the full utilization of 3D printing for membrane manufacturing will require other polymers or monomers ("building blocks") than used by the membrane industry today. On the other hand, this need may provide new opportunities for preparation of polymeric and ceramic membranes. There is a need for lower temperature preparation methods for ceramic membranes (cf. section 5.3), and 3D printing with hybrid precursors could make this possible in the future [206]. Furthermore, new possibilities of functionalization could be feasible leading to concepts of "4D printing" [207], for instance adding stimuli responsiveness to nanofabricated membranes.

6. Potential of utilizing or combining tailored "building blocks" and "advanced tools"

The focus of section 3 was on making membranes more versatile and sustainable, utilizing existing, industrially established membrane manufacturing technologies. The newly emerging "building blocks" (cf. section 4) can either extend the scope of established manufacturing or can be combined with alternative or advanced "tools" for fabricating membranes (cf. section 5). Examples for implementation of such concepts by companies are provided in Table 4.

As demonstrated in the two previous sections, many innovations originate from research outside the "membrane community". From the academic perspective (and in the respective scientific publications), new "building blocks" or "tools" are often claimed to have the potential for (largely) improving separation performance of well-known membrane applications such as water desalination or hemodialysis and virus removal. However, from the application point-of-view, the actual demand may be very different. Hence, it is important to not only focus on what is possible but to consider the real demands and how those can be best addressed. Visions for the future should consider both, the membrane industry as well as the various industries and sectors that already benefit from membrane technologies, or will in the future. The requirements for large membrane applications are often standardized, utilizing established manufacturing processes (cf. section 1). This is generally not the case for smaller, specialized or emerging applications. Hence, it cannot be expected that one strategy or methodology will fit all existing and emerging needs. In the following, the potential of innovations will be discussed while considering some important generic aspects, but also with a view towards adapting or even tailoring membranes to the needs of specific separation (or integrated) processes. Thus, the "rational design" of the membrane should ideally begin with input on the essential requirements of the application process. At the same time, the assembly of materials toward an improved or novel membrane should also follow the same principles. Over-arching criteria will be intrinsic membrane separation performance but also simplicity and sustainability; both will often (but not always!) also require robustness (cf. Table 3). Until now only the very first examples for model-supported or even model-based membrane design and fabrication to satisfy the needs in a real application are emerging (e.g. Ref. [112]; cf. section 4.2). However, in the future the implementation of advanced and novel membrane materials and manufacturing processes in lab and industrial scales (see section 6.1) must be guided by model-based design (see section 6.2).

Table 4
Overview on recent approaches to advanced or novel membranes by companies or taken from academia to start-up companies.

Innovation	Company	Section
Chemically resistant nanofiltration hollow fiber membranes	Seppure; https://www.seppure.com/	3.1
Isoporous ultrafiltration membranes by SNIPS of block copolymers	Terapore Technologies, Inc.; https://teraporetech.com	4.1
Zwitterionic copolymer-based membranes for treatment of organics-loaded wastewater	ZwitterCo Inc.; https://www.zwitterco.com	4.1
Nanofiltration hollow-fiber membranes by layer-by-layer deposition of polyelectrolytes	NX Filtration BV; https://www.nxfiltration.com	4.2
Nanofiltration hollow-fiber membranes by layer-by-layer deposition of polyelectrolytes	Pentair X-Flow; https://xflow.pentair.com/en/spectrum/nanofiltration	4.2
Grapheneoxide coated membranes for water purification	G2O Water Technologies Limited; https://g2o.co	4.4
Grapheneoxide polymer hybrid membranes for water purification	Via Separations; https://www.viaseparations.com	4.4
Polymer-nanocrystal composite membranes with improved and stable CO_2-separation performance under harsh feed conditions	Flux Technology; http://fluxtech.io	4.4
Molecular sieving flat sheet membranes for various gas separation applications	Unisieve Ltd.; https://www.unisieve.com/	4.4
High-flux ultrafiltration membrane by solvent-free „3D printing" and compressing a PVDF nanofiber non-woven	Nano Sun Pte Ltd.; https://www.nanosun-main.com	3.3; 4.5; 5.4
3D printed polymeric spacers directly on RO membrane surface	Aqua Membranes Inc.; https://aquamembranes.com	5.4

6.1. Implementation strategies

Current membrane technologies are successful by utilizing established membranes, flat, capillary or tubular, in modules adapted to the membrane shape; the combination of membrane and module fits to the respective application. It is well recognized that the actual separation performance can be largely influenced by optimizing parameters both on the membrane and on the module level. The key functionality on the module level is to provide the appropriate space for at least two compartments which are separated by the membrane, and to ensure efficient mass transfer toward and away from the membrane. This is typically realized with help of tubes or plates and spacers in suitable housings with connections for feed, permeate and retentate. Typical membranes consist of at least two parts: a mechanically supporting layer and a perm-selective barrier layer (this is obtained by one- or multi-step shaping processes of the membrane material(s); cf. section 1). The membranes are permanently integrated into the modules, typically with the help of adhesives. Such "traditional" membrane separators, composed of different materials in various shapes at largely different length scales (from meter to Angstrom) can be characterized with respect to intrinsic properties, but those are typically static, i.e. determined by the membrane and the module fabrication processes. The only dynamic aspect when using such traditional separators is actually undesired, namely membrane fouling and/or module performance deterioration or failure. As outlined in section 3.4, new developments go beyond anti-fouling and anti-aging strategies, aimed at extending the module operation time by re-use (typically down-cycle) or re-cycle strategies, enabling applications not originally intended by the manufacturer.

It should be noted that there is significant research and development beyond such "static membrane separators". The most prominent example is the extensive academic work on stimuli-responsive membranes [93,208], which can change their surface or barrier properties as a function of chemical or physical triggers; but usually conventional modules are used or considered. Developments beyond the membrane material level – in some cases also implemented in industrial applications – are, for example, devoted to vibrating or rotating membranes or modules [209,210], in order to reduce polarization or fouling, but conventional membranes are usually employed.

Future membrane technologies may also be based on hierarchically assembled separators, where module and membrane functions are integrated and can be utilized in a dynamic manner, all with much larger ("4D") design flexibility than the state-of-the-art. Optionally, the membrane separator function can be implemented "on demand" (when needed) or "in place" (where needed, even in remote, not well accessible, places; e.g.: "injectable membranes"). With a view on applications, such membrane separator systems should enable the same functions as conventional ones, i.e. provide separate compartments, facilitate mass transfer to and from the membrane and comprise a perm-selective membrane barrier. In terms of materials and fabrication, such a system comprises just two different kinds of elements in a suitable housing (with respective connections, see above):

- ***scaffolds***: structural materials, defining compartments and providing porous morphologies in desired shape, with sufficient stability to support the function of the actual membrane;
- ***barrier layers***: selective layers constituted by functional materials that enable the desired membrane-based separation.

Regarding *barrier or selective layers*, the "building blocks" introduced in section 4 can in principle lead to superior properties compared to established membranes based on dense amorphous polymers, randomly phase-separated organic polymers or inorganic materials. The implementation of building blocks as selective membranes is achieved by self-assembly (between building blocks or on a surface) in/from a liquid, visco-elastic or liquid-crystalline state, optionally in combination with additional forces (e.g. mechanical when utilizing filtration onto a support). The porosity and pore size for most materials result from the packing/stacking of the building blocks during the assembly (with building blocks yielding liquid crystalline phases providing the highest "precision"; cf. Fig. 13), and this consequently depends on operating conditions during assembly. In contrast to their "latent" porosity, some 2D materials have permanent pores (useable for mass separation) defined by covalent bonds (2D organic polymers [211]) or combinations of covalent and ionic bonds (e.g., zeolite or MOF nanosheets), i.e. accessible by molecular design. Importantly, most of the materials which are self-assembled based on non-covalent or reversible covalent bonds can, at least in principle, be dis-assembled (cf. Fig. 12).

Regarding *scaffolds*, there is obviously a very wide range of options, from conventional porous materials (spacers, non-wovens, wovens) to established porous membranes (analogous to the support in TFC membranes). "Advanced tools" such as 3D printing (cf. section 5.4) will allow to create porous scaffolds of any shape and, if desired, also the housing of the membrane separator. Some of the "building blocks" can be utilized not only as a barrier layer, but also as a scaffold for a "tighter" barrier layer. For example, a layer made of 1D materials can be used as a scaffold for deposition of 2D materials; and both layers can, in principle, be assembled or dis-assembled "in place" and "on demand". Finally, it has also been shown that self-assembling block copolymers can enable the formation of a 2D nanosheet with self-assembled small molecules, forming synthetic water channels, and thus also act as scaffold (i.e. an internal mechanical support of the 2D nanosheet with domain sizes in the lowest nanometer range); this is an essential precondition for utilizing the perm-selective properties of the synthetic water channels in the hierarchically assembled membrane (cf. Fig. 14). Overall, conventional and alternative scaffolds are available with characteristic lengths (e.g. domain sizes or layer thickness) from the millimeter down to the sub-nanometer range.

Using tailored combinations of scaffolds and barrier layers as design concept, a very large degree of freedom with respect to shapes and architectures on all relevant length scales may be utilized for advanced or novel membrane separations. A few example cases are briefly outlined below, beginning with already demonstrated concepts and then moving to more complex, "futuristic" ones.

Using established membranes (in standard modules) as scaffold for self-assembly of permanent or regenerable barrier layers. Nanofiltration membranes can be obtained using two different polymers with complementary anionic and cationic groups as building blocks via layer-by-layer assembly of the membrane barrier layer on a UF membrane (flat-sheet of capillary); this can be done in either adsorption or filtration mode. It has already been shown that the removal and re-application of the barrier layer is, in principle, feasible (cf. section 4.2). Nanofiltration membranes can also be obtained by filtration/deposition of various 2D materials on UF supports (cf. section 4.4). Membranes with tunable pore sizes, from the microfiltration to the tight ultrafiltration range, can be obtained by filtration/deposition of 3D or 1D materials on support membranes with suitable pore size (cf. sections 4.3 and 4.5). Under filtration conditions, a dynamic membrane system is established (cf. section 5.1), and the flux can be used to monitor the formation of the barrier layer. With an eye towards sustainability, it is important that most systems can be assembled from water as the (main) solvent (cf. section 3.3). In all cases, it is possible to extend the stability range (regarding temperature or aggressive chemical environment, i.e. extreme pH values or certain organic solvents) by using ceramic membranes as the support (if needed in combination with carbon or inorganic building blocks for the barrier layer). However, the development of polymer membranes with higher stability (cf. section 3.1) will also provide alternatives. Furthermore, depending on the application, increased stability through chemical cross-linking of the barrier layer (in combination with robust supports) or the use of reversibly assembled barrier layers in combination with an easily degradable membrane (or entire membrane module; cf. section 3.2), are two different alternative scenarios for the life cycle of the membrane separator.

Using 3D-printed separator modules as a scaffold for self-assembly of permanent or regenerable membrane barrier layers. Considering the current and foreseeable state-of-the-art, it is not feasible to fabricate entire functional membrane modules for colloid or molecular separations only by 3D printing (cf. section 5.4). However, it is certainly possible that modules of any desired shape, containing porous scaffolds which also can have any wanted shape, can be fabricated by currently available 3D printing capabilities. The macroscopic shape and architecture will be designed to optimize the membrane area to module volume ratio, the feed and permeate compartments and the mass transfer to and from the membrane. The actual barrier layer can be assembled by any of the above-mentioned methods. When the ultimate barrier layer is in the nanofiltration range, a suitable scaffold interlayer (preferably from 1D materials) will be required because pores of 3D-printed scaffolds are unlikely to be smaller than 100 nm. All options mentioned above with respect to reversibility/reusability or stability can also be realized if needed (e.g. with 3D-printed ceramics vs. 3D-printed regenerable polymer as scaffold).

Fine-tuning the barrier properties to a specific separation. There are several options to develop standardized methodologies to adjust the barrier layer properties in fine steps as required. This may be achieved by a tool box comprising building blocks with adjustable properties (size, shape, linker groups, optionally porosity) in combination with additional ingredients (e.g. pH, specific salt) of solutions or dispersions used for self-assembly along with specific deposition conditions. That this is possible in a LEGO®-like manner can already be seen – still in a limited way – for some polymer LbL- or graphene oxide-based systems where salts can be used to fine-tune pore size (cf. sections 4.2 and 4.4). It can be envisioned that with other systems, in particular block co-polymers, different and wider ranges of barrier pore sizes can be addressed. However, realizing such systems will require considerable efforts in materials synthesis and further improved detailed understanding of self-assembly mechanisms. Such LEGO®-like approaches are of interest for the manufacturing of membranes with “static” structure and properties (to be then assembled in traditional modules), but also for “dynamic”, “on demand”, “in-place“ membrane formation in modules as outlined above.

Many more opportunities for advanced or novel membrane-based separations will emerge from the possibilities to switch the barrier properties with help of external stimuli, to let the membrane’s selectivity adapt to a certain separation conditions and targets, or to establish self-cleaning or self-repairing membranes. Such membranes are accessible by adaptations of established manufacturing processes, but the further development toward real applications will also very much benefit from combinations with the “dynamic” assembly approaches outlined above.

6.2. Model-guided design of tailored membranes

The basic premise of a "tailored" membrane lies in the ability to:

(a) predict a desired structure, and
(b) reliably create it.

At first instance, one must be able to identify materials and morphological features that promote a given separation. This is not only subject to the choice of material, but may also be used to guide this choice by screening through possible candidates. The second point reflects the fact that membranes are "macroscopic" and the ability to control and obtain a desired morphology is non-trivial and, in some cases, extremely challenging. Both aspects may be considered as underdeveloped (not for lack of trying) and possess a very high potential gain if developed successfully. Clearly, the ability to screen through a large parameter space in order to reduce the number of potentially viable materials/structures (let alone predict exact cases) is desirable in order to guide fabrication. The following section briefly outlines several of these aspects, as related to future membrane fabrication techniques and approaches.

A recent, inspiring account of various ways in which data science may be integrated into the design scheme, from tailored molecular structure up to system scale, may be found in Ref. [212]. Particularly, relevant features are the prospects of "inverse design“, referring to the identification of desired properties and structures that would achieve a target performance, as well as the use of statistically-driven methodologies for guiding the experimental efforts, and optimization methodologies that could facilitate the transfer of parameter input over a range of scales. In the present context, a good example would be optimizing the module-scale design, based on the membrane transport properties (in turn obtained from the micro-scale), or inversely dictating the required membrane properties, based on the desired module-scale performance.

The need for multi-scale models. “In-silico”, high-throughput screening, is gaining popularity in material science, particularly for catalysis and adsorption applications [179,213,214]. While this may be used to identify molecular-scale structures, membranes present an additional challenge – the need to consider length and time-scales beyond those accessed by molecular simulations. In particular, when considering porous membrane structures, one must consider the interplay of the “pore scale” interaction, which may involve truly molecular-level interactions, with the morphology of the membrane on the scale of many pores. Often, this also includes continuum-scale transport of a fluid phase requiring hydrodynamic considerations. The challenge lies in connecting these scales. This would require the “coarse graining” of interaction potentials into a form useable, for example, as boundary conditions or bulk material properties for continuum-scale differential equations. Multi-scale models, such as a combination of dissipative particle dynamics and self-consistent field theory [215–217], would be helpful for better predicting the structure formation of membranes based on block copolymers and other self-assembly systems.

Predicting interactions and their impact on transport. For nanofiltration, pervaporation and gas separation membranes, it would be helpful to better predict the interaction between the membrane material and the various components of the mixture being separated, and its influence on transport and selectivity. Furthermore, model-based quantification of interactions based upon the combination of classical polymer thermodynamics, permeant diffusivity and polymer mobility and relaxation could be useful. The development of multicomponent membranes, as “mixed-matrix”, in great part follows a semi-empirical approach, considering information collected for the single components, such as sorption measurements, which are insufficient for performance prediction as a membrane. Representative examples of recent efforts to tailor such interactions, in order to promote selectivity, may be found in Refs. [218–220] and, particularly, in a recent review [25]. While these are not all model-driven efforts in the quantitative sense, they do follow the stream of thought by which one may exploit known chemistries that promote selectivity, and then fabricate the appropriate membrane material, or modify the surface of an existing membrane scaffold.

Fabrication – predicting conditions leading to desired layered and complex structures. Many of the experimental approaches under current investigation consist of depositing 1D, 2D, or 3D materials on a porous support. It would be helpful to predict the best selection of materials and conditions that would lead to the most successful structures. For each of the approaches mentioned in sections 4 and 5, the selective layer is formed by different mechanisms and would require different modeling considerations. For industrial applications, ideally these approaches should be feasible at module scale. Even better would be the possibility of having a recyclable module, *in situ* create or regenerate the selective layer as outlined in section 6.1. In terms of modeling, there is still a long way to go. The performance predictions, even in the case of more classical membranes, which in most cases have a porosity gradient or multilayer structure, are frequently oversimplified. More detailed predictions are frequently disregarded, since they currently demand excessively time-consuming procedures and are not always well-

correlated with experimental observations. Modeling is still more successful in understanding, rather than predicting, performance (for a recent review see Ref. [221]). Furthermore, the ideal membrane for specific applications should fulfill not only the requirements of flux and selectivity, but be mechanically, chemically, thermally stable and have a low susceptibility to aging and fouling. A holistic analysis should be possible in the future, combining aspects of thermodynamics, polymers relaxation, and rapidly advancing computational capability.

7. Conclusions

Through exploration of the emerging concepts outlined above, the future of membrane materials and manufacturing will rely on innovation, scalability and sustainability of new approaches, stability of resulting membranes, feasibility of delivering fast prototypes and iterative work with risk-taking visionary industries. There are challenges and opportunities for membrane technology on different levels and sectors.

In the water sector, membranes are well-established mainly for seawater desalination (RO), pretreatment processes (UF), and wastewater treatment (MF/UF, membrane bioreactors). RO membranes with satisfactory flux and salt selectivity have been highly successful. Innovation concerning the use of new materials in this sector is challenging with the state-of-the-art, if cost and production at large scale are to be considered. In this field, the main improvement required for RO is still the resistance to fouling (bio-, organic and scaling) and to chlorine as cleaning agent. Decades of investigation have been dedicated to this topic [3]. The use of renewable sources of energy (e.g. solar) is under consideration worldwide as a way to reduce the fossil-fuel consumption for desalination. Membranes for desalination have a high rejection of sodium chloride, but if the selective separation of different salts is required, progress would require better RO/NF membranes. This will provide opportunities for approaches discussed in this article.

Liquid separations in the chemical, petrochemical and pharmaceutical industry constitute a growing opportunity for membrane technology (RO, NF, UF and pervaporation). However, here are also some of the largest challenges. Many of the processes would require temperature and solvent-resistant membranes and a rapid growth of research activities in this field is needed to accelerate the implementation of membrane technology for separations currently dominated by energy-consuming methods, such as distillation. Furthermore, NF/UF membranes with narrower pore size distribution (sharp molecular weight cut-off) would facilitate separations not possible today. Working in close collaboration with risk-taking progressive industries in this sector would be important to identify the processes with the highest chance of success whether performed with membranes alone or integrated with other technologies. Membrane development could be better tuned with specific knowledge of the requirements. With that feed-back, several of the approaches discussed in this article will lead to advanced or new membrane technologies.

Gas separation membranes have been successfully operating at large-scale for hydrocarbon vapor recovery or CO_2 separations. A rich variety of new polymeric materials and composites have been populating the Robeson plots of CO_2/N_2, CO_2/CH_4 or O_2/N_2 selectivity as a function of permeability, in a frantic competition for the highest combination of these properties. However, most membranes under operation in large-scale industrial applications are based on only a small number of polymers (e.g. CA, PSU, polyimide, polyetherimide) applied as selective coatings on porous asymmetric supports in flat-sheet modules. The reason for that has been emphasized by Baker many times: “a film is not a membrane” and finding a new material with good selectivity and permeability is only the first step [222]. Clear and honest statements on how feasible would be the implementation of academic new approaches as industrial membranes should be encouraged in publications. More efforts should be dedicated to go a step forward in the preparation of real membranes demonstrated with the needed reproducibility, as well as with a solid estimation of acceptable cost and scalability demanded for a successful industrial product.

Biomedical applications offer opportunities for advanced membranes; however, the demands are for perfectly defect-free membranes passing rigorous quality control. Selectivity and pore size control could be a valuable advantage to decrease the number of steps in purification processes and biocompatibility must be addressed. Hollow fibers used for hemodialysis have one of the largest markets in membrane technology, but membranes and porous materials have a lot of open opportunities in the biomedical sector for biomolecule purification, drug delivery, diagnostics, scaffolds, etc. Multi-functional membranes could revolutionize therapies, where cost is not as restrictive as, for example, in large-scale applications such as desalination.

Having said that, it should be kept in mind that existing and potential applications of membranes are much broader than what is mentioned in the previous paragraphs (cf. Table 1 and section 2).

Although methods of performance characterization have long been used in the membrane community with dead-end and cross-flow cells, a better standardization and broader dissemination of these methods in a scale that represents the requirements of future industrial application would be important, to avoid overestimated expectations.

Sustainability in membrane manufacture and processes will be needed, worldwide, with increasing concern on waste reduction and environmental protection, ultimately considering the entire life cycle of materials and processes.

In conclusion, there are many different opportunities, each related to a given sector of application and time scale for implementation. For the “evolutionary” approaches in section 3 there is a profound impact on a wide range of applications, and implementation will happen in near future. The range of more specialized approaches in sections 4 and 5 will have a case-specific impact; an active development in laboratories is ongoing and the first scaled-up implementation is expected within the next decade. By further establishing and consolidating “building blocks" and “tools” for membrane fabrication, “revolutionary” visions for *in situ*, “in place” and “on-demand” membrane systems (section 6) will be realized step-by-step in the next decades. There is a very large portfolio of materials currently under investigation with potential for application as membranes. It would be naïve to bet on only one or very few classes of materials. The next decades will tell us the advances achievable with new membranes and manufacturing processes.

Declaration of competing interest

The authors of this article have no conflict of interest.

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List of abbreviations

[EMIM]DEP	(ethyl-methyl-imidazolium) diethylphosphate
ALD	atomic layer deposition
CA	cellulose acetate
CAPEX	capital expenses
CNT	carbon nanotubes
COF	covalent organic framework
CVD	chemical vapor deposition
DMSO	dimethylsulfoxide
GO	graphene oxide
LbL	layer-by-layer

LLC	lyotropic liquid crystalline
MBR	membrane bioreactor
MF	microfiltration
NF	nanofiltration
NG	nucleation and growth
NIPS	non-solvent induced phase separation
OPEX	operational expenses
P4VP	poly(4-vinyl pyridine)
PA	polyamide
PC	polycarbonate
PDMS	polydimethylsiloxane
PE	polyethylene
PEEK	poly(ether etherketone)
PES	polyethersulfone
PET	poly(ethylene terephthalate)
PIM	polymer of intrinsic microporosity
PLA	poly(lactic acid)
POXI	poly(oxindole biphenylylene)
PP	polypropylene
PSμM	phase separation micromolding
PS	polystyrene
PSU	polysulfone
PTFE	poly(tetrafluoro ethylene)
PVDF	poly(vinylidene difluoride)
REACH	registration, evaluation, authorization and restriction of chemicals
RO	reverse osmosis
SD	spinodal decomposition
SEM	scanning electron microscopy
SNF	silk nanofibrils
SNIPS	self-assembly and non-solvent induced phase separation
SW	sea water
TEM	transmission electron microscopy
TFC	thin-film composite
TIPS	temperature-induced phase separation
UF	ultrafiltration
VIPS	vapor induced phase separation

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