

Thin film deposition techniques for polymeric membranes– A review

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ABSTRACT

Thin film deposition (TFD) allows for precise tuning of the chemical and physical properties of a membrane to improve performance, including the selectivity, flux, chemical resistance, and antifouling and antimicrobial properties. TFD techniques have a unique advantage over other traditional surface modification methods (e.g., grafting) vis-à-vis their applicability to low-surface energy polymers, which usually resist modification through other techniques. TFD is also an economical approach to surface modification as inexpensive base materials can be functionalized with small amounts of more expensive active chemistries. Here, we review a range of TFD techniques and their applicability for the modification of polymeric membranes to improve durability and performance across water treatment applications. The discussed techniques include sputtering, thermal evaporation, chemical vapor deposition, atomic layer deposition, electrochemical deposition, electron beam deposition, Langmuir-Blodgett deposition, and colloidal deposition. We review how recent developments in TFD techniques have made these methods a competitive alternative to other methods of membrane modification and discuss how modified membranes lead to improved performance for water applications, including micro-filtration, nanofiltration, reverse osmosis, and membrane distillation. Relative advantages of each coating process are discussed. We also discuss how process parameters for the various TFD techniques (deposition speed, versatility, conformality, thickness, bonding strength, temperature, etc.) influence the final chemical and physical properties of modified membranes. We conclude with an outlook for how further developments in TFD techniques will continue to introduce new possibilities for unique membrane properties and applications.

1. Introduction

1.1. Motivation

Freshwater scarcity is worsening in many parts of the world due to both natural and anthropogenic causes [1]. This situation is further aggravated by accelerating population growth, combined with the impacts of climate change [1]. The United Nations estimates that 1.8 billion people will experience absolute water scarcity and that two-thirds of the global population will live under water-stressed conditions by 2025 [2]. A sustainable water management plan involving diversified sources of water is essential in combating this escalating

problem of water scarcity [3]. Such a strategy will likely include reducing water consumption, reusing and recycling treated water, and producing freshwater via desalination. Membrane technologies are widely used for both desalination and the treatment of wastewater due to their lower operational cost and higher efficiency compared to alternative treatment methods [4–6]. Nevertheless, membrane fouling still poses a key economic limitation to membrane processes [7,8]. Therefore, improvement of membrane anti-fouling properties and selectivity via economically and scalable techniques is a critical step towards widescale implementation of membrane methods.

Thin film deposition (TFD) methods exhibit great promise as economic and scalable techniques for modifying membranes via application of thin coatings that can profoundly influence a material's chemical and

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Abbreviations list

6FDA	Hexafluoroisopropylidene-2,2-bis [phthalic acid anhydride]	PA	Polyamide
AACVD	Aerosol-assisted chemical vapor deposition	PAN	Polyacrylonitrile
ALD	Atomic layer deposition	PDMS	Polydimethylsiloxane
BSA	Bovine serum albumin	PE	Polyethylene
CA	Contact angle	PECVD	Plasma enhanced chemical vapor deposition
CVD	Chemical vapor deposition	PEFC	Polyelectrolyte fuel cell
DEZ	Diethylzinc	PES	Polyethersulfone
ECD	Electrochemical deposition	PET	Poly(ethylene terephthalate)
ESAVD	Electrostatic spray assisted vapor deposition	PFDA	Poly(1,1,2,2-perfluorodecyl acrylate)
G-PEMS	Graded proton exchange membranes	PIAM	Poly(isobutylene-alt-maleic anhydride)
HEMA	Hydroxyethyl methacrylate	PiCVD	Photoinitiated chemical vapor deposition
iCVD	Initiated chemical vapor deposition	PMMA	Poly(methyl methacrylate)
MB	Methylene blue	PP	Polypropylene
MD	Membrane distillation	PSf	Polysulfone
MF	Microfiltration	PST	Polystyrene
NF	Nanofiltration	PTFE	Polytetrafluoroethylene
N-PEMS	Normal proton exchange membranes	PVDF	Polyvinylidene fluoride
P	Pressure	RO	Reverse osmosis
		TFD	Thin film deposition
		UF	Ultrafiltration
		ZnO	Zinc oxide

physical properties. These coatings can impart a range of desirable properties, including suppressed adhesion of foulants, anti-biofilm/biocidal properties, and chemical resistance. However, it is also vital that the coatings can be applied without compromising other membrane performance criteria such as permeability and selectivity [9]. While TFD techniques have been quintessential across industries for centuries, application of these methods to polymeric membranes has thus far been limited due to harsh process parameters which can degrade the underlying membrane structure. New developments in the field of TFD have enabled these techniques to be applied to polymeric membranes without compromising performance. In this work, we review these recent developments and discuss the advantages and limitations of using TFD for water treatment membranes.

1.2. Alternative approaches for membrane surface modification

The surface properties desired for a water treatment membrane are dependent on the application and quality of the source water. Hydrophobic membrane materials lead to fouling issues in many filtration processes, including microfiltration (MF) and reverse osmosis (RO), as organics and biological matter are more likely to adhere to hydrophobic membranes [10–12], albeit with some exceptions [13]. Meanwhile, superhydrophobic membranes are desired in membrane distillation (MD), an emerging membrane technology for desalination and brine treatment, to prevent intrusion of water into the vapor-filled pores [11, 14]. Organic solvent nanofiltration (OSN), a membrane process for separating molecules in harsh organic solvents, despite being prone to higher fouling, applies hydrophobic membranes due to their better permeability for non-polar solvent [15,16].

Modification of membranes has been widely studied as a method to improve performance. Composite membranes are useful for maximizing as many desired properties as possible while minimizing the fabrication cost [17,18]. Approaches such as physical blending and graft polymerization have been employed for modifying membrane surfaces [19]. However, there are several drawbacks to these techniques. For instance, blending of hydrophilic and hydrophobic materials often affects the membrane structure [20]. Furthermore, the polymer matrix may encapsulate the blended materials, which then restricts their efficacy in modifying the surface properties. Post-fabrication modification is often a better option for effective surface modification [21–23], mainly because imparting the desired surface chemistry across the entire base

polymer can be expensive. Beginning with a low-cost base membrane and applying only a thin layer of the more expensive active material can significantly reduce costs [17].

Graft polymerization is one post-fabrication process which involves the covalent attachment of the modifying material to the base membrane via chemical reactions. To create these bonds, membranes require some method of pre-treatment to induce radicals, which may entail plasma modification, ultraviolet (UV) exposure, piranha treatment, ion beam, or γ -ray irradiation. Thin film deposition techniques have a unique advantage over grafting methods in that they apply to low surface energy polymer membranes, which often resist modification via covalent bonds [24]. Besides, some grafting techniques are not scalable, are difficult to fine-tune, and may result in a heterogeneous deposition that reduces membrane permeability [25,26]. Alternative techniques such as TFD that are efficient, scalable, and do not compromise the membrane performance could, therefore, present substantial improvements over traditional methods.

1.3. Background on membrane surface deposition techniques

Membrane surface deposition methods with appropriate modifying materials offer several opportunities for fine-tuning membrane surfaces while also preserving the underlying structure [27–29]. The addition of a thin layer can drastically alter the way a membrane or other substrate interacts with its environment [30]. Deposition of a thin layer alters the chemical and physical structure of the membrane surface to create changes in solute rejection [31], solvent flux [32], inorganic fouling properties [33], thermal resistances [34], chemical stabilities (e.g., acid or chlorine resistances) [35] or even antimicrobial properties [36]. Deposition techniques are an emerging alternative to the popular grafting/irradiation techniques of creating functionalized membranes [37] and can be more robust and permanent [38]. Vapor phase methods, in particular, prevent surface energy effects that may lead to nonhomogeneous coatings during wet phase depositions [39].

The basic steps of any deposition technique include: (i) synthesis of the deposition material, (ii) transport of the material to the substrate, and (iii) surface deposition and film growth [40]. Depositing 2-dimensional surface layers with a sub-micron thickness are usually referred to as TFD, whereas deposition of surface layers thicker than 1 μm are classified as coating [41,42]. TFD deals with the surface deposition of distinct atoms or molecules, while surface coating involves depositing

particles [41].

A variety of deposition techniques exist to controllably create a thin film on a substrate. The deposition techniques that have thus far been used for modification of polymeric membranes (and which are reviewed in the present work) are shown in Fig. 1. The choice of deposition technique will largely depend on the substrate and process requirements [40]. For example, some techniques such as thermal evaporation require high process temperatures that are unsuitable for some polymer materials. Thus, some of the criteria to consider include: limitations of the substrate (such as thermal and chemical stability), desired deposition rates, potential for scale-up, cost, and safety [43]. Even in the case that multiple processes can be used to deposit the same source material onto the same substrate, care should be taken in selecting the most optimal process(es), as the specific process will influence the final structure and properties of the coating [40,44]. Deposition techniques can be used to coat ultra-thin layers (as low as ~5 nm) [45]. These coatings may be conformal and coat the interior of membrane pores or non-conformal and only add a layer on the membrane's top surface. While many factors play a role in the variation of coating properties between deposition methods, the most important is the energy of the deposited molecules (called adatoms) upon arrival at the surface. For example, energies for physical vapor deposition (PVD) processes can range from tenths of an eV (thermal evaporation) to hundreds of eVs (sputtering) [40]. Other important factors include the way atoms are incorporated into the existing structure and how a deposited layer responds to the continued deposition of new layers. Many atomic deposition processes are non-equilibrium, meaning that the deposited materials may have significantly different properties from the source materials, thus enabling the creation of unique surface properties [42,43].

1.4. Status of research on thin film deposition on polymeric membranes

Initially, research on the deposition of thin films on polymeric membranes for water treatment applications was limited, as polymeric substrates are often not suitable for the conditions required in deposition reactors. For example, surface deposition processes generally operate at high temperatures and use high energy atoms, which in many cases can damage polymeric materials and cause membrane degradation [46,47]. Nonetheless, new methods have been developed to overcome such limitations. This includes, for instance, the initiated chemical vapor

deposition (iCVD) processes that can deposit materials at much lower temperatures [48,49], and magnetron assisted sputtering method, which can accelerate sputtered particles without substantial addition of thermal energy [40]. Consequently, a growing interest in applying TFD techniques for modifying polymer membranes has been observed recently.

A literature search on various deposition techniques has resulted in 30 journal articles on polymeric membrane deposition techniques prior to 2000, of which 26 articles focused on physical vapor deposition, 2 on CVD, and 2 on electrochemical & electrostatic spray. However, the last two decades have seen the advent of new deposition techniques and a substantial rise in publications in this area. This is reflected by the 760 journal articles published between 2000 and 2019 on emerging TFD techniques, as shown in Fig. 2. To create this figure, papers were classified according to the technique utilized. The more traditional coating techniques (e.g., dip-coating, etc.) were excluded from the counts in Fig. 2. Sputtering, thermal evaporation, and CVD have been the most popular deposition techniques for modifying polymeric membrane surfaces thus far, while electrochemical deposition and atomic layer deposition (ALD) have been emerging more recently.

In this work, we review recent developments in the field of polymeric

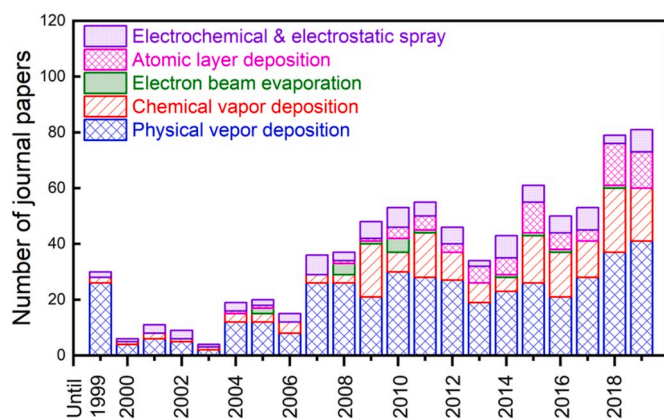


Fig. 2. Chronological literature mapping of the use of TFD techniques for modifying polymeric membranes in academic research (retrieved from Scopus).

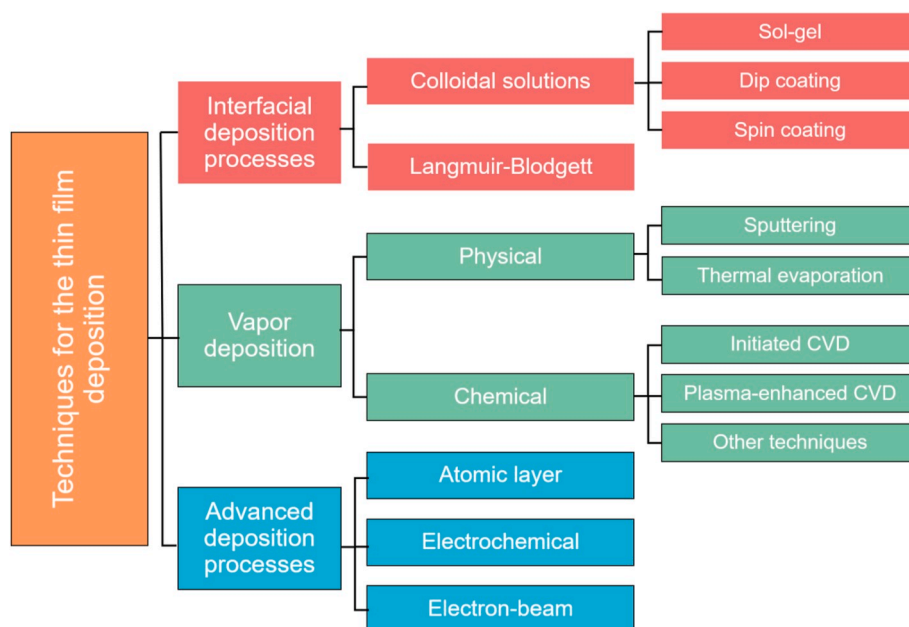


Fig. 1. Classification of thin film deposition techniques applied for modifying polymeric membranes.

membrane modification via the TFD techniques outlined in Fig. 1. This review includes an overview of TFD process fundamentals and how these processes can be modified or improved for creating membranes with desirable properties. We focus on water treatment applications for modified membranes, including microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), and membrane distillation (MD). However, the techniques and strategies reviewed here have application across a large number of industries which rely on membrane separation processes. Finally, we discuss future directions in this area and highlight some of the opportunities that TFD can enable.

2. Methods

The data presented in Fig. 2 were gathered via the Scopus search tool. Each deposition technique was searched along with the term “polymer membranes” by using the “AND” feature in the advanced search options. Search terms were put in double-quotes to restrict the search result to the specific phrases. The search field was specified to search only abstracts, title, keywords; and was restricted to only peer-reviewed journal articles.

3. Key terminologies

Since several different definitions, equations, and symbols are used throughout literature to describe membrane properties (sometimes interchangeably), some key terminologies used throughout this article to refer to membrane performance and properties are briefly defined.

Contact angle (CA) quantifies the wettability of a membrane surface by a specific liquid (assumed water if not specified). It is defined as the angle between the liquid-vapor interface and the membrane surface of a liquid droplet placed on the membrane surface.

Flux refers to the flow rate of the permeate stream through a unit membrane area.

Permeability is the driving force (e.g., pressure) normalized flux.

Selectivity is conveniently expressed in terms of the retention (R) of a particulate solute in the feed stream, in the case of dilute aqueous solutions. The value of R can vary from 0% (complete transport of solute and solvent through the membrane) to 100% (complete retention of the solute).

In the case of mixtures of organic liquids and gas mixtures, selectivity is usually expressed in terms of separation factor α . For a mixture of components A and B, the selectivity factor $\alpha_{A/B}$ is defined in Eq. (1), as:

$$\alpha_{A/B} = \frac{Y_A/Y_B}{X_A/X_B} \quad (1)$$

where Y_A and Y_B are the concentration of components A and B in the permeate, while X_A and X_B are the concentration of components A and B in the feed.

4. Interfacial coating techniques

Interfacial coating techniques make use of an interface between different phases, such as the air-water interface, to assist with the deposition of regular films on surfaces. This is enabled by the ability of interfaces to align particles or molecules into single layers, often called monolayers. The subsequent sections highlight different methods of interfacial deposition techniques, including Langmuir-Blodgett, sol-gel methods, spin-coating, and dip-coating.

4.1. Langmuir-Blodgett method

4.1.1. Process overview

Langmuir-Blodgett (LB) techniques are used to deposit successive series of monolayers by taking advantage of the air-water interface. Layers formed via this technique are highly crystalline and composed of

amphiphilic macromolecules [50]. The deposition is enabled by surfactants, which spontaneously spread into a monolayer when placed at the air-water interface. LB monolayers are typically characterized using pressure-area curves to determine the correct amount of surfactant [51]. A solid or polymeric substrate can then be either raised or lowered into the solution so that it penetrates the surfactant-laden interface and entrains the monolayer (Fig. 3). The rate of substrate movement must be low enough to allow the water (or another solvent) to drain so that the monolayer can move onto the substrate without entraining solvent [50]. Multiple layers of the same or different, macromolecules can be formed via successive dipping processes, and alternation of molecule type can result in unique material properties [52].

LB films have found widespread use in coating technology due to their simplicity, repeatability, and predictability of the structures of deposited films. Some applications include sensors and the creation of biological membranes [53–55]. Because only amphiphilic entities are suitable for LB coating, the materials for deposition are limited; although nanoparticles attached to hydrophobic tails expand the number of applications and properties [56]. Films can be very thin (with a thickness of just one constituent molecule), and often range from several to tens of nanometers. However, adhesion/delamination is a concern. The deposition conformality is highly influenced by interfacial effects, including surface energy of the substrate and pore geometry of the membranes coated. While these films are well-bound to themselves, covalent bonding to the substrate may be lacking, which can lead to holes in the coating layer [57,58].

4.1.2. Applications of LB

The LB method is among the oldest forms of thin-film deposition used for polymeric membrane modification, with reports first demonstrating improved performance of surfactant-treated membranes in the 1980s [59,60]. Like other thin-film chemistries, nonionic surfactants can increase membrane resistance to the flow of solvents. LB layers can also reduce the binding of foulants due to surface smoothness, dense surface packing, and the amphiphilic chemistries. The stability of LB layers on polymeric membranes is heavily dependent on the chemical properties of the surfactant and the base polymer. Strong secondary interactions are sometimes sufficient to resist delamination of LB films from membranes despite the lack of covalent bonding [61].

LB techniques have been used to coat PM30 UF membranes (Amicon Corp.) with a variety of non-ionic surfactants [62]. The deposition reduced the surface roughness and the number of visible pores; and was able to increase the CA from 60 to 91° via deposition of stearic acid. These effects increased with the increasing number of deposition layers. The modified hydrophobic membrane exhibited larger amounts of organic fouling, yet still achieved 12% better flux than the virgin membrane. Despite the larger amount of protein deposition, the flux improvement by the stearic acid-treated surface can be attributed to the smooth and homogeneous surface. However, further increases in the number of LB layers caused a correlated linear decrease in water permeability due to an associated reduction in porosity. The authors, therefore, recommend the use of a single monolayer coating for best performance [62]. This highlights that increasing film thickness does not always lead to associated performance improvements, and that thin films are sufficient to alter membrane properties.

Anionic surfactants have also been successfully deposited using LB techniques to reduce fouling during UF of proteins [63]. The reduced fouling was attributed to the modified electrostatic interactions between the small anionic surfactant groups on the membrane surface and the protein in the feed. Another investigation showed improved flux by a polypropylene membrane, which was altered by plasma treatment followed by deposition of a polyelectrolyte layer via LB deposition [64]. This enhancement was attributed to the partial degradation of the membrane structure and the introduction of hydrophilic groups on the membrane surface during plasma treatment. However, addition of the LB layer significantly reduced the flux as compared to the membrane

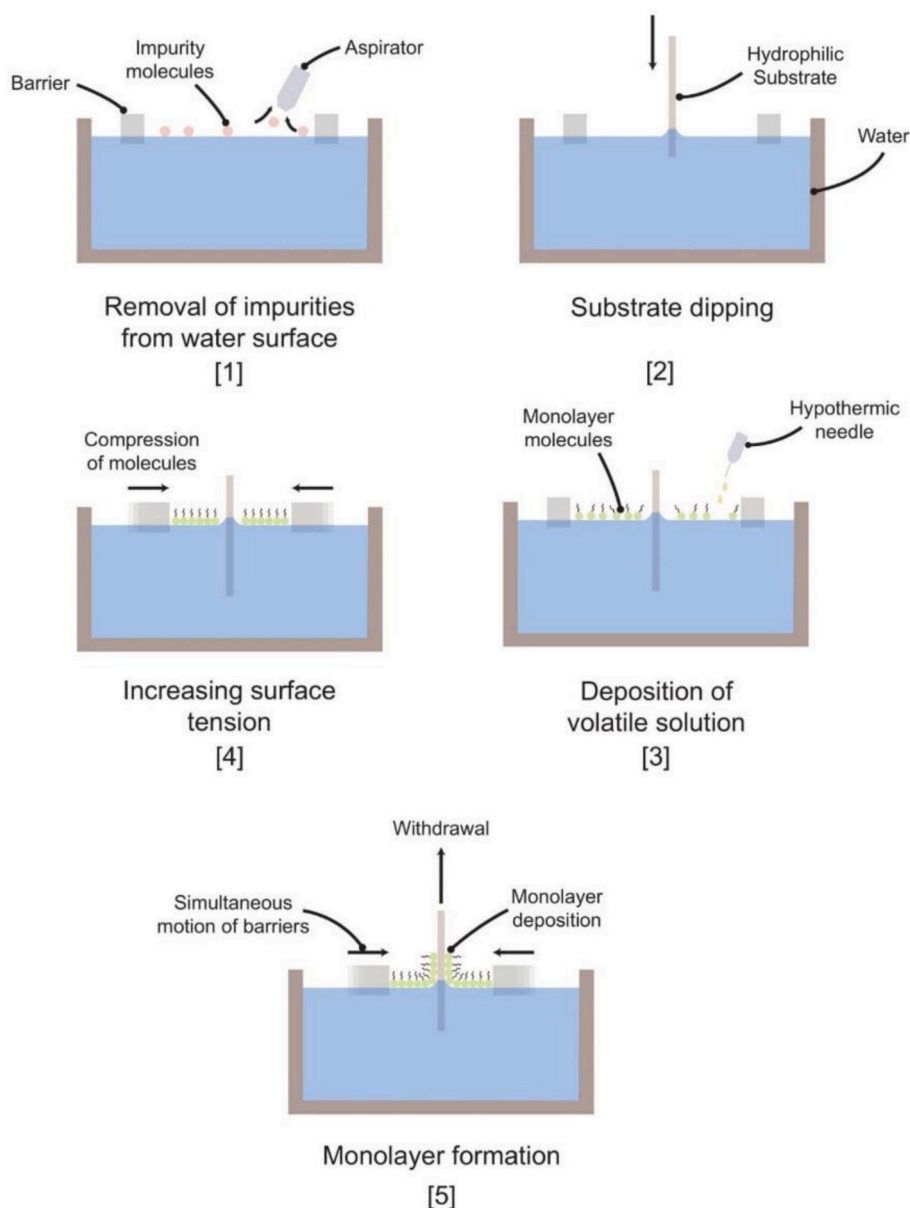


Fig. 3. Schematic showing monolayer deposition of a surfactant film using the Langmuir-Blodgett method (inspired by Ref. [50]).

treated by plasma alone, as the layer blocked the largest pores and decreased the surface hydrophilicity. Despite this disadvantage, the plasma-treated membrane with the LB layer exhibited low deposition of protein due to electrostatic repulsion between the protein and the membrane surface. Interestingly, LB deposition of a second polyelectrolyte layer enabled recovery of the original flux due to a stretched conformation of the polyacrylic acid chain which increased the pore diameter. The flux declined with additional polyelectrolyte layers because of decreasing pore diameters and eventual pore plugging [64], making two LB layers the ideal number for maximizing desired properties. Another study found that layering of alternating polyelectrolytes can allow for selective ion transport in a nanofiltration membrane [65]. Porous alumina coated with 5 layers of poly(styrene sulfonate)/poly(allylamine hydrochloride) exhibited a water flux of 42–83 LMH at 4.8 bar with a 96% rejection of $MgSO_4$. It was also found that the rejection of divalent ion increased when the membrane surface had a similar charge.

Although LB methods generally involve the deposition of amphiphilic molecules, the latter can be functionalized with nanoparticles at their hydrophobic tails. This technique vastly increases the possible

applications for LB methods and allows facile deposition of monolayers of metallic particles [66]. For example, TiO_2 nanoparticles can be deposited on membranes to impart bactericidal properties. Another creative use of LB methods is to directly deposit carbon nanotubes onto alumina membranes [67]. Such a technique could also be applied to polymeric membranes by dispersing the carbon nanotubes in an amphiphilic polymer matrix and spreading it on the water surface followed by horizontal lifting or vertical dipping of the membrane [68,69].

In addition to surface modification, LB methods have also been used to produce membranes assembled on top of porous base layers. LB methods are ideal for this application due to their uniformity that allows for the creation of uniform pore properties, which are associated with high water permeability and well-defined rejection coefficients [70]. A filtration membrane was developed by depositing a non-cross linked LB monolayer on a pre-formed UF membrane, with cross-linking performed after [70]. Another investigation started with polypropylene (PP) and polyethylene terephthalate (PETP) base UF membranes, then adding polydiacetylene (PDA) layers via LB deposition for use in reverse osmosis [71]. The researchers found that more hydrophobic base

materials resulted in a better deposition, and that polymerization of the monolayer was vital for membrane stability.

Overall, LB techniques are cost-effective processes that can effectively apply fairly consistent monolayers, which allows for functionally useful coatings that minimally block pores. However, these approaches require amphiphilic molecules, making them ideal for biologically relevant materials, but somewhat limited in material choices otherwise. Notably, they have the potential for multilayer designs and nano-engineering. However, such films don't necessarily covalently bond to substrates, making durability and delamination a concern.

4.2. Coating with colloidal solutions

Processes applying the deposition of colloidal solutions containing reactants include the sol-gel method, dip coating, and spin coating. These processes can be used to create unique material coatings such as metal oxides, although their ability to impart thin conformal layers on membranes is relatively limited. Agglomeration (also called gelling) limits the use of the sol-gel method, and the surface roughness of membranes impairs coating uniformity. Thus, though colloidal coating techniques are used for a wide variety of materials coatings, they are generally unsuitable for membranes given their tendency to form thick coatings and block pores [72]. Such coatings tend to have low porosity. Nevertheless, because these processes require lower process energy and costs than the thin film deposition techniques reviewed in sections 5-8, they can be advantageous for situations where the base material is sensitive or where the coating material requires solution-based reactions to form. This niche is especially applicable to applying thin layers that are catalytic (e.g., TiO_2) or have semiconductor properties.

4.2.1. Sol-gel

Sol-gel processes are a set of material fabrication techniques where a solution (*sol*) containing colloidal monomers becomes *gel-like* as the monomers form a network [73]. They can create metal oxide coatings and nanostructures (e.g., SiO_2 , TiO_2) and are capable of doing so at far lower temperatures than alternative techniques, making these materials compatible with membrane materials such as polymers [74].

Sol-gel coating processes have several steps, some of which may be simultaneous. These steps are: 1) preparation of a colloidal solution that functions as the precursor for forming gel of either polymer networks or discrete particles (e.g., with mixing, causing hydrolysis), 2) deposition of a thin film, 3) networking of the colloids (e.g., via condensation), 4) evaporation of the solution, and often 5) a higher temperature step to increase networking and enhance mechanical strength (e.g., via grain growth) [75]. When coating polymeric membranes, the final heat treatment must be performed at a temperature that will limit polymer degradation.

Applications of the sol-gel technique for membrane coatings include developing hybrid metal oxide-polymer membranes, coating photocatalytic particles (e.g., TiO_2) on the surface and within the membrane pores [76], imparting unique membrane properties (e.g., electrical, optical, superhydrophobic), creating chemical-resistant layers [77], enhancing the elasticity of metal oxide coating materials [78] and creating ceramic or glassy membrane layers themselves. For instance, Chakraborty et al. compared spray-, vacuum- and sol-gel- techniques for coating TiO_2 on PES and polyvinyl-chloride/polyacrylonitrile hollow fiber UF membranes to impart photocatalytic properties for degradation of organic components in wastewater [79]. When compared to the other two techniques, the sol-gel coating was able to impart the TiO_2 without significant reductions in permeability. When compared to pristine membranes, sol-gel coated membranes achieved a degradation of 30+% and 40+% of methylene blue and chlorhexidine digluconate, respectively.

In another study, Song et al. utilized the sol-gel coating for functionalizing PVDF membrane surface with uniform zwitterionic organosilica xerogel [80]. The stability of the coating was tested via ultrasonic

and chemical cleaning with sodium hypochlorite solution. No morphological changes were found between coatings before and after the tests, suggesting a strong adhesion and good integrity of the coating on the membrane surface. Organosilica coated membrane showed excellent anti-bioadhesion capability in bacterial attachment tests, thanks to the smooth, zwitterionic surface. Moreover, modified membranes showed better flux recovery rates of 68% and 91% in the 3-cycle filtration with protein and polysaccharide.

Sol-gel processes can also allow for the design of depositing particle size, porosity, layer thickness, and particle separation. Precursors are typically metal alkoxides, but may also include metal acetates, nitrates, sulfates, and chlorides [81]. Such coatings can help improve membrane properties like thermal stability and hydrophobicity (e.g., with TiO_2 -PVDF membranes [22]). They are also very common in catalytic membrane processes and other applications relevant to semiconductors. Important process parameters include the concentration of the precursor, solvent and additive choices, solution aging time, substrate morphology, and heating steps [74]. Because sol-gel processes cannot impart sufficiently thin films compared to other techniques, sol-gel techniques should be used for applications in which thin films are not mandatory.

4.2.2. Dip coating

The requirement of a colloidal suspension of the precursors (e.g., through prolonged stirring in solution, often at elevated temperature) limits the sol-gel deposition techniques, thus requiring other forms of coating to form thin films [75]. Dip coating is an impressively versatile technique for coating surfaces, with high flexibility with regards to what can be coated but with the reduced ability for minimizing coating thickness. As shown in Fig. 4, dip coating involves immersing the substrate in a solution which contains the precursors, then withdrawing it at a constant speed [82]. Film formation takes place due to a combination of hydrodynamic and evaporative effects in the solution [75]. The process can be qualitatively explained as follows: 1) a hydrodynamic boundary layer is formed as the substrate is withdrawn, which separates the entrained fluid (eventually participating in film formation) from the rest of the bath, 2) volatile solvent is evaporated from the entrained fluid film resulting in the deposition of materials on the substrate, and 3) heat treatment can be applied to remove the solvent completely and modify the coating characteristics to achieve the required properties [83]. As with the sol-gel technique, the final heat treatment during coating on the polymer membranes has to be performed at a temperature which avoids degrading the polymer.

Coating thickness is mainly governed by process parameters such as withdrawal speed, solution viscosity, concentration, and the evaporation rate. Several forces are at play in this process, including viscous drag, inertial drag, surface tension, and gravity [84]. The initial precursor concentration has the largest influence on final membrane porosity in dip coating processes [85].

Dip coating processes are susceptible to defects caused by contamination, aggregation of precursors, microscopic air bubbles in the solution, and irregularities in the supporting substrate surface [86,87]. Because of this, dip coating is often carried out in a cleanroom (controlled environment) and is repeated several times to minimize the defects. Substrate selection also plays a major role, and it is optimal to have chemical compatibility and an identical coefficient of thermal expansion for the membrane and substrate [88]. Dip coating can coat membranes by adding layers with 100 nm to 100 μm thickness and is suitable for creating additional layers with pore size in the micropore (1–2 nm), mesopore (2–50 nm), and part of the macropore range (50 nm–5 μm) [88]. But in the majority of cases, the minimum thickness of the film should be of the same order as the maximum surface roughness of the substrate to minimize defects [89,90]. Notably, in dip coating (and spin coating), the coating thicknesses are generally much larger than the pore sizes of the dipped material, so the added layer must be inherently porous, or porosity must be created within the dipped layer.

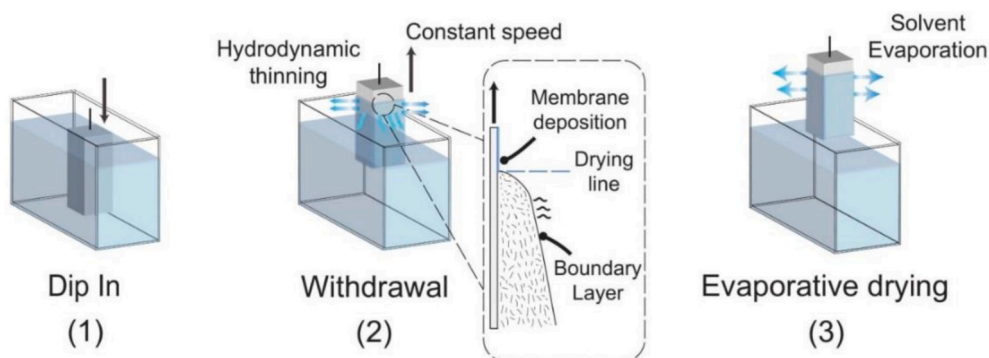


Fig. 4. Schematic of the dip coating process in which a substrate is immersed in a suitable precursor solution and then withdrawn at a constant speed to leave a regular film after solvent has evaporated.

Techniques for creating such porosity include phase separation, crystallization [91], and etching.

Like other deposition processes, dip-coating can be used to improve membrane surface energy and roughness for decreased fouling. Yu et al. dip-coated polyamide RO membranes with the natural polymer sericin followed by *in situ* cross-linking [92]. Results showed that coating enhanced the surface hydrophilicity, increased surface negative charge, and smoothed surface morphology. Fouling tests with bovine serum albumin (BSA) aqueous solution showed a high fouling resistance and low flux decline of the coated membrane. In another study, PP hollow fiber membrane was modified with a rough PP layer via a 2-step dip-coating process (nonsolvent coating followed by PP coating) to create a superhydrophobic membrane with a CA of $149.0^{\circ} \pm 2.3^{\circ}$ [93]. Increasing the drying temperature from 25 to 70 °C resulted in a reduced overall crystallinity and a decreased water CA from $139.7 \pm 2.6^{\circ}$ to $125.1 \pm 2.5^{\circ}$. Increasing the concentration of the PP solution increased the coating layer thickness and decreased membrane porosities. For instance, when the PP solution concentration was increased from 10 to 35 mg/mL, membrane porosities decreased from 35 to 24%. Despite improved hydrophobicity, the pristine PP membrane exhibited a higher flux than the PP-modified membrane for separation of a water-in-oil emulsion due to the increased thickness and reduced porosity of the modified membrane. Therefore, capitalizing on the increased contact angle would require a thin film coating with minimal influence on the porosities. In another study, authors prepared a hierarchically structured, low surface energy, superhydrophobic coating with a static water CA of $155.7^{\circ} \pm 1.4^{\circ}$ and a CA hysteresis of $5.5^{\circ} \pm 0.4^{\circ}$ [94]. Dip coating followed by non-solvent induced phase separation was employed to coat biodegradable PLLA polymer and SiO₂ nanoparticles on a PU sponge, which was then tested in water-oil separation. The microstructures of PLLA along with the hydrophobic SiO₂ nanoparticles increased the surface roughness and enhanced the hydrophobicity. Pristine sponge absorbed both the water and oil, whereas the modified sponge retained its high separation efficiency (>99%) even after 10 cycles.

The dip coating process has excellent homogeneity of layers and can create uniquely smooth coatings, evening out roughness with successive coatings [88]. The technique is common for ceramic membrane fabrication, and also for dispersing particles (not films). The process has several drawbacks: i) multiple coating and baking steps can be uneconomical, ii) thickness cannot be monitored in-situ but can only be measured after baking the coated layer, iii) thicker layers and dense coated structures risk greatly impaired permeability, and iv) metal films are difficult to be produced by this method, and it is usually limited to oxide films [181,184].

4.2.3. Spin coating

Spin coating is a widely used method for depositing uniform films over flat substrates and provides excellent control over their thickness [95]. The process capabilities, coating properties, and potential

applications are very similar to those of dip coating, except that the gravitational force of dip coating is replaced by centripetal force in spin coating. Control of rotational acceleration enables greater control of the final film thickness. Both methods rely on a fluid dynamic balance between a body force (gravity or centripetal) with viscous and surface tension forces.

Spin coating can coat membranes with thickness in the range of 70–500 nm and have a pore size continuously varying from 4 to 200 nm [96,97]. As illustrated in Fig. 5, spin coating involves four main steps: 1) deposition of solution at the center of the substrate, 2) spin up in which the substrate is rotated at a certain speed to get a near-uniform distribution of sol, 3) spin off where the speed is further increased so that excess liquid drains off from the side as droplets (this speed is determined according to the desired film thickness), and 4) evaporation: volatile solvent gets evaporated from the solution leaving behind a polymer film [75].

Like in dip coating, the film thickness is mainly governed by the solvent evaporation rate, viscosity, and concentration of the solution [98]; with spinning speed adding an additional variable. Film thickness varies inversely with the square root of rotational velocity. The film thinning can be understood as occurring in two stages [99]:

- I During the spin off process, centrifugal forces on the liquid result in a radial outflow and subsequent thinning of the deposition. As the thickness decreases, the solution becomes enriched in non-volatile solute, which increases its viscosity, countering the centrifugal force.
- II When the liquid is no longer flowing radially, solvent evaporation becomes the only means for thinning. The choice of solvent is thus important as differences in vapor pressure of solvent will result in different rates of evaporation.

The input parameters can be extremely variable and thus provide a wide range of coating thicknesses for the same material; for instance in a study where the polymer concentration in Toluene was varied (a PS and PMMA combination) from 0.001 to 0.15 w/w, viscosity had an exponential relationship, varying from 7×10^{-7} to 5×10^{-5} m²/s. By varying concentration and spin time from 0 to 7 s, coating height ranged from a few nm to >8 μm [100]. Rotation rate was varied less (1000-300 rpm with a 5 cm diameter).

Membrane characteristics are significantly affected by process parameters during spin-coating. At lower spin velocities, the films have a non-uniform thickness distribution, whereas, at higher velocities, there is a greater volumetric loss of the precursor [101]. Cracking and defects are a risk caused by stresses (centripetal, viscous, thermal, etc.) from preparation [96] as well as rapid evaporation rates, which can cause uneven fluid concentrations [101]. Deposition of continuous thin films on porous substrates requires solutions to issues such as pore bridging and penetration of polymer into the pores [102]. Coating parameters (thickness, speed, etc.) may need iteration to minimize such concerns

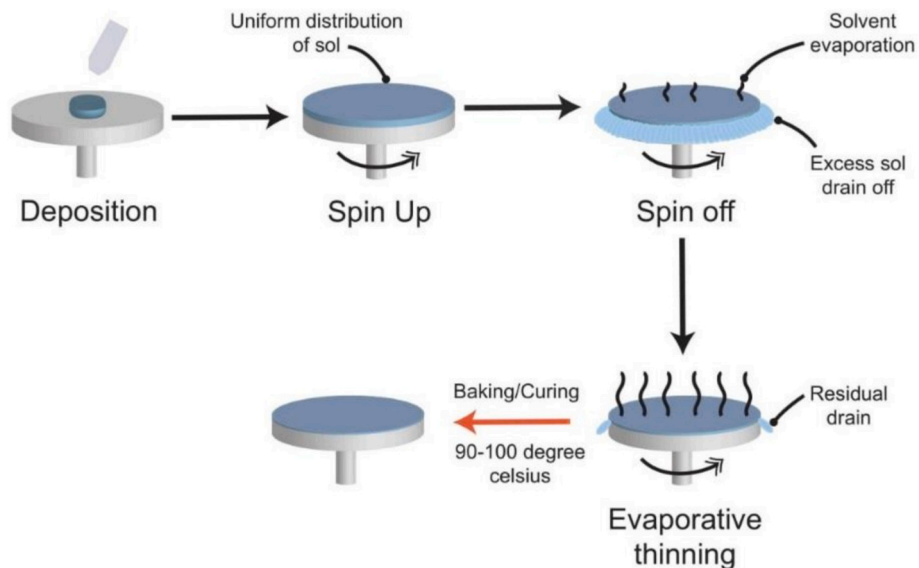


Fig. 5. Schematic illustration of a typical spin coating process in which deposition solution is rotated at a controlled rate to achieve a desired film thickness before the solution is cured to leave a solid film on the substrate (inspired by Ref. [75]).

and the resulting defects.

Forced convection may enhance solvent evaporation, so high-speed air streams are often used to speed up spin-coating processes. Because of the geometry, spin coating has challenges with substrates that are cylindrical (e.g., hollow fibers), have complex shapes, have depressions, or are not axisymmetric [103]. Complexities arise with shear thinning (non-Newtonian) fluids to ensure uniform thickness [104]. Overall,

creating very thin layers is often more challenging in dip and spin coating than in other processes. Because of these limitations, dip and spin thin-film coating applications to membranes are usually limited to processes that can't be done with other techniques, such as the sol-gel coating of metal oxides like TiO_2 and ceramics like $\alpha\text{-Al}_2\text{O}_3$ on polymeric membranes [105]. These coatings often have lower porosities (<36%) [88,91]. However, these methods have wide applications to

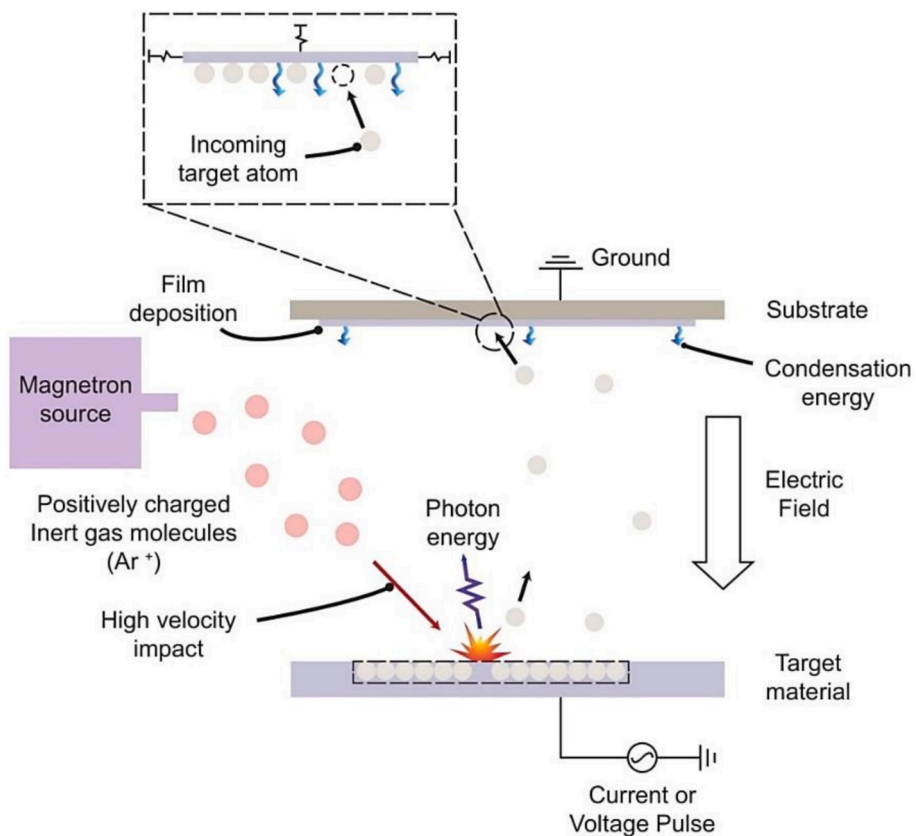


Fig. 6. A diagram illustrating the sputtering process. High energy ionized (and inert) gas (left) bombards the sputtering target (bottom) to create a spray, driven by an electric field. This sputtered material then condenses on the substrate (top) to form the thin film (inspired by Refs. [111]).

nanocomposite membranes, including depositing photocatalytic particles, graphene, graphene oxide, and carbon nanotube on membranes, which are reviewed extensively elsewhere [106].

5. Physical vapor deposition

Physical vapor deposition (PVD) was first developed in the 1960s and refers to any method involving physical deposition of material via the vapor phase onto a substrate to form a thin film coating. In PVD, the source material is converted into the vapor phase by evaporation, sputtering, or through a carrier gas/plasma (i.e., ion plating) [40]. Within these three main categories of PVD, several hybrid processes and variations exist. Some of the historically common applications for PVD include deposition of electrically conductive films [107] or corrosion-resistant coatings [108]. PVD is widely used because of its versatility in terms of the types of coatings that can be applied as well as the variability of substrates that can be coated. The subsequent subsections highlight some of the most common methods applicable to polymeric membranes and how these techniques have been used for membrane alteration.

5.1. Sputtering

5.1.1. Process overview

Sputtering is a form of PVD that is perhaps the most versatile in the number of materials that can be deposited. In the sputtering process (Fig. 6), a liquid or solid coating material (known as the sputter target) is bombarded with fast-moving ionized gas particles [40]. The high kinetic energy of the gas is transferred to the target atoms, resulting in a microscopic spray that condenses onto a grounded substrate to form the surface coating [42]. The stability of a sputtered coating is highly dependent on the properties of the substrate [109]. Sputtering a coating onto an incompatible substrate will often lead to delamination, in which the thin film flakes off of the substrate. Process parameters such as the speed of the gas, distance of the substrate from the sputter target and temperature, will all alter the morphology of the final coating [110].

Parameters for controlling sputtering include gas pressure, temperature, the chemistry of the carrier gas, and cooling rate [48]. Sputtering growth results in slow deposition rates compared to other methods of PVD ($\sim 10^{-4}$ g/cm²s) [40]. Although slow deposition rates can be a limiting factor for industrial fabrication, they typically result in more uniform and controlled coatings. Since momentum transfer is the primary mechanism resulting in a deposition, the energy of target adatoms is generally high (1–100 eV) upon reaching the surface, which can significantly affect the film structure. Most importantly, sputtering processes do not require elevated temperatures at the substrate, allowing for the coating of polymeric membranes without modification or melting of the underlying structure [112]. For this reason, magnetron sputtering is often preferred for polymeric modification over other PVD methods [113]. However, investigations have also shown that the high energy of adatoms during the sputtering process has the potential to damage membrane structures [114]. The subsequent subsections highlight applications of sputtering in the surface modification of polymeric membranes.

5.1.2. Applications of sputtering in polymeric membrane modification

One application of sputtering technology is to create hydrophobic membranes for MD via the coating of hydrophilic polymers. For example, Pedram et al. [115] used argon plasma sputtering of polytetrafluoroethylene (PTFE) to create a fluorocarbon film on polyethersulfone (PES) membranes to increase the hydrophobicity of distillation membranes to a contact angle of 115° (up from $\sim 75^\circ$) [115]. The plasma power of the sputtering process was reported to control the functionality and CA of the surface, with higher CA's reported for higher energy sputtering. Thicker coatings were also generally correlated with increased CA. Interestingly, the relationship between the CA and coating

thickness was also dependent on the distance between the sputter target and substrate, with higher CA's occurring at lower thicknesses for an increased sputter distance. For example, a CA of 113° was reached at a thickness of 135 nm for a sputter distance of 10 cm, and the same angle was achieved at a thickness of 300 nm for a 5 cm sputter distance. This effect is due to the size, velocity, and orientation changes induced by altered sputter distance. The resulting MD membrane created by sputter coating of PTFE on PES exhibited a lower porosity compared to untreated membranes as a function of both the sputter parameters and thickness of the coatings [115]. Permeate flux decreased with increased coating depth, while the separation factor increased.

In another investigation, hydrophobic MD membranes were prepared via magnetron sputtering of PTFE on polyethylene terephthalate (PET) membranes [116], where membrane with one hydrophobic side was created. By applying the functional chemistry to only one side, the resulting material had the desired wettability without needing to functionalize the entire material. The sputtered membranes had a noticeably lower roughness (RMS decreased from 7.9 to 3.1 nm) and effective pore size (from 95 to 75 nm) after 25 min of deposition. A deposition time of 10 min was sufficient to increase the membrane CA from 65 to 115° and only decreased the effective pore diameter by 5 nm. Because the hydrophobic sputter coating was conformational (coated the inside of the pores), good resistance to water intrusion into the pores was achieved during MD [116]. However, the thicker coatings also decreased gas flow rates across the membrane.

A similar investigation applied sputtering to increase membrane hydrophobicity without modification of pore size [117]. A polypropylene (PP) membrane was sputter-coated with a thin film PTFE on one side to increase its hydrophobicity. The resulting membrane had a high CA associated with PTFE while using the far cheaper PP material for the bulk of the membrane [117]. The membrane CA increased by 26° to a final CA of 151°, which is higher than the CA of pure PTFE, likely due to an increase in RMS from 149 to 456 nm. The mass transfer rate for the treated membrane was approximately 70% higher than the untreated membrane, though both materials exhibited performance drops with exposure to solvent. The authors also note that their material may have performed better had the pore sizes been decreased in the coating process, as smaller pore sizes decrease solvent intrusion.

Another common use of magnetron sputtering in the modification of polymeric membranes is the creation of composite metal-polymer membranes that can improve either permeability or selectivity. These composite membranes have found two primary applications for water treatment. First, as with fuel cell membranes, sputtered coatings have been applied to improve species selectivity [38]. Second is the enhancement of anti-fouling or anti-microbial properties by sputtering of silver or other anti-microbial metals [118–121]. In some cases, selectivity and anti-fouling can be simultaneously enhanced using metal-polymer composites [31]. Metal-polymer hybrid membranes have previously been prepared for fuel cell applications to improve the selectivity of hydrogen [122]. Nafion (a membrane material used for selective hydrogen permeation) sputtered with Pd was able to increase the selectivity for hydrogen by reducing methanol permeability, but also decreased the permeation of hydrogen [123,124]. As with other sputtering effects, the reduced permeation increased with film thickness.

Metal-polymer composite membranes were also studied for food processing, with one investigation demonstrating that a palladium coating sputtered onto polyethyleneimine can increase the mass transfer of hydrogen [125]. Another investigation applied sputtering to create a thin film of carbon on a polysulfone (PS) membrane [38] using a sacrificial polyvinylpyrrolidone (PVP) layer for creating a more resilient RO membrane. Sputtering parameters were varied by altering the proportions of Ar, CH₄, and N₂ carrier gases, and it was reported that the presence of CH₄ was crucial for successful membrane modification. A 30 nm carbon-coated PS membrane sputtered in an Ar:N₂: CH₄ gas mixture was able to reject 96% of salt from a 0.2 wt% saline water, as compared to 70% rejection by a membrane prepared in the presence of only Ar and

N₂. These carbon-coated membranes were also able to reduce damage caused by chlorine radicals by reducing the nitrogen gas in the sputtering process. The authors concluded that such a membrane would be an improvement to those currently used in RO [38].

Another metal-polymer composite membrane prepared via reactive magnetron sputtering of TiO₂ on a cellulose acetate membrane demonstrated increased pollutant rejection in drinking water treatment [31]. Since TiO₂ is well-known for its anti-fouling and photocatalytic properties [126], polymer-TiO₂ composite membranes have the potential to fulfill the dual goal of fouling resistance and high pollutant rejection. Previous investigations have suggested that a surface coating of TiO₂ is more effective than the incorporation of TiO₂ nanoparticles within the polymer matrix [127]. In one study, a fouling-resistant composite membrane was prepared via room temperature sputtering with argon as a working gas under an O₂/N₂ atmosphere for 5–8 h. The best performing (i.e., highest flux) membrane was the one with the lowest deposition time and, therefore, the lowest film thickness [31]. The deposition of the TiO₂ layer decreased DI water flux from 650 to 250 L/m²h, but led to a better flux performance when *E. coli* – contaminated water was used due to inhibition of biofilm formation. While the membrane with the smallest TiO₂ film had the highest flux, it also exhibited the lowest amount of turbidity (NTU) reduction with a 45% rejection, while thicker coatings were able to achieve 80% rejections. Although the flux performance of the treated membrane was decreased compared to that of the native material at first, the addition of anti-fouling coating led to a better long-term performance, which is of clear importance across water treatment fields where fouling is often a limiting factor.

In another study, a TiO₂-sputtered PVDF MF membrane was prepared as a fouling-resistant membrane for membrane bioreactors in wastewater treatment [119]. The sputtered layer decreased the CA of the intrinsically hydrophobic PVDF polymer to improve biofouling prevention. Furthermore, the authors reported that the modified membrane took twice as long to foul compared to the unmodified one [119]. This effect is likely related to TiO₂'s well-established anti-fouling properties [128]. TiO₂-polymer composite membranes have a secondary benefit in that the photocatalytic properties of TiO₂ may allow for the simultaneous catalytic degradation of contaminants in water [126]. Similar sputtering techniques can be used for silver deposition, which also has anti-microbial properties, though silver coatings are likely more cost-prohibitive than titanium [118]. TiO₂ films have also been successfully applied via reactive sputtering to increase the CA and reduce biofouling for polydimethylsiloxane (PDMS) surfaces [129].

5.2. Thermal evaporation

5.2.1. Process overview

Thermal evaporation is one of the most common methods of PVD due to its simplicity. In this process, the coating material (known as source) is heated under vacuum to induce evaporation [40]. Vaporized particles move towards the substrate and are deposited as a thin coating. This is contrasted by sputter coating (section 4.1), in which deposition occurs due to the high energy bombardment of the target. Thermal evaporation processes are relatively fast when compared to other PVD methods (10⁻³ g/cm²s) but have several limitations. For example, the material can only be deposited where there is a straightforward path for the evaporated atoms to reach the surface, which means that coating can be challenging on complex surfaces such as membranes, as the pores will not be conformally coated [40]. Furthermore, the types of materials which can be deposited are limited as the source material must be volatile under the given operating conditions. One advantage of the process is that the energy of atoms is relatively low (0.1–0.5 eV) when compared to sputtering processes, which can be beneficial in reducing the damage of the substrate and/or to the growing thin film. Fig. 7 shows a schematic overview of the process.

Controlling the process parameters in thermal evaporation enables

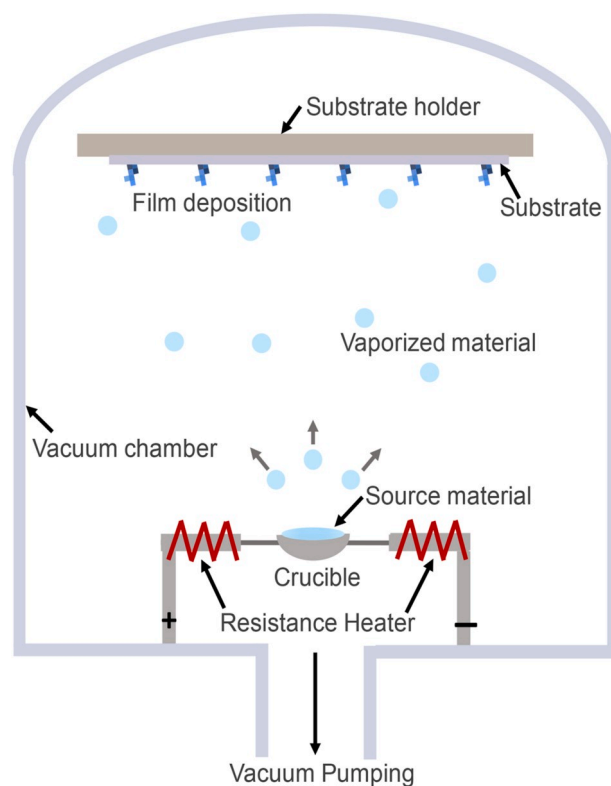


Fig. 7. Process overview of thermal evaporation deposition. The deposition material is heated for evaporation under vacuum and then condenses onto the cooler substrate (inspired by Refs. [40]).

fine-tuning of film deposition on a membrane material. For example, increasing the distance between the membrane and the source material improves uniformity across the substrate (i.e., the thickness of the coating will be the same across the area of the substrate) and decreases the film thickness. In an ideal evaporation chamber, the area of the source should be larger than or equal to the area of the substrate for uniform surface deposition. This ideal arrangement is not common in practice [42]. Thermal/vacuum evaporation PVD is most commonly used for the deposition of metallic thin films and is only compatible with the source material with low melting points [40]. Alloys and organic compounds are generally less suitable because the extreme process temperatures can lead to material degradation and loss of functionality [130].

5.2.2. Applications of thermal evaporation in polymeric membrane modification

Thermal deposition techniques have so far found only limited use in polymeric modification, mainly because of the high operating temperatures. The materials (both source and substrate, but especially the coating materials) suitable for thermal evaporative deposition have traditionally been limited to metals or other materials with high thermal resistance. Despite this limitation, thin metallic films have found application in membrane coatings due to their anti-biofouling nature and to the fact that evaporative deposition can be used to coat polymeric materials by minimizing heat degradation at the substrate material. For example, thermal PVD was used to create a thin film (50 nm) of copper on a polysulfone: poly(isobutylene-alt-maleic anhydride) (PSF: PIAM) composite membrane [131]. The polymeric membrane was situated far from the crucible to prevent heat decomposition and rotated for a more even coating [131]. The copper-coated membrane exhibited similar salt rejection levels as the uncoated membrane and performed better than the virgin membrane at resisting biofilm formation (Fig. 8). The initial flux of the coated membrane was slightly lower than the virgin one;

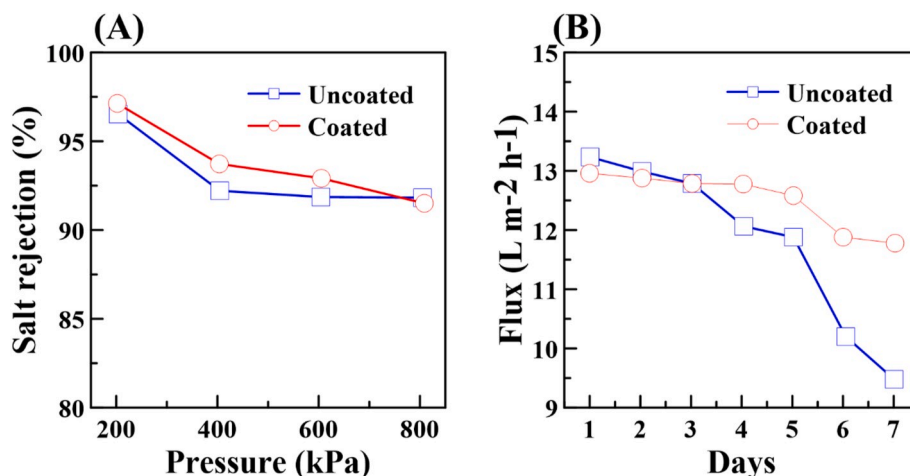


Fig. 8. (A) Salt rejection as a function of pressure for coated and uncoated membranes, and (B) Flux over time for both membranes (redrawn based on the data from Ref. [131]).

however, over seven days, the coated membrane flux decreased by 7% due to the fouling. In contrast, the virgin membrane had a 27% flux decline over the same period. It may also be possible to circumvent issues related to the temperature stability of polymeric membranes by evaporating the adatoms under high vacuum rather than under very high temperatures [132].

Another application for thin metallic films in water technology is the modification of the physical structure of membranes [133–135]. Padaki et al. [134] used the evaporative PVD of aluminum to transform a PSF MF membrane into a NF membrane by decreasing the pore size and thereby increasing the rejection. However, the membrane also exhibited an order of magnitude decrease in flux [134], which is expected given the reduction in pore size. The addition of aluminum also increased the CA of the resulting membrane from 66.8 to 89.5° [134], which would likely alter fouling on the material. The pore size modification in this study highlights another possible use for using PVD as a fabrication method.

Another creative use of thermal evaporation in the modification of polymeric membranes is the purposeful creation of conductance asymmetry (a directional gradient in electric properties) by deposition of a metal to resist ion transport in RO membranes [136]. Aluminum foil was evaporated in a thermal vacuum unit for deposition on a poly(ethylene terephthalate) (PET) membrane. The membrane was shielded until the foil had been completely melted to avoid thermal decomposition. The membrane pore diameters were decreased from 35 to 15 nm after 3 min of deposition, with a correlated 90% decrease in flux. The pore size and

flux were modulated by deposition time. The one-sided deposition of aluminum allowed for conduction asymmetry in saline solutions, which significantly increased the resistance to ion transport across the membrane [136].

5.3. Summary of PVD methods

Table 1 provides a summary of PVD techniques, along with the types of membranes that have been successfully modified. We find that sputtering is an ideal method for imparting anti-fouling properties by addition of either another polymer or of a metallic layer for applications where the modifier is not overly concerned with damage to the membrane material or pores. Sputtering is therefore not ideal for RO applications in which pore sizes and structures must be precisely controlled, but could find application in MF/NF for wastewater applications in which membrane durability suffers from biofouling. Sputtering can also be used for creation of superhydrophobic MD membranes, where pores are large enough that clogging is not of concern. Thermal evaporation is generally less suitable than sputtering for modification of water treatment membranes due to the limited coating materials and high process temperatures. However, like sputtering, there exist applications for coating of metallic layers for improved biofouling performance in MF and NF. Limitations to PVD techniques in membrane modification are primarily related to limitations on the types of materials that can be deposited, as well as to their potential for damage to the underlying structure.

Table 1
PVD techniques - advantages and disadvantages in membrane modification.

Modification technique	Membrane type and membrane material	Advantages(s)	Disadvantage(s)	Ref.
Sputtering	Type: MF, NF, MD	- Simple	- Potential damage to membranes by high-speed adatoms	[104–109, 111,121]
	Material: cellulose acetate, PES, PP, PE, PVDF	- Cost-effective	- Limitations on materials that can be sputtered	
	Applications: Changing wettability, fouling properties, porosity, imparting electrical conductivity, and improving resilience by adding physical layer	- Already scaled for industry - Low-temperature processing - Fast	- Potential for clogging pores and/or reducing porosity	
Thermal evaporation	Type: MF, NF	- Fast	- Uneven coverage	[8,123]
	Material: PS, PSF, PET (polymers with higher temperature resistance) Applications: Metal-polymer composites for anti-fouling properties, ion rejection, or altered pore sizes	- Lower adatom velocities improve deposition - Even coatings	- Coating may not enter pores - High operating temperatures - Strict limitations on deposited materials – must be volatile enough for evaporation	

6. Chemical vapor deposition

Like PVD processes, chemical vapor deposition (CVD) techniques carry a reactive vapor to a surface for deposition. CVD differs from PVD in that a chemical reaction occurs upon deposition at the substrate, chemically producing the desired coating. In these processes, reactive gas species are fed to the recipient substrate via a carrier gas, as shown in Fig. 9 [138].

All three deposition steps (material synthesis, transport, and nucleation) occur at the substrate interface in CVD [40], as shown in Fig. 8. CVD processes produce relatively thin and uniform coatings that can attain strong adherence to a substrate [139]. Key process control parameters include gas mixture composition, pressure, gas flow rate, substrate temperature, and materials for the reactive compound and substrate.

CVD processes have several advantages, including high coating uniformity [140], few defects in the coatings, thin coating capabilities, scalability to larger substrate materials, the ability to cross-link *in situ*, which enables novel chemistries, and strong chemical bonding to a substrate [45]. Film thicknesses can vary from 4 nm to >10 μm [141, 142], and pore sizes after coating can be as small as 5 nm [45]. Deposition kinetics and morphology are altered by thermodynamics (minimization of free energy/chemical potential), the extent of supersaturation of the source material in the vapor, nucleation of liquid on the substrate [143], and the grain size of deposited adatoms [144]. The properties of the resulting composite material can be limited by the degradation of substrates, film cracking, and stress of thin films.

High-temperature CVD reactions are generally not suitable for polymeric membrane coatings. For example, one synthesis of a hydrophobic carbon coating on a ceramic membrane substrate required an activation temperature of 1000 $^{\circ}\text{C}$ [145], precluding the use of this coating technique for polymeric membranes. Many CVD reactions using inorganic coatings are not compatible with polymeric membranes for this reason. Popular materials such as graphene and carbon nanotubes created with CVD are limited by temperature degradation as well. However, it is possible to operate CVD processes at lower temperature. The purpose of the high temperature in CVD is to initiate reaction; however, the reaction energy can be provided in other ways. Some methods to induce reaction at lower temperatures include CVD polymerization, initiated chemical vapor deposition, and plasma-enhanced chemical vapor deposition. The reduction in temperature of the latter processes is due to the use of non-heat controlled initiation, and/or because the deposited materials have lower activation energies (polymers or other organic compounds) [146].

One example of a low-temperature CVD process that does not rely on

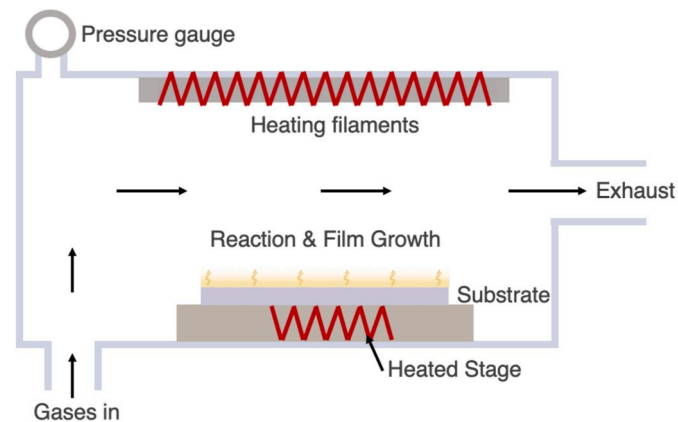


Fig. 9. Reaction chamber schematic for CVD, in which reactive species are carried by a carrier gas into the chamber, and the reaction is initiated (usually by heat) within the chamber so that a thin film grows by reaction at the substrate.

an advanced technique such as initiation or plasma is the addition of low-boiling point organics to modify polymeric membranes. For example, the deposition of hydrophobic organic silanes with a low boiling temperature (80 $^{\circ}\text{C}$) has been used to modify a polyvinylidene fluoride (PVDF) membrane for application in oil/water separations [147]. This membrane exhibited better selectivity for a kerosene/water separation than the native membrane. Applications of the advanced techniques with non-thermal initiation are discussed in subsequent sections.

6.1. Initiated CVD (iCVD)

6.1.1. Process overview

Initiated chemical vapor deposition differs from other CVD processes in that a chemical initiator is used to begin the polymerization process. This is in contrast to the typical CVD process, in which the reactions are initiated by heating. iCVD can form films from almost any monomer that can undergo free radical polymerization, given sufficient volatility [148]. The initiator disintegrates (either due to a high temperature or due to selection of a highly volatile initiator) inside the CVD reactor and forms radicals on the substrate, which then react with vaporized species [149]. iCVD reactions are catalyzed by the initiator and can, therefore, vastly increase the reaction rate while operating at lower temperatures [49]. Furthermore, techniques for solvent-free iCVD have been developed [150], eliminating concerns regarding compatibility between polymeric membranes and solvents. Grafted polymers from iCVD retain the functionality of the monomer precursors, allowing for predictability of surface coating performance that can be lacking in other deposition methods. Polymer films can be formed using iCVD for any monomeric species that are moderately volatile and undergoes free radical polymerization [47]. These processes can create even and very thin coatings on irregular surfaces [149]. The major limitation to iCVD techniques is how new the technique is compared to more established techniques such as sputtering, meaning that commercialization and scale-up of the process is still an ongoing effort.

6.1.2. Applications of iCVD in polymeric membrane modification

Initiated CVD deposition techniques have been successful at coating commercial RO membranes. For example, in a study by Matin et al. [151], iCVD was used to coat copolymers HEMA and PFDA on commercial polyamide RO membranes [151]. The two polymers were heated to 70 and 80 $^{\circ}\text{C}$, respectively, and the initiator was kept at room temperature. The vapors of the three species were controlled with mass flow controllers to optimize the final polymer composition. Membranes formed via this technique exhibited decreased flux decline under sodium alginate fouling conditions and generally exhibited a slow rate of fouling [152]. Similar techniques were also used to modify commercial RO membranes to reduce bacterial adhesion [48].

iCVD was also used to create highly hydrophobic membranes for use in MD [34,153,154]. Conformality (uniformity at minimal thickness) of iCVD coatings is critical to minimize pore-clogging [155] while attaining the desired properties of hydrophobicity and high liquid entry pressure for the MD application [34]. A study by Servi et al. [34] reported that nonconformal coatings (Fig. 10c) produced from iCVD had reduced permeability compared to thick uniform coatings (Fig. 10b) [34]. In contrast, thin conformal coatings exhibited no decrease in permeability (Fig. 10a). Furthermore, iCVD has proven to be an effective technique for making MD membranes superhydrophobic for improved antifouling. For example, a 96% reduction in adhered biofouling was achieved by coating a hydrophobic PVDF membrane with poly-(1H,1H,2H,2H-perfluoro-decyl acrylate) (PPFDA) [156]. The authors reported an exceptionally hydrophobic CA of 157 $^{\circ}$ and stated that their membrane could maintain air layers at the membrane-water interface [156]. Similar techniques have also been applied towards reducing wettability and roughness on PVDF hollow fiber membranes [157].

iCVD techniques were also demonstrated for applying fouling-

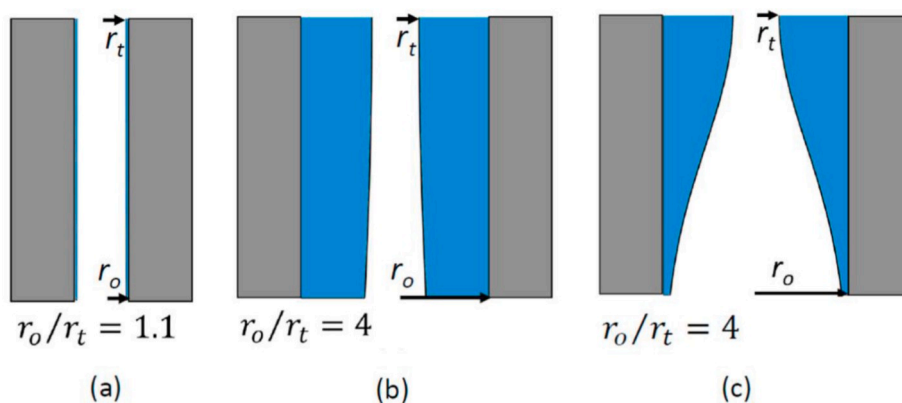


Fig. 10. iCVD coatings (blue) of a membrane pore (grey) with varied conformality and coating thickness. a) Conformal thin coating, b) Uniform thick coating, and c) Nonconformal coating with a narrow opening. Here, r_t is the radius of the coating at the pore entrance, and r_o is the substrate pore thickness (obtained from Refs. [34]). (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

resistant zwitterionic coatings on RO membranes [158]. In this application, the zwitterionic coating was reported not to impair salt rejection and successfully reduced fouling, though thicker (100 nm) coatings did reduce permeation [158]. Such a strategy was also successfully applied for creating a roughness-independent superoleophobic coating on an open mesh (700 μm) to separate oil and water [159]. Oleophobicity relies on the strong electrostatic interaction between the zwitterionic surface and molecules. The surface CA of oil (1,2-dichloroethane) and water reached nearly 180° , and the authors report improved separation by an order of magnitude [159].

In addition to using iCVD to coat pre-formed membranes, methods were also developed to fabricate membranes using iCVD polymerization reactions [45,148,160–162]. iCVD has been used to produce grafted polymeric layers over a nanoparticle template in a colloidal lithography process [160]. In colloidal lithography, spherical colloidal particles are layered on the substrate and treated with oxygen plasma to create hydroxyl groups for bonding polymer deposits. These groups enable consistent structure across multiple layers of deposited polymer. Membranes synthesized via this process are free of wetting defects, are strongly adhered to the underlying substrate, and are chemically robust. Through colloidal lithography, pore sizes are highly controllable, with a minimum size of 25 nm [160].

Intrinsically hydrophobic membranes composed of fluorinated polymers have also been synthesized with iCVD using a porous track-etched polycarbonate substrate [45]. Such track-etched substrates allow for fast and scalable fabrication and can produce tiny pores (down to 5 nm diameter) of cylindrical morphology and narrow pore size distributions. This technique is particularly amenable to hydrophobic coatings with selectivity for small molecules [163], with reported selectivity as high as 234:1 (number of desired molecules transported to the number of undesired molecules transported) for molecules of similar size but different polarity [45]. In another study, polymer deposition using iCVD over a fabric membrane support was used to create a uniform membrane surface for selective transport of chromium, which resulted in a maximum transport of 81% for Cr(VI) ions [148]. A completely dry iCVD process without the use of a support has also been recently demonstrated to be useful in the fabrication of membranes with tunable pore sizes [162].

6.2. Plasma-enhanced CVD

6.2.1. Process overview

The most-applied CVD technique for surface modification of polymers is plasma-enhanced CVD (PECVD), also referred to as plasma deposition or plasma polymerization [164]. In PECVD, the free radicals of the plasma act as the initiator rather than temperature or a chemical

initiator. The plasma is a mixture of normal gas particles, radicals, ions, and electrons formed when inert gas is exposed to a strong electric potential, causing high electrical conductivity. Plasma can be near-equilibrium (high-temperature plasma) or in non-equilibrium (glow discharge, also called low-pressure plasma, or “cold” plasma) [40,165]. In PECVD, plasma (most commonly glow discharge) is used to enhance deposition rates, which allows for lower substrate temperatures [165]. Besides, plasma can help normalize thin film growth. The high energy plasma bombards the growing deposit, which breaks the bonds and creates active sites for further growth [40]. This method is ideal when a highly cross-linked film is desired as a barrier coating, but maybe less ideal when a more controlled process is desired. Decreasing the energy of the plasma can help reduce breakages and defects [166].

The gentleness allowed by PECVD makes it one of the universal approaches to coating fabrics [167], and it should therefore also be well-suited for polymeric membranes. Inductively coupled plasma (in which plasma is produced by electromagnetic induction) deposition can further decrease damage to the growing film, as the high-electron density plasma achieves similar results at lower temperatures than regular PECVD [168].

While there are many benefits to using PECVD, care should be taken in properly cleaning the substrate before coating, as impurities at the polymer substrate can significantly influence the properties of the coating [40]. The use of plasma will create a film with chemical and physical properties distinct from polymeric thin films grown without the use of a plasma [40]. In addition to other CVD process parameters, the reactor power generating the plasma will also influence the final properties of plasma-deposited polymer films. Plasma polymerization differs from regular polymerization processes because of the high energetics of the radicals involved in the reactions. While regular polymerizations show repeating structural units, plasma polymerizations are better described as networks of homologous chemical groups [169].

6.2.2. Applications of PECVD in polymeric membrane modification

Like iCVD, there are a variety of possible applications for PECVD methods in polymeric membrane fabrication. For instance, PECVD (via O_2/Ar plasma) was used to functionalize membranes with poly(methyl methacrylate) (PMMA) followed by deposition of silver nanoparticles (an effective biocide) via sputtering to create anti-bacterial membranes [36]. This membrane was tested for disinfection by NF and successfully resisted biofouling for both gram-negative and positive bacteria with a greater than 4 log removal. The coating reduced the CA of the PES substrate from 68.9 to 37.1° , but also increased the work of adhesion by up to 31%, decreased the permeability by 48%, and increased the pore size by a factor of 2 [36]. Other investigations used PECVD to create hydrophobic membranes [170–172], with one investigation concluding

that the addition of hydrophobic coating did not alter porosity [172].

This technique has also been used to make cellulose surfaces that are sticky (i.e., exhibiting high degrees of CA hysteresis) [150]. These properties were obtained by domain selective etching in an oxygen plasma and coating of the etched surface with a fluoropolymer (pentafluoroethane precursor) film through PECVD [170–172]. Cellulose filter papers were coated with double layers of HMDS (hexamethyldisilazane) and n-hexane (via PECVD) to fine-tune its wettability properties for selectively separating water and oils [172]. This work demonstrated selective permeability in which non-polar compounds dissolved in water were able to pass while water did not [172].

6.3. Other CVD techniques

A variety of other CVD processes exist, although in most cases, their application to polymeric membranes has been limited. This is due to a variety of factors, but primarily because the field of using TFD techniques for polymeric materials is still developing; and thus far most published studies make use of only the most popular TFD techniques. Other CVD processes include aerosol-assisted CVD (AACVD) and atomic layer CVD (ALCVD), in which alternating layers of different substances are deposited. Other variants are similar to the above, but may differ in their methods for initiating precursors (e.g., with a hot filament), methods for surface bonding (e.g., oxidative as in iCVD) [47], the pressure applied in the reaction chamber, the method for creating plasma and the methods for heating substrates for deposition [144]. CVD techniques are often used for semiconductor and metallic applications, and even for the creation of carbon nanomaterials. Thus, a wide range of variations and material-specific variants exist. In one technique, carbon nanotube membranes were created using CVD within the pores of an alumina template to create the membrane structure [173]. Smooth graphene sheets are also created with CVD and can be used as membranes; however, such techniques currently do not use deposition, and instead grow the graphene on a smooth surface before transferring it to a substrate [174]. In the following sections, we highlight some other forms of CVD that are promising alternative techniques for polymeric membrane modification, but which have limited studies on their application.

6.3.1. CVD polymerization

Another application of CVD for designing advanced membrane materials is to use it as a polymerization process. For most polymer synthesis processes, liquid-phase techniques (such as spin-coating, dip-coating, etc.) are used due to their simplicity and low cost. However, these techniques use solvents, which can limit the types of materials polymerized and influence the chemistry of the resulting material [40]. CVD is useful in augmenting polymeric surfaces because it allows for delivery of monomers of limited solubility, such as polytetrafluoroethylene (PTFE) [166]. CVD polymerization, on the other hand, can also be used for delicate substrates such as paper and fabrics by eliminating the need for solvents and operation at low temperatures [166]. Furthermore, because the polymerization takes place directly on the surface, the chemical influences of the liquid solvents can be avoided and the polymeric coating can be highly controlled [146].

The first step of any polymerization process is initiation, or creation of highly reactive free radicals. The second step is propagation of the chain by addition of monomers to the polymer chain. Polymerization ends with a termination process. Initiation can be induced by a variety of methods, including high temperature (regular CVD), an initiator chemical species (initiated CVD, iCVD), light (photoinitiated CVD, piCVD) and plasma (plasma-enhanced CVD, PECVD). Temperature activated CVD polymerization is not generally used for membrane coatings for the reasons mentioned previously. However, one study used CVD polymerization at a temperature of 250 °C to deposit 6FDA (hexafluoroisopropylidene-2,2-bis [phthalic acid anhydride] monomers onto a polyamide membrane backbone to create a heat-resistant polymeric membrane [175]. While the process did allow conversion to a

polyimide selective layer, it degraded the membrane performance compared to the base material, with selectivity fractions for gas and ethanol decreasing by 25–40% [175].

In a recent study, Xiao et al. fabricated a free-standing, ultrathin polymeric carbon nitride membranes via CVD polymerization and investigated their ionic transport properties [176]. Suitable amounts of guanidinium carbonate (Gdm_2CO_3) or melamine was used as the precursor. Following the thermal polymerization in the test tube, yellowish transparent polymeric carbon nitride membranes were formed on the surface of glass. The membranes were then delaminated from the glass substrate by soaking in water. Membranes with thickness ranging from 140 nm to 1 μm were prepared by varying the amount of melamine. At lower ionic concentrations (10^{-3} M), ionic conductivity of these membranes became independent of the nominal ionic concentrations due to their cation selectivity and thus exhibited surface charge controlled ionic transportation properties. These membranes are promising for applications such as generating electric energy from salinity gradients.

6.3.2. Electrostatic spray assisted vapor deposition

Another form of CVD that has the potential to reduce process temperatures is via the use of electrostatics. Electrostatic spraying techniques were developed in the 1950s to deposit ionized particles onto charged or heated substrates [177]. Electrostatic spray assisted vapor deposition (ESAVD) is used for deposition of both micro- and nano-scale film layers. In this technique, liquid precursors are aerosolized using an electric field to spray the desired chemistry on a heated substrate (Fig. 10). The aerosol spray reacts while in the vapor phase to form the final chemistry that will be deposited. This technique can be categorized as a form of CVD because the reaction occurs within the vapor phase. ESAVD is widely applied in both industrial processes and for scientific instrumentation because of the cost and operational advantages over techniques such as plasma and e-beam CVD. Specifically, ESAVD does not require the use of vacuum or other high energy equipment, which significantly reduces both the manufacturing and operating costs [144, 178]. The main compartments of a typical ESAVD device include a spray nozzle, heated surface, power supply, and liquid precursors (Fig. 11) [179].

ESAVD is emerging as a popular technique for thin film deposition due to its consistent production of stable films with excellent adhesion in a single production run [180]. ESAVD is used for a variety of applications, including catalytic, bioactive, glass, thermal barrier coatings for

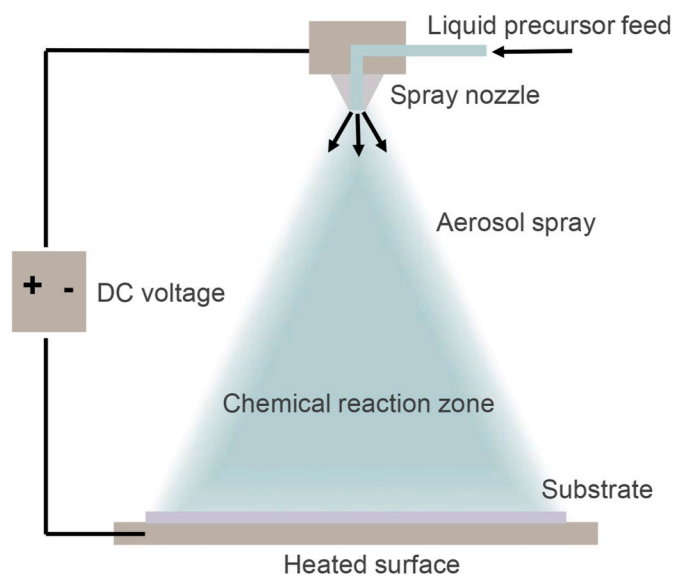


Fig. 11. Schematic illustration of a typical ESAVD device, where liquid precursors are fed into a charged nozzle to create a charged aerosol spray that reacts *in situ* before reaching the surface (inspired by Ref. [179]).

solid oxide fuel cell components, ceramic membranes for selective gas separation, and optical/ferroelectric films for sensors and memory devices [133]. TiO₂-based films doped by Cr or Nb have been successfully deposited onto silicon substrates by the ESAVD technique at different deposition temperatures varied from 400 to 600 °C [132]. While these process temperatures prevent the use of many polymeric materials, they still represent an improvement over traditional thermally-initiated CVD processes. They may find future application in creating metal-polymer composite membranes with anti-fouling properties, such as the ones formed by sputtering [119].

6.4. Summary of CVD methods

Table 2 presents a summary of some of the previous studies applying different CVD methods. Because these methods are more versatile than PVD, the listed applications and materials within this table should not be taken as comprehensive. Rather, these are the applications/materials which are already demonstrated by prior investigations. The relative dearth of investigations for some of these methods present opportunities for future research in these areas, especially for PECVD, which is a gentle and versatile technique that could be applied for a wide range of goals. Although it is an emerging technique, iCVD has already been widely applied for water treatment applications, including RO and MD, with great reported success. The novelty of the technique is its main disadvantage, as commercialization of the process is still ongoing.

7. Atomic layer deposition

7.1. Process overview

Atomic layer deposition (ALD) is a chemical gas-phase thin film deposition based on sequential surface reactions [181]. It is sometimes considered to be a form of CVD and is distinguished from other methods by the special pulsing technique that grows the film layer by layer in a self-limiting fashion [181]. In each pulse (typically lasting 1–2 s), a precursor chemical is introduced to the substrate to form a monolayer. The pulses are typically followed by a purge, removing excess gas that was not deposited. Precursors are added one at a time in subsequent pulses. The sequence of chemical pulses/purges creates the final coating, as shown in Fig. 12 [182]. By introducing one chemical at a time, uncontrolled gas-phase reactions are avoided. Furthermore, the surface reactions are self-saturating, creating extremely conformal and uniform layers. Most ALD processes use only two chemical precursors alternating between pulses. Similar to CVD processes, most ALD processes use an inert carrier gas, such as nitrogen, and most processes run between 200

and 400 °C, though they can go as low as room temperature.

Advantages of ALD for membrane applications include the formation of pin-hole free films (due to the bottom-up growth) with excellent conformity, repeatability, scalability, and the creation of ultrathin yet dense films. Importantly, ALD can be used to coat deep trenches with an even layer, allowing for coating the inside of membrane pores without significantly modifying pore size [135]. ALD also has the advantage of being able to combine different materials at the nanoscale to create artificial materials with unique features, allowing for innovation in surface functionalization. ALD, however, has some restrictions for polymeric membranes due to the limitations on material choices and thermal stability. The precursor requirements for ALD differ from those in CVD because the reactions happen only at the surface and not in the gas phase. This allows for the possibility of using more reactive precursors in ALD than possible for CVD since gas-phase reactions are eliminated. Solid and liquid precursors used in ALD must be volatile under the operating temperature and pressure.

Because of the non-equilibrium nature of many ALD coatings, stability can be an issue. Like many PVD/CVD processes, the high temperatures of several ALD reactions are problematic for polymeric membrane applications [183]. Also, the mechanism of ALD growth on polymeric membranes differs from those on other substrates [184]. For instance, the specific chemical groups on the polymer surface can make nucleation of deposited Al₂O₃ films challenging [185]. Density functional theory (DFT) calculations have shown that Al₂O₃ can readily nucleate and grow on –NH₂ and –OH terminated self-assembled monolayers (SAMs), whereas growing on –CH₃ terminated SAMs will be challenging [186]. As adhesion of the deposited film to the polymer surface and the film strength are important in the functional polymer membranes, routes such as plasma pre-treatment of the substrate could be used to improve the adhesion and avoid delamination issues [187].

7.2. Applications of ALD in fine-tuning polymeric membranes

Metallic coatings are popular applications for ALD in polymeric membrane modification, as ALD allows for the incorporation of metals into polymers due to the low temperatures and high reactivity of ALD precursors [187–189]. Several studies have successfully applied metal oxides to polymer layers with ALD. Specifically, ALD of metallic species has been used for enhancing hydrophilicity (for fouling resistance) and separation performance. In one study, alumina was coated on a PTFE microfiltration membrane (mean pore size of 0.2 μm) to improve its hydrophilicity and water flux [190]. The hydrophilicity of the PTFE membrane increased with an increasing number of ALD cycles, with a CA of 20° reported after 500 cycles. A lower number of cycles resulted in

Table 2
CVD techniques - advantages and disadvantages in membrane modification.

Modification technique	Membrane type and membrane material	Advantages(s)	Disadvantage(s)	Ref.
Traditional CVD	Material: PVDF Application: Water/organic separations	- Simple - Already scaled for industry	- High processing temperatures - Limited materials	[147]
iCVD	Type: RO, MD Material: PA, PVDF (most polymers suitable) Applications: Alteration of CA for fouling, grafting polymers to create a membrane, tuning pore size	- Conformation - Low temperature	- New technique without established scale-up - Cost	[34,48,151,163]
PECVD	Material: PMMA, PES, CA (most polymers suitable) Applications: Alteration of CA for fouling, separating oil/water	- Predictability of layer properties - Extremely thin and even coatings on irregular surfaces - Versatile	- Sensitive to process parameters - Plasma alters properties of deposited material; non-predictable properties	[36,170–172]
CVD Polymerization	Material: delicate structures	- Gentle technique - Normalized film growth - Low temperature - Established procedure for coating flexible materials	- Moderate process temperatures	[175,176]
ESAVD	Material: Polymers with good temperature stability	- Gentle technique	- Low energy and financial costs - Moderate process temperatures	N/A

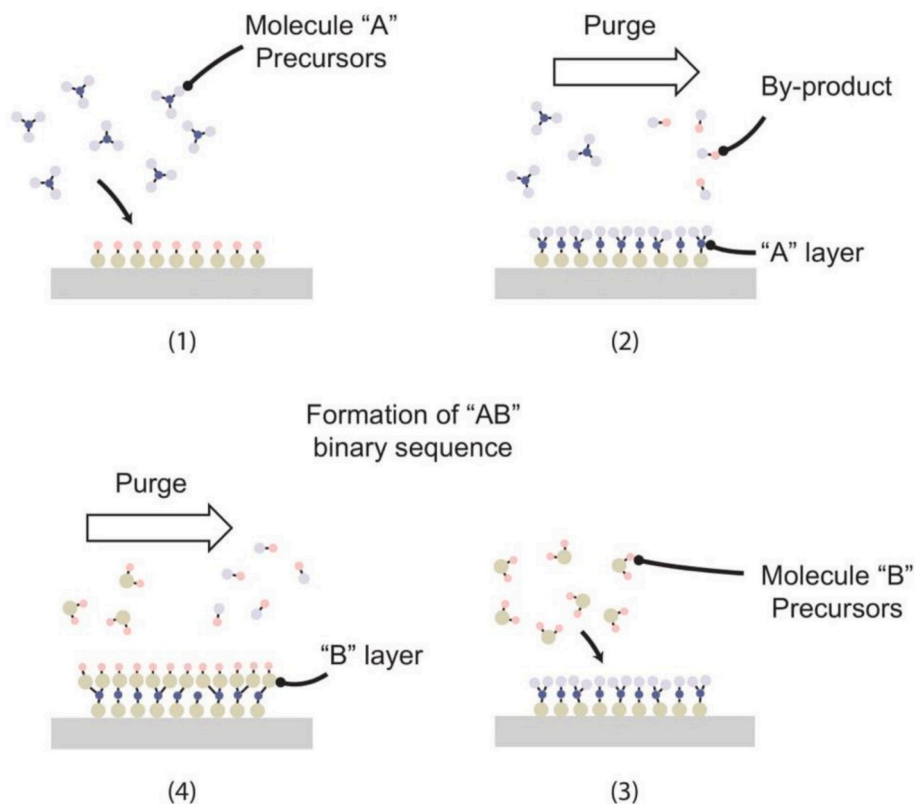


Fig. 12. Schematic representation of ALD using self-limiting surface chemistry and an AB binary reaction sequence (Inspired by Ref. [182]). One layer of A or B is deposited at a time, with rapid cycling between these precursors, enabling extremely uniform layers.

the formation of fine particulates, whereas higher cycles yielded a continuous dense layer. An optimal modification, which occurred at 500 cycles, yielded a 50% increase in water flux and a 12.4% increase in the rejection of polystyrene nanospheres when compared to the pristine membrane due to reduction in fouling.

Another study tested the deposition of TiO₂ on a PTFE MF membrane and demonstrated a reduced contact angle and increased water flux with increasing ALD cycles [191]. There was an interplay of hydrophilicity enhancement and pore blockage, which resulted in an initial increase of SiO₂ nanospheres rejection along with the pure water flux up to 150 cycles, beyond which flux started to decline. A TiO₂ deposition of 150 cycles drastically reduced the CA from 131 to 28° without causing

significant pore blockage and resulting in an initial increase of both flux and rejection. The pore blockage started to become significant with more than 150 ALD cycles because of the overgrowth of TiO₂ deposition layer on the membrane pore walls, which resulted in a gradual decline in flux and an increase in rejection. In another study, ZnO was deposited onto a PTFE membrane via ALD and was shown to be effective in removing dyes and other organic matter via adsorption from aqueous solutions [129]. The adsorbed species were removed via ethanol to regenerate the membranes without loss of performance, which was enhanced by ZnO through better solution diffusion through the membrane and increased adsorption [192].

TiO₂ was deposited by ALD on PP UF membrane to increase

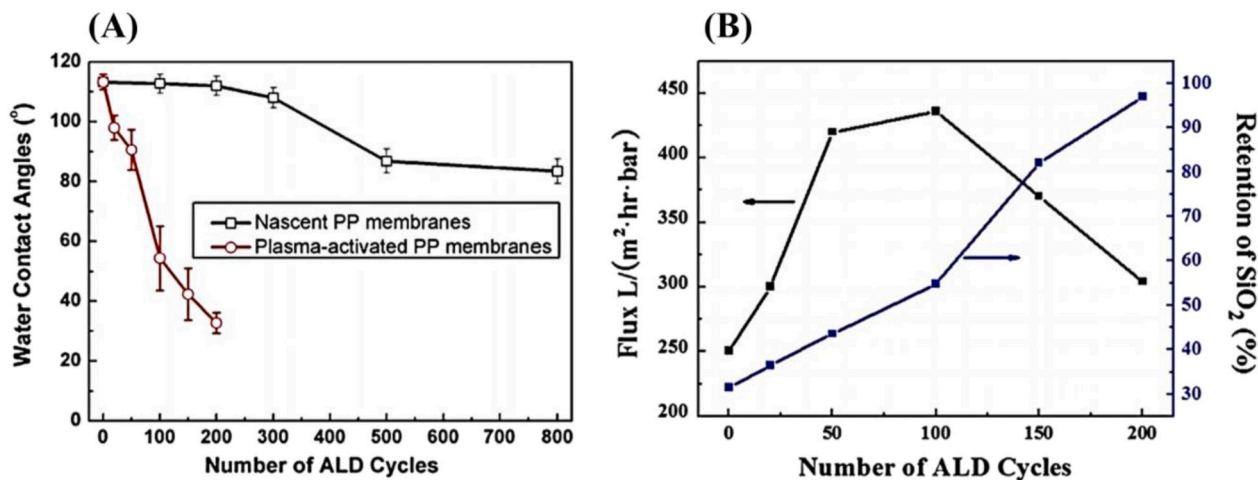


Fig. 13. (A) Water CA of the nascent and plasma-activated PP membranes deposited with TiO₂ over different cycles, (B) water flux and SiO₂ retention of the deposited membranes [193].

hydrophilicity [193]. Initial deposition on the pristine membrane did not yield a functional coating due to the absence of sufficient reactive groups on the membrane surface. This was overcome by a short plasma activation prior to deposition, which generated active radicals on the membrane surface to enable a smooth and conformal deposition of TiO₂ (Fig. 13A). Increasing the number of ALD cycles increased the amount of deposited TiO₂ and consequently improved the hydrophilicity, flux, retention of SiO₂ nanospheres, and fouling resistance of the membranes (Fig. 13B). Although rejection of SiO₂ nanospheres was increased with the increasing ALD cycles, flux started to decline beyond 100 cycles, which can be attributed to pore blocking by the deposited TiO₂. Thus, the optimum number of TiO₂ deposition cycles was found to be 150, which resulted in a 60% increase in water flux and a doubling of the retention ratio, as well as improved resistance to protein fouling. In another study, Chen et al. [32] used ALD in tandem with nitric acid activation to deposit either aluminum oxide (Al₂O₃) or titanium dioxide (TiO₂) to enhance the water permeability and hydrophilicity of polypropylene membranes [32].

TiO₂ has also been deposited on PVDF membranes using TiCl₄ and water as precursors to enhance flux and selectivity [194]. The PVDF membrane became hydrophilic with a sharp decline of CA from ~67° to ~27° after 120 ALD cycles, exhibiting a 5-fold increase in water flux. Selectivity was improved, too, with the retention of a proteinaceous contaminant, BSA, increasing from ~73% to ~95%. A further increase beyond 120 ALD cycles resulted in a sharp decline in flux (190 and 75 L/m² h bar for 120 and 150 ALD cycles, respectively) as smaller pores were blocked completely. Interestingly, the thermal stability of the PVDF membrane was also enhanced with the deposition at a lower number (30) of cycles. Although the pristine PVDF membrane started to degrade at 300 °C, the TiO₂ deposited membrane (at 30 ALD cycles) continued to be stable until 400 °C, thanks to the shielding effect of TiO₂ layer against the direct oxidation of the polymer. However, this trend was reversed at higher temperatures. For instance, the thermal degradation of the pristine PVDF membrane was completed at ~500 °C, whereas that of membranes deposited with 30 and 200 cycles were completed at 460 and 410 °C, respectively. This is due to the catalytic effect of the TiO₂ at elevated temperatures, which enhanced the polymer degradation.

ZnO deposition by ALD has been used to reduce fouling on PVDF membranes [195,196]. In an investigation that used ALD to deposit both TiO₂ and ZnO onto PVDF membranes, the coated membrane was reported to become hydrophilic, had high permeability, and had good fouling resistance [197]. The modified membrane exhibited photo-induced superhydrophilicity, which was evident in a sharp (82.6%) reduction in the water CA and a 33.5% increase in water flux. Also, it showed excellent photocatalytic properties in the degradation of methylene blue (MB). Removal rate of MB was around 80% even after reusing 5 times. A TiO₂: ZnO modified PVDF MF membrane also possessed excellent fouling resistance against humic acid (HA), which was ascribed to a synergistic action of enhanced hydrophilicity and photocatalytic activity under visible light [197]. The authors attributed these enhanced performances to the formation of a type II heterostructure formed by the layer-by-layer deposition of hexagonal wurtzite ZnO and amorphous TiO₂, which effectively improved the segregation of photo-generated electron-holes. In another study, ZnO was deposited on a PVDF membrane to improve its hydrophilicity and separation performance [196]. Diethyl zinc (DEZ) and deionized water were used as precursors for zinc and oxygen, respectively. Pre-treatment using nitrogen dioxide (NO₂) resulted in the generation of more oxygen-containing active functional groups on the membrane surface, enabling a better deposition even after only 100 ALD cycles. In a fouling test using BSA [196], report that ALD of ZnO on the PVDF membrane cut the mass of BSA accumulated on the membrane by three. The authors attribute this result to the decreased hydrophilicity of the modified membrane (Fig. 14A) [196]. Furthermore, the retention rate of the modified membrane after 200 ALD cycles was increased from ~73% to

97%, as seen in Fig. 14B. The authors report that the increase in the retention did not compromise the membrane permeability. Although a pore size reduction, and hence reduced permeability, is expected to have happened after 200 ALD cycles, it is possible that such pore size reduction was compensated for by the enhanced hydrophilicity of the coated membrane. Al₂O₃ deposited by atomic layer deposition similarly improved the anti-fouling performance of a polyamide RO membrane [198].

While the layers deposited by ALD can be incredibly thin, it is still possible to use the ALD technique for pore size modification [199]. For example, Li et al. [135] used ALD of Al₂O₃ to simultaneously tune the pore size and improve the hydrophilicity of polycarbonate track-etched UF membranes [135], presenting a method for very precise fine-tuning of membrane pore sizes with a precision of less than 1 Å. The initial pore size of ~33.9 nm started decreasing after 130 cycles, and the pores began sealing after 300 cycles.

While metals are commonly applied as coating materials in ALD of polymeric membranes, some investigations used ALD to deposit other materials. For example, one group deposited polyimide onto a PES membrane and subsequently crosslinked the deposited polymer. They demonstrated tunability of pore size and higher mechanical/thermal stability [200].

Table 3 gives a summary of ALD applications for polymeric membranes. In general, ALD is advantageous over other TFD techniques due to its versatility and ability to generate very thin and well-controlled layers. This fine tuning enables modifiers to simultaneously design a material with desirable fouling and/or selectivity properties while also minimizing flux reductions associated with addition of layers to a porous membrane. The primary disadvantages include process costs, energy requirements, and stability issues, which may necessitate plasma pre-treatment – which then further increases process costs and complexity.

8. Electrochemical deposition

8.1. Process overview

Electrochemical deposition (ECD) is a process in which metals, oxides, or salts are deposited from a solution containing ions onto an electrically conducting surface (an electrode) by electrolysis. The ECD process requires three electrodes (working, counter, and reference), and involves the reduction of metal ions at the working electrode due to the current passed through the solution. A typical ECD processing device is shown in Fig. 15 [201].

Electrochemical deposition, also known as electrodeposition, electrophoretic deposition or electroplating, is used for depositing conducting/semiconducting materials onto a suitable substrate using an electrical current and redox reaction. Cations or a monomer of the target material in the electrolyte are reduced by an electrical current and deposited on the surface of the cathode [202]. Electrochemical deposition involves moderate temperature, high deposition rate, relatively low cost, effective, easily portable, and effectively controlled process [203]. Moreover, this technique allows growing a conductive film from nanometers up to several hundreds of microns in a single step [202]. Optimizing multiple parameters such as bath (electrolyte) composition, pH of electrolytic bath, deposition time and temperature, current density or applied voltage, anode, and cathode materials are essential for the desired layer thickness and the synthesis of homogeneous coating [204, 205].

The requirement of a conductive substrate for ECD does not necessarily preclude the use of this technique for polymeric membranes. A thin metal film (that does not disintegrate or block pore structures) can first be vapor-deposited on one side of the membrane to serve as a cathode for electrodeposition. Then, the desired chemistry can be electrodeposited onto the other side of the membrane. ECD methods do not have the challenges with high process temperatures that other forms of TFD do, and are therefore a competitive alternative for creating metal-

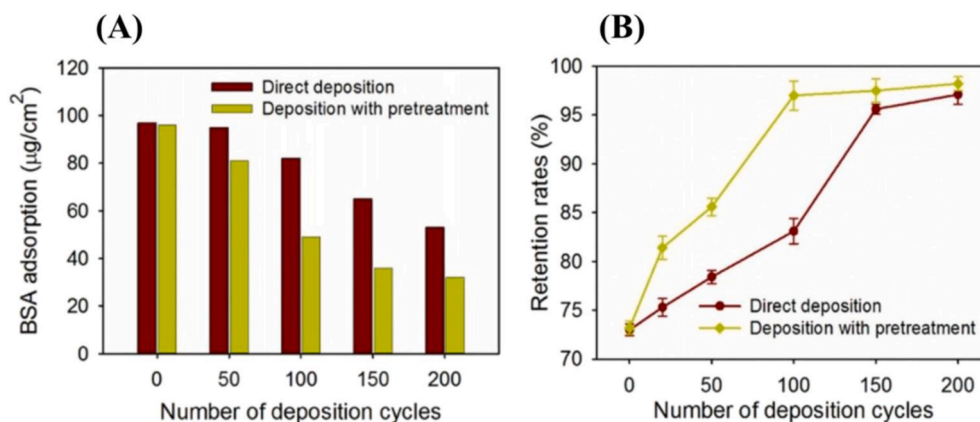


Fig. 14. (A) Fouling propensity and (B) Separation performance of pristine and ZnO deposited PVDF membranes with different ALD cycles [196].

polymer composite materials.

8.2. Applications of ECD in membrane preparation

As with forms of PVD, preparation of metal-polymer membranes is one potential application for ECD. In one study, TiO₂ particles were electrophoretically deposited to produce a composite titanium dioxide membrane using carbon-cloth as a conducting substrate [206]. The mean pore size of the developed membranes was about 0.28 µm and was tested in photocatalytic water treatment. Four different target molecules (4-nitrophenol, caffeine, acetaminophen, and uracil) were treated under simulated solar light in aqueous solutions. The results indicated a 100% degradation of 4-nitrophenol, above 80% of acetaminophen and uracil, and 60% of caffeine. Moreover, they also achieved the photodegradation of pre-adsorbed methylene blue (MB) both under simulated solar radiation and visible light [206]. The successful preparation of the photocatalytic membrane using ECD suggests that it could be used as an alternative to more expensive TFD methods for metal-polymer composites.

Hybrid UF membranes have also been developed for water purification using ECD. A PSF membrane with graphene nanoplatelets modified with poly(styrene) (G-PST) was ECD-coated with ZnO [207]. The ECD of ZnO on the PSF-G-PST membrane surface was carried out in the presence of water-soluble polymers, polyvinyl alcohol (PVA), poly(acrylic acid) (PAA), 2-hydroxyethyl cellulose (HEC) at different concentrations (2.5 and 10 wt%). The surface morphology of the hybrid membrane was affected by the polymer type and concentration. At low concentration (2.5 wt%) of water-soluble polymers (PVA, PAA), the ZnO nanostructures were generated mainly at the edges of the bottom macropores. At high PVA concentrations (10 wt%), the ZnO nanostructures were embedded inside the porous structure of the composite membrane rather than only at the edges [134]. The use of HEC improved the deposition rate, increased the amount of ZnO deposited in the whole structure, and decreased the size of inorganic structures of the composite PSF-G-PST-membrane. This highlights how sensitive ECD processes can be to solution characteristics, which is simultaneously advantageous due to the versatility enabled and disadvantageous due to the number of iterations that can be performed before finding an ideal solution.

In another study on metal-polymer composites using ECD, Chou et al. [208] deposited platinum (Pt) ions on the interior pores of a Nafion membrane placed on an electrode. By moving through the hydrophilic channels of the membranes, Pt ions deposited at the end of the hydrophilic channels of the membrane. The results showed that the deposition of Pt in this way achieved good Pt utilization when compared to the Pt deposition on the bare electrode and subsequent placement of the membrane on top [208]. This further demonstrates how ECD can be an effective process for producing a metallic coating on a membrane surface.

ECD is simple, fast, can be done at low temperatures, and be ideal for depositing specific materials. However, coating uniformity can be challenging, and a small thickness can be difficult to achieve. In addition, the materials that can be used are limited in electrochemical processes. Many of these materials, with the notable exception of metals, are of limited application for modification of water treatment membranes. Another limitation is the challenge associated with scaling these processes and creating continuous rather than batch processes.

9. Electron-beam deposition

9.1. Process overview

Electron-beam (e-beam) technology has enabled special applications across a wide range of fields, including nanotechnology, microbiology, contamination control, electron microscopes (scanning and transmission), curing, welding, surface treatments, additive manufacturing, metal powder production, semiconductor manufacturing, solar-cell production, fabrication and modification of polymers and more [209, 210]. The technology is so broadly used because of its energy efficiency and ability to precisely control small volumes of matter.

E-beam technology (also called electron irradiation or cathode rays) uses beta radiation to treat materials and is usually operated under elevated temperatures and inert atmosphere [211]. In e-beam processes, a target material is bombarded with high-energy electrons that move through the target material. Electrons are ejected from their orbits and generate free radicals that initiate reactions. The released energies, normally ranging from 3 to 10 million electron volts (MeV) and coupled with 1–50 kW of power, have sufficient energy to penetrate through the materials [212–216]. In e-beam evaporation, normal evaporative deposition processes are enhanced by the addition of an electron beam that heats the material target. With e-beam heated sources, deposition rates can reach 25 µm/s for Zn and Al [42].

A typical e-beam processing device is shown in Fig. 16 [209]. The main component of the device is an e-beam gun (consisting of a cathode, grid, and anode), which is used to create and speed up the primary beam. In operation, the gun cathode is the source of thermally emitted electrons. The electron beam emerges from the gun through an exit hole in the anode. The use of direct high voltage to produce a high-energy electron beam allows the conversion of input electrical power to beam power at greater than 95% efficiency, making e-beam material processing a highly energy-efficient technique.

Advantages of e-beam deposition on polymeric membranes include shorter exposure period and processing time, less oxidative damage, reduced color change and no chemical residuals on the produced products, which makes this process clean, safe and environment friendly [217]. Drawbacks of e-beam deposition include high capital equipment cost, polymer degradation, and energy loss due to backscattered

Table 3
Use of ALD - its advantages and disadvantages.

Deposited material	Precursors	Membrane material, Mean pore size	Remarks	Ref.
Al ₂ O ₃	- Trimethylaluminum - Deionized water	PTFE	- Improved hydrophilicity - 50% increase in water flux - 12.4% increase in retention of polystyrene nanospheres with a uniform diameter of 190 nm	[190]
TiO ₂	- Titanium isopropoxide - Deionized water	PP 0.043 μm	- Better deposition was achieved using pre-treatment by plasma - Enhanced hydrophilicity, flux, retention and fouling resistance	[193]
TiO ₂	- Titanium tetrachloride - Deionized water	PTFE 0.2 μm	- Prior activation of the membrane surface yielded better deposition and performance in filtration	[191]
TiO ₂	- Titanium tetrachloride - Deionized water	PVDF	- Enhanced hydrophilicity and resistance to fouling by proteins - Performance was best at higher numbers of ALD cycles	[194]
Al ₂ O ₃ and TiO ₂	- Trimethylaluminum (for Al ₂ O ₃) - Titanium isopropoxide (for TiO ₂) - Deionized water	PP 0.043 μm	- Demonstrated the use of nitric acid (without affecting the microstructure and mechanical stability) in activating the PP membrane surface	[32]
Al ₂ O ₃	- Trimethylaluminum - Deionized water	PP 0.03 μm	- Al ₂ O ₃ and TiO ₂ deposited showed higher hydrophilicity and water flux - Al ₂ O ₃ improved the hydrophilicity and membrane resistance to acids and organic solvents - Pure water flux decreased, and retention of protein increased with increasing the ALD cycles, implying its applicability in fine-tuning the	[135]

Table 3 (continued)

Deposited material	Precursors	Membrane material, Mean pore size	Remarks	Ref.
Polyimide	- Pyromellitic dianhydride - Ethylenediamine (both as a precursor and cross-linking agent)	PES 0.1 μm	- Retention was enhanced by reducing the pore sizes - Hydrophilicity and fouling resistance were improved due to the amide bonds after crosslinking - Thermal and mechanical stability and corrosion resistance were improved due to crosslinking of the polyimide chains	[200]

electrons [218]. The high energy of the e-beam impacting the surface can modify substrate electron shells and bonds in ways that other processes cannot, opening them up for a wide range of chemical reactions.

9.2. Applications of e-beam deposition

E-beam modification has been applied to polymeric materials to modify their mechanical strength, swelling and dissolution properties, surface topography, wetting properties, surface reactivity, and other material properties [219]. However, even though many studies have reported increased use of e-beam technique for irradiation, curing, and grafting, there has been very little research reported on the deposition of materials on polymeric membrane surfaces [220–226]. In one study, nylon 6 was treated with e-beam radiation under the doses of 100–600 kGy in the air at ambient temperature in the presence of triallyl isocyanurate to reduce water absorption. The samples were irradiated by 2 MeV e-beam from both sides of the specimen in two passes. All irradiated Nylon 6 samples were compared for mechanical properties with the un-irradiated virgin sample. Water absorption, Rockwell hardness, tensile and flexural properties, and impact strength of Nylon 6 were determined [221]. The results showed that the crosslinker played an important role during e-beam irradiation of Nylon 6, resulting in a larger improvement of properties (flux wettability, power density, and robustness) compared to virgin Nylon 6.

Function-graded proton exchange membranes have also been fabricated by e-beam grafting for polymer electrolyte fuel cells (PEFCs). A heterogeneous energy deposition technique was used and a sulfonic acid group gradient was observed. Normal proton exchange membranes (N-PEMs), graded proton exchange membranes (G-PEMs), and Nafion®212 membranes were prepared at 30 and 60 °C with dry H₂/O₂ gases and compared for PEFC operations. It was reported that the fabricated G-PEMs showed a higher power density and performance at low temperature under non-humidified conditions, and a lower deterioration and cost than Nafion®212 and N-PEMs [222].

PES PVDF, PSF, and PAN membranes have also been functionalized directly using e-beam irradiation. Aqueous solutions containing fifteen different functional molecules were immobilized on the membrane surface by e-beam treatment. The resulting membranes showed significantly increased flux and water wettability of the hydrophilic membrane surface, accompanied by decreased protein adsorption. It was also

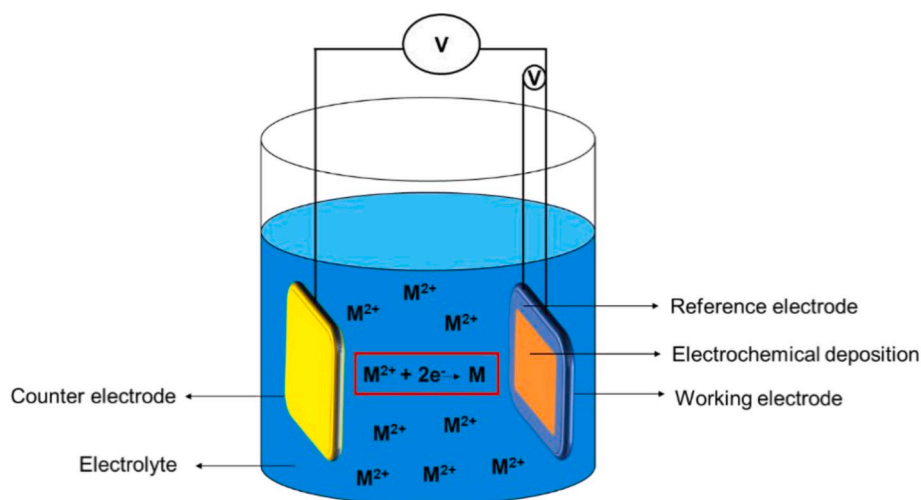


Fig. 15. Schematic of a typical ECD process, which uses a current applied through an electrolyte solution with 3 electrodes. Metal ions (M^{2+}) are reduced at the working electrode.

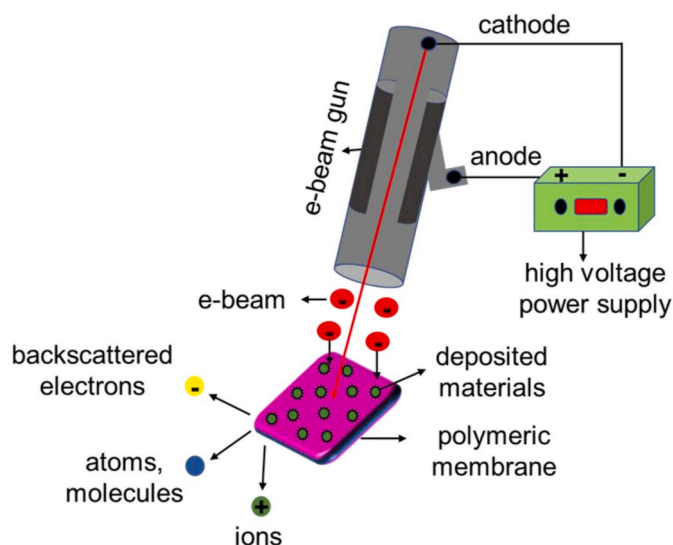


Fig. 16. Schematic illustration of a typical e-beam processing device. The substrate is bombarded with high energy electrons, generating free radicals that initiate the reactions.

shown that the membrane pore structure was open and that nearly no filter cake had been formed on the PVDF membrane modified with glucose [224].

In another study, PSF membranes were prepared by e-beam curing via the addition of acrylate monomers as cross-linkers to obtain a solvent resistant nanofiltration membrane [149]. Due to optimization of curing efficiency, the effect of different parameters, such as e-beam dose (100, 300, and 500 kGy), cross-linker type (trimethylolpropane tri-acrylate, pentaerythritol tetra-acrylate, dipentaerythritol penta-acrylate) and cross-linker concentration (10, 12.5, 15, and 20%), were investigated for membrane performance, morphology, double-band conversion, and solvent stability. SEM cross-section images (not reproduced here) of the different PSF membranes show that the membrane microstructure exhibited small changes. Finger-like macrovoids became longer in the membranes with the presence of the additive compared to the reference membrane. The obtained e-beam cured PSF membranes showed good solvent stability with 96% Rose Bengal (1017 Da) retention at isopropanol permeance of $0.062 \text{ L/m}^2 \text{ h bar}$ [223].

A composite membrane was created by e-beam sputter deposition of

PTFE to create a superhydrophobic membrane using a typical polypropylene track-etched (PPTe) membrane. It was reported that the modified membrane sample thickness increased from 60 to 1400 nm and the effective pore diameter decreased from 275 to 150 nm. However, water CA increased from 120 to 154° when the thickness of the deposited PTFE layer increased up to 1400 nm. The air flux significantly decreased from 210 to $25 \text{ mL/cm}^2\text{min}$ when the thickness of the modified membrane increased. The e-beam sputter deposition of a PTFE layer onto the PPTe surface yielded an asymmetric shape of pores [227]. The same group reported another application of e-beam evaporation to create a micro/nano-fluidic diodes on a PET membrane to alter pore size/geometry for directed ion transport. Enhancements similar to the previous PPTe membrane study were shown, with drastic pore size decreases ($85\text{--}28 \text{ nm}$) but large CA increases ($65\text{--}120^\circ$) [228]. Table 4 provides a summary of e-beam deposition applications for polymeric membranes.

10. Associated challenges with TFD on polymeric membranes

Membrane surface properties, such as hydrophilicity/hydrophobicity, roughness, surface charge, and surface-exposed functional groups, can be fine-tuned by choosing a suitable deposition technique. These modified membranes can then be used for enhanced performance in a variety of water treatment applications (MD, RO, NF, etc.). Examples of desirable membrane performance parameters include, among many others, higher flux and selectivity, low/anti-fouling surfaces, anti-wetting and narrow pore size distribution in membrane distillation, etc. Although similar properties could be achieved via different deposition techniques, the extent of modification, resulting surface morphology and the durability of the coating can be process-specific. Many challenges are restricting the wide-scale use of TFD techniques for modifying polymer membranes. One of the major challenges is the compatibility of the material properties of the coating and the base membrane. Specifically, the coefficients of elongation at break and the thermal expansivity must be well-matched to avoid delamination of the coating [138]. The instability of the coated layer due to the weak interaction of the coating layer with the substrate membrane is also of concern. This instability results in gradual delamination of the coating layer during membrane operation or cleaning. In such cases, the stability of the coating can be enhanced by anchoring the coating layer on the substrate membrane via a chemical bond. Another issue is the formation of cracks on the coating layer, which is mainly dependent on the film thickness. Crack formation becomes energetically favorable beyond a certain film thickness. Therefore, fine-tuning of thickness is essential to

Table 4
Application of e-beam deposition applications for polymeric membranes.

Modification technique	Membrane type and material	Advantages(s)	Disadvantage(s)	Ref
e-beam curing	PSF, NF	<ul style="list-style-type: none"> - More defined top layer - Formation of slightly larger macrovoids - Unimpaired membrane structure - A distinct densification of the selective layer 	<ul style="list-style-type: none"> - More brittle - Instantaneous demixing 	[223]
e-beam grafting	Poly(tetrafluoroethylene-co-hexafluoropropylene) films ion exchange membrane	<ul style="list-style-type: none"> - Lower cost - Higher power density - Lower deterioration 	<ul style="list-style-type: none"> - Prevented from drying-up - Back water diffusion - Unclear water distribution 	[222]
e-beam irradiation	PES (UF), PVDF (MF), PSF (MF), PAN (UF)	<ul style="list-style-type: none"> - Increased flux - Increased water wettability - Decreased protein adsorption - Inner surface activation 	<ul style="list-style-type: none"> - Necessity of the aqueous solution of corresponding functional molecule 	[224]

avoid the formation and propagation of cracks on the membrane surfaces.

Coupling of polymer membranes with photocatalytic processes is a strategy that could enable continuous membrane filtration while also degrading organic micropollutants in wastewater [229]. There are numerous TFD techniques that can be used, including PVD and ECD. However, the addition of a photocatalyst can damage the polymer membranes. This limitation may be overcome by carefully TFD coating of porous, inorganic material on the polymer membrane prior to the photocatalytic coating, which can improve adhesion and prevent direct contact between the free radical and the polymer material. Although it is possible that such a deposition could reduce the porosity and permeability of the membrane, it improves longevity and therefore enables the coupling of photocatalytic activity with membrane filtration.

The developing field of TFD of polymeric membranes is also affected by challenges related to characterizing the membrane properties. The development of robust characterization methods is of utmost importance to truly understand the connections between the coating, structure, and performance of the membrane. The invention of new membranes necessitates the expansion of characterization methods and tools to ensure the precision and accuracy of the characterization results. Globally accepted standard methods for measuring properties such as porosity, hydrophobicity/philicity, surface charge, roughness and mean pore size, etc. have to evolve in order to avoid the problems of irreproducible characterization results. For instance, wettability and CA are vital parameters in membrane distillation, yet, finding the CA of porous materials is more complicated than it is for solid, nonporous surfaces. One of the widely used methods for characterizing wetting is the simple and quick sessile-drop goniometry method. However, in many cases, static CA readings from the sessile-drop method are misleading for membrane materials. Characterization is even more challenging in the case of fouled membranes. Therefore, a more robust, and field-standardized, method for determining the advancing and receding CA should be developed to ensure consistency in reported wetting behavior of membrane surfaces across studies [230].

Another challenge for the field of TFD for polymeric membrane modification is the scale-up of these processes. Many of these techniques have already been adapted for industrial-scale fabrication [40], which somewhat eases this transition. However, newer developments such as iCVD that have enabled coating of polymeric materials are still primarily confined to lab-based settings. One significant challenge currently limiting the scale-up of these techniques is the sensitivity of the process to variations in process parameters. This sensitivity makes it difficult to reproduce the successes of lab-based efforts on industrial scales. Another challenge to technology scale-up is the economic feasibility of the technologies by weighing the projected benefits of the processes against the costs associated with fabrication. Industrial-scale deposition systems can cost up to USD 20 million [40], and the processes best suited for

polymeric materials such as iCVD, PECVD, and ALD tend to be more expensive than less-suitable processes such as thermal evaporation PVD.

11. Conclusions and future perspective

The capabilities and applications for TFD processes are rapidly evolving as new technologies and methods are developed. These new technologies have the potential to enable wide-scale application in fine-tuning various properties of polymeric membranes, whereas such techniques were previously inappropriate for polymers due to harsh operating conditions. In this review, we have summarized the process fundamentals of basic deposition techniques, including sputtering PVD, CVD, e-beam, ALD, ECD, LB, and Sol-Gel methods. The applications of these techniques to modifying polymeric membranes were reviewed, with special emphasis placed on new developments that have enabled new surface modifications to improve the performance of membranes for water treatment. We described the key advantages and disadvantages of each process. The technology landscape offers many niches as certain techniques are better for certain coating types (e.g., metals, oxides, polymers, carbon materials, colloids) and substrate characteristics (maximum temperature, hydrophobicity, pore size, etc.). However, coating thickness, conformality, and material compatibilities can make certain techniques better generalists.

PVD techniques are generally advantageous because of their low cost, simplicity, and potential for scale-up. Some disadvantages include poor ability to coat the interior of pores and non-uniform thickness distributions. Furthermore, many of the coating materials suitable for use with PVD are metallic. While metallic coatings have several applications (anti-microbial resistance, catalysis, modification of permeability/selectivity by modification of electrochemical binding, etc.), the lack of versatility in coatings is a major drawback for the use of PVD in polymeric membranes modification. Sputtering is the most versatile of the PVD processes discussed, but even then, sputtered coatings may not be compatible with polymeric substrates. For example, differences in material flexibility or weak binding can lead to delamination and membrane destruction.

CVD techniques, and iCVD in particular, have seen great improvements over the past few years that have enabled modification of polymeric membranes. Use of the initiator in iCVD means that any monomer with sufficient volatility can be reacted onto a surface without the use of aggressive solvents or extreme temperatures. Because species grafted via iCVD maintain the functionality of the monomers, the final properties of a modified surface are easily predicted. The ability of a grafted zwitterionic via iCVD compound to prevent fouling of a reverse osmosis membrane without reducing salt rejection or water permeation is a very promising development. Two primary advantages of e-beam heated targets are (i) the very high-power density, giving a good deal of control over the evaporation rate, which in turn allows for more control over the

film properties, and (ii) the sources of contamination from the heated crucible used in thermal evaporation are eliminated.

E-beam evaporation allows for a wider range of source materials than does thermal evaporation and is, therefore, more versatile. However, E-beam evaporation is also more complex than thermal evaporation and can present safety hazards due to x-ray generation by the high voltage electron beam. The safety requirements contribute to making e-beam evaporation a much more expensive process compared to thermal evaporation. Because of this, e-beam deposition is an infrequently used technique for the modification of polymeric membranes. E-beam techniques show promise for polymeric membranes modification applications, but the high-cost issue remains to be addressed. Other problems include the limited control of deposition thickness, inability to conformally coat pores, and damage to the polymer structure. Future developments in the e-beam deposition field might be in the production of polymeric membrane coatings.

ALD is effective in modifying the surface properties and fine-tuning the pore size of porous polymeric membranes. The thickness of the deposited layer is directly proportional to the number of ALD cycles, and thus the effective pore size of the membrane can be optimized by simply varying the number of ALD cycles. ALD is also advantageous in balancing the pernicious and ubiquitous trade-off between permeability and selectivity of membranes, as evidenced in the simultaneous improvement in the permeability and selectivity of a TiO₂-deposited PVDF membrane [133].

LB methods had a surge of applications between 1980 and 1990, although studies related to their use in modification of water treatment membranes in the past 20 years have been limited. Given recent developments in nanotechnology (for example, the development of biphilic Janus particles), it may be worth revisiting these techniques for thin-film deposition on polymeric membranes. LB techniques are scalable, environmentally-friendly, cost-effective, repeatable, and are more tolerant to variable processing conditions as compared to PVD, ALD, or CVD processes, though also do not provide the unique advantages of these TFD techniques such as fabrication of novel chemistries and precise control over coating thickness.

The prospect of wide-scale implementation of deposition techniques is promising for polymer membranes. An endless variety of substrate-coating combinations can enable unique properties using suitable deposition methods. Future directions include the use of novel homo- and copolymers, which ensure better selectivity, use of compounds that are more environmentally benign, and improvements in the deposition process for obtaining more uniform and thinner films. There has been a special focus on the development of new compounds that can increase hydrophobicity, preferably for applications in membrane distillation. Another major focus has been on improving the solute selectivity, without compromising the permeability.

There is a great number of potential directions for future research, exploring both the processes and economics of TFD based membrane modification. For example, researchers could aim to make coatings amenable for smaller pore sizes without blocking the pores. Such a development would increase the number of applications amenable for TFD techniques. The mechanism of the interaction between the deposited layer and the substrate could also benefit from further investigation in order to improve integration and avoid delamination. Progress could also be made in scaling up the successful lab-based techniques for industrial-scale fabrication. As with any scale-up procedure, future work could also explore the economics of constructing advanced membranes using TFD, to verify whether or not the benefits to be gained from membrane durability and performance outweigh additional costs of fabrication.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence

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