








REVIEW

Advances in surface modification and functionalization for tailoring the characteristics of thin films and membranes via chemical vapor deposition techniques

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Abstract

Advanced materials are among the prime drivers for technological revolutions and transformation in quality of lives. Over time, several modification techniques have emerged enabling development of novel materials with extraordinary features. The present review aims to introduce various promising chemical and physical surface modification techniques instrumental for tailoring the characteristics of thin films and membranes. Meticulous discussions are provided over chemical vapor deposition (CVD) techniques evolved for addressing the demands for materials with desired functionalities. Also, essential criteria for the selection of substrates, modifying and precursor materials for an effective CVD modification are elaborated. Investigations are extended to unraveling the role of various process parameters on the quality and properties of deposition. Special attention is paid to the significance and performance of CVD-based membranes and thin films for industrial applications ranging from desalination and water treatment to energy and environment, biomedical and life science as well as packaging. The goal has been to establish a scientific platform for a timely tracking of the prevailing trends in exploitation of CVD techniques and highlighting the unexplored opportunities. This also helps in

identification of the scientific and technical gaps and setting directions for further progress in the fields of thin films and membranes.

KEYWORDS

chemical vapor deposition, advanced materials, functionalization, surface modification, membranes, thin films

1 | SIGNIFICANCE OF SURFACE MODIFICATION FOR THIN FILMS AND MEMBRANES

Since their emergence, thin films and membranes have undergone several revolutionary transformations, which resulted in evolution of new features and extending their applications. One of the radical elements in this journey has been diversification in the nature and type of materials employed for fabrication of a wide variety of thin films and membranes. This has been the consequence of the numerous investigations on the exploration of candidate materials with attractive characteristics.^{1–5} However, the chance of success in identification of materials that could simultaneously meet the physicochemical as well as the performance requirements for the intended applications merely based on their inherent characteristics has been very low. So far, only limited number of materials have succeeded to be techno-economically viable without needing any sort of modification or alternation for thin film or membrane applications. Therefore, numerous materials could only enter into development, commercialization and market phases after undergoing appropriate manipulations to overcome their shortcomings or to improve certain features based on the requirements. Therefore, parallel to the continued research on discovery and synthesis of new materials possessing advanced features, significant opportunities have been emerged for extensive examination of existing materials to boost their properties with the aid of modification techniques.

As an essential enabler, substantial progress and advances have been accomplished on the modification techniques in order to enable tuning the properties and structure of thin films and membranes. For instance, reverse osmosis (RO) membranes employed for desalination are required to exhibit certain combinations of water flux and salt rejection aside to having sufficiently high chemical and mechanical stability. Similarly, special attention must be paid to their surface properties due to their high tendency toward fouling which has serious impacts on the performance and longevity of the membranes. Another example is the packaging films which are extensively used especially in food, medical and electronic industries. In fact, the barrier characteristics of

such films must be extremely high against the diffusion of target species (e.g., water vapor, oxygen, etc.) to protect the content. Often, it is required to consider some delicate aspects such as the difference between the types of gases that could permeate through the film due to the different transport properties of gases in permeation. Aside from the possibility for the modification of the entire material used for the film fabrication, a smart option would be to impart the desired property in a smaller scale but with a same efficiency via surface modification. Obviously, there exists many more cases that can highlight the significance of surface modification techniques for thin films and membranes in order to achieve the expected properties.⁶

Selection of an appropriate surface modification technique depends on the prevailing scenarios. One is that the material opted for surface modification is expensive so that it is not economically justifiable to extend it for the formation of the entire bulk phase of the film or the membrane. In this case, just a thin layer of such performance material would be sufficient to be applied on another affordable material serving the bulk phase. Another case is when formation of bulk phase from the performance material is not possible due to technical or processing limitations, complexity of processing, or imparting undesirable effect to the morphology, operation, or performance. Another prevalent scenario for the surface modification is the need for exploitation of distinct features of materials into a single integrated unit. This can be especially advantageous for the polymeric materials due to their low surface energy, which prevents them from the employment of conventional modification techniques. All above situations have contributed to the widespread growth and diversification of surface modification and functionalization techniques applicable to thin films and membranes.

Classically, modifications of thin films and membranes, and other similar structures, can be accomplished through adoption of either chemical or physical routes. According to the chemical techniques, one or multiple materials with chemical functional groups are needed to initiate the modification. In majority of chemical techniques, the extent of modification can be limited to a single atomic layer up to nanometers and sometimes with progression into the bulk depending on the conditions. On

the other hand, the physical route for the modification of surface can be accomplished through heat treatment, annealing or pyrolysis, with or without the involvement of external materials. In contrast to the chemical route, the physical modifications often can have impacts on the bulk phase though it might not be favorable. Therefore, the nature, degree, and the consequences of modifications by chemical and physical routes is different and can be controlled by adjusting process parameters.

Another peculiar aspect with regards to the surface modification arises from the consideration of shape and geometry which distinguishes thin films and membranes from other systems due to presence of a relatively large surface to volume ratio. Considering this and due to the distinct characteristics of surface phenomena, the behavior and physicochemical properties of thin films and membranes should be explained with special attention. Importantly, often the functionality and performance of thin films and membranes are largely associated to the interactions occurring between the component and the membrane at the interface. All these properties regulate the transport properties of species through them depending on the governing mechanisms. This has motivated numerous investigations and innovations. For instance, instead of using a highly expensive material for membrane fabrication, only the surface of a regular membrane can be modified by a fraction of a functional material to obtain desirable surface characteristics at an affordable costs.^{7,8}

Parallel to the rapid growth in diversity and applications of thin films and membranes, the relevant modification methods have evolved to address the new needs.^{9,10} Among them, techniques based on chemical vapor deposition (CVD) have received a great attention in recent years.¹¹ This is largely due to the exclusive features offered by the CVD techniques that enable formation of highly selective, uniform, and conformal thin coatings onto the surface. On account of these merits, application of CVD techniques for modification of thin films and membranes has grown significantly.^{12,13} Figure 1 shows the number of publications as documents and patents generated in the field of CVD modifications of thin films and membranes during the period of 2010–2022. It is interesting to note that the number of patents filed in this period are considerably larger than that of research and scientific documents. This corresponds to more than 193,000 patents filed on CVD modification of thin films and more than 69,000 patents concerning membranes. This sums to more than 262,000 patents filed by the United States Patent & Trademark Office (USPTO) as well as the Japan Patent Office (JPO). This may be regarded as the large potentials and attractiveness of CVD modification of thin films and membranes for industrial applications. This may also be an indication of the considerable number of research activities in the field

that have enabled transition into the development and commercialization phases. From another perspective, the number of scientific publications on CVD modification of thin films (~5300 documents) is more than 2.5 times of membranes (~2000 documents). These are to some extent reasonable records and match the expectations especially by considering the fact that often membranes are categorized as a sub-category of thin films.

Another interesting observation from Figure 1b is that in the selected period, the number of patents filed on the CVD modification of thin films by the USPTO has been considerably larger than that by JPO. However, the trend has been slightly different in the case of CVD modification of membranes. It can be noted that during 2010–2018, the number of patents filed by JPO has been greater than that by USPTO. Interestingly, after this period till now, the trend has reversed. These numbers provide useful insights on the directions in the industrial progress in the field and may be an indication of the amount of investments and resources devoted to these highly demanding subjects.

Overall, these trends confirm that the pace of growth in the field is remarkably high, and this makes it essential to continuously monitor and track the status of progresses and achievements. A survey in literature reveals that a few reviews have been released over the past years that directly or indirectly cover the progresses in some of the important aspects of CVD modification for thin films and membranes. Among the most relevant ones, Mavukkandy et al.¹⁴ provided a review focusing on different thin film deposition techniques including their general features. In this review, CVD processes were discussed as a sub-section though without providing details and conditions governing the process of modification. In addition, the review was limited to the progresses made in the field of membranes and focusing on the water treatment applications. Thus, no information was provided related to thin films. The review conducted by Chen et al.¹¹ focused on two techniques of CVD modification including iCVD and oCVD polymerization dedicated to thin films. In this review, some of the applications of these techniques for surface engineering, device integration and protective layers were analyzed by highlighting some exemplary cases. On the other hand, the focus in the reviews by Zhao et al.¹⁵ and Yu et al.¹⁶ was on the materials and general applications though among the wide variety of CVD techniques, only iCVD was taken into consideration for extensive discussions. Analysis of the other review papers released in this subject shows that they were successful in covering no more than progresses in some specific applications of CVD modified films and membranes.

Table 1 provides an overview of the review papers available as of now. A careful analysis of the coverage and contents of these reviews motivated the authors to plan for

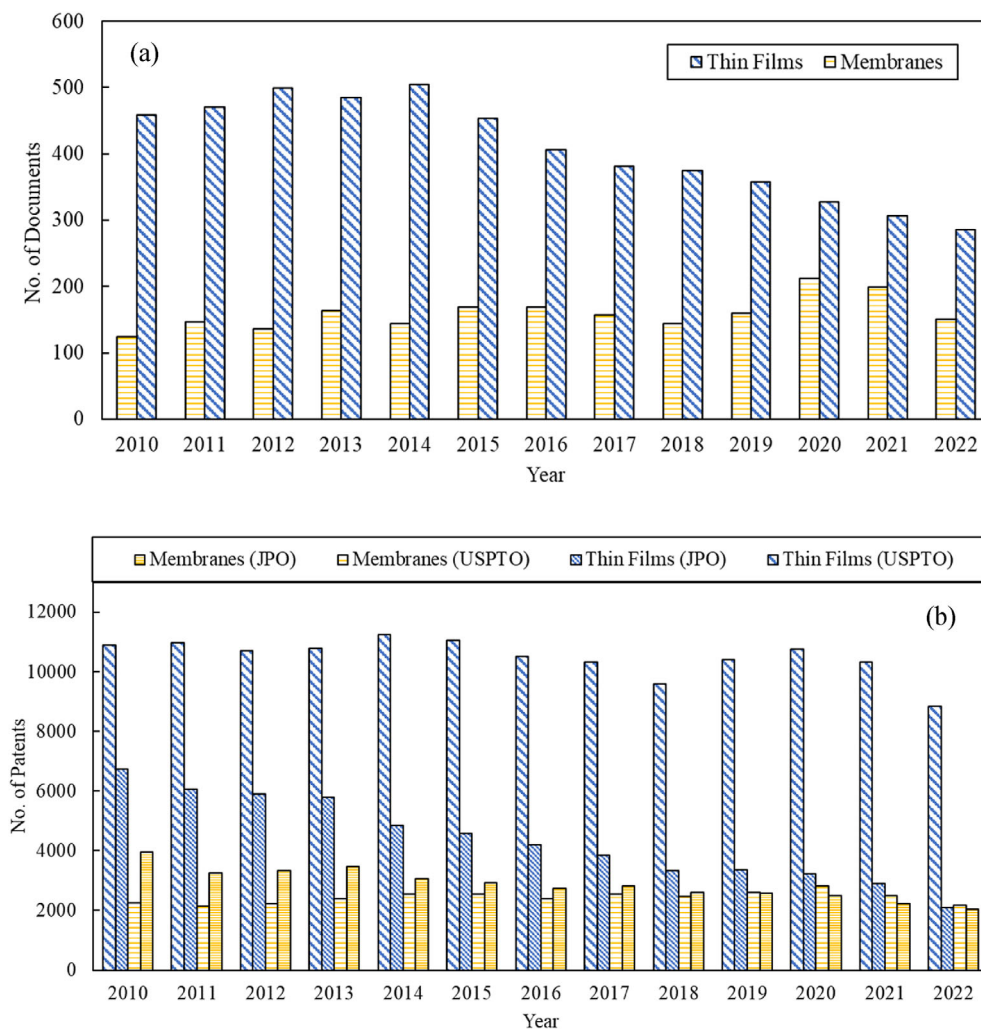


FIGURE 1 An overview of the number of (a) published documents (research, scientific, technical, etc.) and (b) filed patents in the field of CVD modification of thin films and membranes in the period of 2010–2022 (Source: Scopus, Updated: November 20, 2022; USPTO: United States Patent & Trademark Office; JPO: Japan Patent Office). [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/app.53720)]

the present review with the aim of providing an update on the research activities conducted in the field, especially in the recent years, in a more structured classification. Another objective was to fill the identified gaps by devoting comprehensive discussions. This review also serves to highlight the prevailing trends and to set direction for the future activities in the field especially in the domains of technique, materials as well as applications.

In the present review, firstly, the essence and significance of modification techniques for functionalization of thin films and membranes are elaborated. This is followed by providing a classified introduction of prominent chemical and physical modification techniques applicable to thin films and membranes and discussion on the principles, features, and prominent aspects of each technique. In subsequent sections, contents are focused to the CVD-based modification techniques and its derivatives and underpinning the differences in between. A separate section is devoted to the principles of material selection for CVD processes including discussions on the role and functionality of substrates, modifying materials and precursors in the characteristics and performance of CVD

process. Insights are also provided on the crucial parameters involved in the implementation of CVD techniques by scrutinization of the effect of each individual parameter on the ultimate product. Furthermore, special attention is paid to the extended applications of CVD modified and functionalized thin films and membranes divided into four main categories of desalination and water treatment, energy and environment, biomedical and life science, as well as packaging. Elaborative explanations are made for each category along with the provision of notable examples. Finally, conclusions drawn based upon the analysis of the examined works in tandem with providing recommendations for future activities in the field.

2 | CHEMICAL MODIFICATION TECHNIQUES

2.1 | Chemical vapor deposition

Surface modification and functionalization by chemical vapor deposition (CVD) is accomplished by direct

TABLE 1 An overview of the review papers released during the past two decades directly devoted to chemical vapor deposition (CVD) modification of thin films and membranes.

Year	Key subject(s)	Technique(s)	Focus and applications	No. of references covered	Ref.
2003	Coatings	CVD	Techniques, systems, comparisons, principles, thermodynamics and kinetics, mass transport, process parameters, morphology, and microstructure	421	17
2003	Barrier coatings	CVD	Thermal, plasma, and laser CVD	31	18
2005	Thin films	CVD	Dielectric materials	139	19
2005	Engineering surfaces	CVD	Corrosion and wear protection, thermodynamics, kinetics, design, and technological	90	20
2006	Films	CVD	Precursor design and novel CVD technologies	79	21
2011	Films and membranes	CVD	Chemical design, deposition mechanism, sensors, biotechnology, microelectronics/organic electronics, microfluidics, MEMS, composites, and membranes	235	22
2013	Silica membranes	CVD	Hydrogen separation	129	23
2013	Polymeric films and coatings	iCVD	Functional and responsive coatings	63	24
2015	Films and droplets	iCVD	iCVD for liquid substrates, optics, sensing, and separations, free-standing films, nanoparticles, encapsulated droplets, polymer–liquid gels, and heterogeneous films	109	25
2016	Thin films	iCVD oCVD	Novel nanostructures, process studies and tuning CVD polymers, antibiofouling, biomass extraction, anti-icing, anti-hydrate, stimuli-responsive polymers, biocompatible polymers, device integration, protective layers	116	11
2018	Films	iCVD	Electronic devices, surface treatments (hydrophobic, membranes, adhesives, microstructures, patterning, microfluidics), biomedical applications	178	16
2019	Thin film	PVD, CVD	Simulation, electronic component and display solid surface coating and biomedical, optical coating and optical data storage devices	139	26
2020	Polymeric membranes	Interfacial coating, CVD, PVD, ALD, ECD, EBD	Water treatment	230	14
2020	Membranes	iCVD, iPE-CVD, SLID, ALD/MLD	Sustainable separations	78	15
2021	2D materials and polymer thin films	CVD	Instrument construction, process control, material characterization, reproducibility, scale up	209	27
2021	Thin films	CVD	Green CVD and Sustainability aspects of CVD	41	28
2022	Membranes	PECVD, PPECVD, iCVD	Polymer electrolyte membranes for fuel cells	186	29
2022	2D materials	CVD	Modeling, simulation, and machine learning	174	30

Abbreviations: ALD, atomic layer deposition; CVD, chemical vapor deposition; EBD, electron beam deposition; ECD, electrochemical deposition; iCVD, initiated chemical vapor deposition; iPE-CVD, initiated plasma-enhanced chemical vapor deposition; MLD, molecular layer deposition; oCVD, oxidative chemical vapor deposition; PECVD, plasma-enhanced chemical vapor deposition; PPECVD, pulse plasma enhanced chemical vapor deposition; PVD, physical vapor deposition.

deposition or coating of certain functional materials onto the surface of a substrate involving a chemical reaction. The process is often followed by

immobilization and stabilization steps for completion. Typically, a gas mixture containing volatile precursors and reactants is flown over the surface of intended

substrate with the aid of a carrier gas. This creates the opportunity for immediate interactions to begin through nucleation and growth mechanism which leads to the formation of a coating. For example, a mixture of NH_3 and SiH_4 can be used for deposition of a thin layer of silicon nitride (SiN_x) on the surface.

The advantageous features of CVD are enabling formation of the uniform, conformal and controlled thin layers onto the surfaces at an acceptable deposition rate at affordable costs. Such layers can be impermeable or highly selective due to the presence of tunable tiny pores. Thus, CVD based films and membranes are well suited specially for the retardation or separation of a diverse range molecules sizing in the angstrom to nanometer size. However, some aspects such as operation at high temperatures, need for high vacuum as well as toxicity of some of the precursors have been among the disadvantages of CVD-based coatings. Thanks to the progresses made over the years, some of the challenges such as high vacuum and temperatures have been addressed to a great extent. Importantly, extensive investigations in this field have led to the emergence of novel CVD-based techniques and are discussed in the following sections.^{31–33}

2.2 | Atomic layer deposition

Atomic layer deposition (ALD) is among the most resembling techniques to CVD since they share several features with just minor differences. Like CVD, a volatile precursor is used in ALD as the source to perform deposition. However, in contrast to simultaneous introduction of precursors and reactants to the chamber in CVD, each precursor and reactant is entered in sequence in ALD. This gives the opportunity to precisely control the deposition properties as well as to tune the thickness in the atomic range.³⁴ Although ALD brings many advantages such as uniformity and conformity, the precursors used in ALD often need to be more reactive than those used in CVD due to the sole presence of surface reactions.¹⁴ In recent years, ALD has been used for the modification of various organic and inorganic thin films and membranes particularly to impart hydrophilic characteristics and for accomplishing tailored surface engineering^{35–37}

2.3 | Grafting

Grafting is a popular modification and functionalization technique and has been applied to a diverse range of thin films and membranes. In this technique, specific molecules create chemical bonds with the functional moieties present at the target surface to enhance the existing

characteristics or to impart new features such as hydrophilicity, certain affinity or functionality, etc.³⁸ The grafting can be accomplished via different methods such as plasma irradiation, photo-induced grafting, gamma ray, electron beam, thermal-induced, ozone-induced, redox, metal ions-initiated and chemical grafting. When there exist functional groups such as $\text{C}=\text{C}$ bond (e.g., in poly(1-trimethylsilyl-1-propyne), PTMSP) in a repeating unit of a polymer, a variety of monomers can be grafted onto the surface via photo- or heat-induced grafting. It has been demonstrated that the surface graft polymerization of poly(ethylene glycol) behenyl ether methacrylate onto the PTMSP membrane resulted into a highly-ordered structure and a lamellar morphology.³⁹ In the case of plasma irradiation for grafting monomers onto the surface, which is very similar to PECVD, the membrane or film is placed in a plasma reactor and by using a specific gas (e.g., oxygen), the formed radicals can readily bound to the modifying material.

However, the great limitation associated to grafting techniques is that they are only applicable to functional polymers. Furthermore, it is difficult to use them at industrial scales since process control can sometimes be challenging and the pores may also undergo substantial changes if not properly adjusted. Also the overall cost can be considerably high.^{40,41} In a study, Rong et al. modified carbon fibers by carbon nanotubes (CNT) with two different methods of chemical grafting and CVD.⁴² In terms of morphology, they found that chemical grafting modification led to a random orientation of CNTs on the surface while in the CVD method, CNTs were vertically attached to the fibers. Although this perpendicular growth reduced the flexibility, a better interfacial bonding could be obtained. Another identified advantage of the CVD method over chemical grafting is the improved tensile and flexural strengths by 11% and 15%, respectively.

2.4 | Sol-gel

Coating by sol-gel is one of the most desirable techniques especially for flat surfaces such as membranes and thin films. Sol-gel possesses wide variety of benefits compared to its rivals. Various metal alkoxides have been used as a precursor for metal oxide membranes. One of the most widely employed precursors is titanium tetraisopropoxide (TTIP), which is deposited onto the porous alumina support and is converted into crystalline TiO_2 upon calcination at $450\text{--}550^\circ\text{C}$.⁴³ The porous crystalline TiO_2 membrane plays a pivotal role as a photocatalyst in removing and filtering pollutants in wastewater treatment applications.

In order to control the morphology and the size and structure of pores, use of nanostructured polymer

templates such as block copolymer and graft copolymer has been recommended.^{44–46} The hydrophilic precursor has preferential interactions with the hydrophilic polymeric chains to form the membrane matrix after calcination while the hydrophobic polymer chains are exhausted to generate the pores. In an investigation, Mombeshora et al.⁴⁷ compared the final characteristics of the nanocomposites made of sol-gel and CVD and realized that those made with latter method had better thermal stability, uniformity, smoothness and crystallinity.

3 | PHYSICAL MODIFICATION TECHNIQUES

3.1 | Electrophoretic deposition

Electrophoretic deposition (EPD) is a method of coating in which charged colloidal particles that exist in a liquid medium (e.g., alcohol) immigrate to an electrode in the presence of an electrical field. This method has some benefits including formation of uniform coatings, a high deposition rate, control over the thickness and effective deposition of ceramic materials.^{48,49} To proceed with EPD, the substrate should be conductive and able to function as an electrode. This is considered as a key limitation of this method for modification of membranes.

3.2 | Sputtering

Sputtering is a technique in which the deposition of elements onto the thin films occurs through ablation of the target by ion bombardment in a plasma phase and redeposition of the ablated material on a substrate. This technique is a physical vapor deposition (PVD) and has been widely used in industry owing to the feasibility of coating large surface areas. Conceptually, materials are extracted from a negatively charged source (cathode) with the help of an inert gas (e.g., argon) for plasma activation. Subsequently, argon atoms are hit by electrons transferring from cathode to anode and the collisions lead to creation of argon ions. Finally, the sputter target is bombarded by a part of Ar^+ ions.

Different methods of sputtering are used including magnetron sputtering, ion beam-assisted sputtering and radio frequency sputtering. Also, if the reaction takes place between bombarding reactive ions and surface, the process is called chemical sputtering or reactive ion etching.^{50,51} Sputtering has some advantages over CVD including operations at lower temperatures, absence of precursors and versatility in terms of materials; whilst CVD techniques have shown in general a better coating performance and higher deposition rates.

3.3 | Dip coating

Dip coating is one of the most popular industrial techniques for surface manipulation. As it can be inferred from its name, the substrate is firstly immersed in a coating solution and then removed to be drained. In this course, solvent is evaporated, and a thin layer of coating material remains at the surface. Despite its simplicity, dip coating can have some drawbacks including low coating quality and nonuniformity depending on the types of samples and process conditions.⁵²

As a sub-category of dip coating, the layer-by-layer (LbL) assembly of membrane has received lots of attention.^{53,54} Membrane with high water flux and salt rejection values were prepared by this method for desalination applications. For example, polyelectrolyte membranes were prepared by repeated dip coating of polycation and polyanion solutions⁵⁵ and graphene oxide (GO) membranes were prepared by dip coating of negatively charged GO on a positively charged membrane surface.⁵⁶ A variety of physicochemical properties such as surface hydrophilicity, charge property, free volume, membrane morphology and pore structure can be tuned by a number of deposition cycles, deposition time, solution concentration, deposition pressure, and temperature.

3.4 | Bar coating

This technique is effective in forming uniform surface and constant thickness together with high reproducibility and has been widely used for in case of gas separation membranes and polymer electrolyte membrane fuel cells.⁵⁷ The thickness can be controlled from 10 μm to 100 nm by adjusting some parameters such as bar thickness, solution concentration and viscosity. Low viscosity of polymer solution often leads to formation of defects due to rough and nonuniform surface topology of the porous support. Accordingly, concentration and viscosity of polymer solution should be precisely optimized to obtain desired membrane thickness. Mixed-matrix membranes (MMMs), in which porous inorganic fillers are dispersed in a dense polymer matrix can be effectively prepared by the bar coating method.^{58–60} A variety of nanoporous inorganic materials such as GO and metal-organic frameworks (MOFs) has been used as filler, resulting in improved permeability and performance of MMMs for gas separations.⁶¹

3.5 | Spin coating

This is a low-cost, simple, facile, and fast method for formation of a thin film onto a porous support. In contrast

to the bar coating, a low viscous solution can be utilized for making a uniform coating with minimum defects using spin coating. The method has been widely used for the preparation of GO-based membranes for desalination and gas separation applications.^{62,63} For instance, poly(dimethyl siloxane) (PDMS) membranes with large free volume and an improved gas/vapor permeability were successfully fabricated by spin coating using a solution containing a mixture of monomer and curing agent in hexane.^{64,65} The thickness of dense PDMS membrane varies depending on the coating speed, duration, and annealing temperature. Nevertheless, due to the nature of this process, it is not scalable and thus its applications have remained limited to the small size samples.

3.6 | Spray coating

Spray coating is another effective and powerful method especially for minimizing the pore penetration and is well appropriate for fabricating inorganic porous membranes. For example, spray coating was used to prepare inorganic alumina (Al_2O_3) membrane with excellent performance for microfiltration (MF).⁶⁶ It was reported that the air gaps inside the porous support play a pivotal role in preventing infiltration of the particles into the surface pores. For the preparation of inorganic membranes, a polymer binder such as PVA or poly(vinyl pyrrolidone) (PVP) is typically added into the inorganic powder suspension in a solvent to increase the viscosity of solution. The calcination conditions such as temperature and time directly affect the membrane morphology, pore size, pore distribution, and pore connectivity. A polymer membrane can also be prepared by spray coating method, for example, polysulfone-poly(ethylene glycol) (PSf-*b*-PEG) block copolymer membranes have been successfully fabricated onto the macroporous substrates.⁶⁷ Pebax block copolymer thin film membranes were also prepared on a porous PSf support using direct spray coating method for CO_2 capture applications.⁶⁸ It is worthwhile to mention that spray coating does not necessarily need a gutter layer, and this simplifies the process. However, it has been claimed that the performance of spray coated membranes, especially in terms of CO_2 permeance, was lower than those with a gutter layer.⁶⁹

3.7 | Thermal evaporation

In this technique, which is also known as vacuum evaporation, a volatile source material is heated under vacuum until it is vaporized and then is brought in contact with a substrate where it is solidified and forms a layer on the

surface. The energy for thermal evaporation can be supplied by diverse sources such as a resistive wire tungsten coil and electron beam. This is a simple method of coating with more affordability than other PVD techniques, but coating complex surfaces like membranes by this technique is not trivial and sometimes can be challenging.^{14,26}

3.8 | Thermal spraying

Thermal spraying is method of coating in which a heat source like an external flame or plasma power is used to melt the fine particles. The molten material is then carried into contact with a substrate surface by spraying and is cooled to form a coating. There are versatile techniques of thermal spray coating namely flame spraying, plasma spraying, warm spraying, cold spraying, high velocity oxygen fuel (HVOF) spraying, high velocity air fuel (HVOF) spraying, vacuum plasma spraying, arc metallization, and detonation gun spraying. The main advantage of thermal spraying over other methods is its high deposition rate.^{49,70} Also, in comparison to CVD, the coating obtained by thermal spraying can offer higher porosities and lower bond strengths.

3.9 | Blending

Blending is one of the most favorable modification techniques by which the intended functional materials such as polymers and nanoparticles are mixed with the main substrate material to impart the desired properties. In this type of modification, the resultant film or membrane will have new characteristics such as hydro-philicity/phobicity, improved mechanical strength, certain affinity etc., which is a shared combination of the properties of constituents.⁷¹ For example, a hydrophilic water-soluble polymer such as PEG and PVP have been blended with hydrophobic polymer matrices such as PSf or poly(vinylidene difluoride) (PVDF) for ultrafiltration (UF) and MF applications. However, the hydrophilic homopolymer can be leached out of the membrane during the operations in aqueous environments and reducing hydrophilicity and water flux. A possible solution to circumvent this problem is to blend an amphiphilic block or a graft copolymer consisting of both hydrophilic and hydrophobic chains. During the phase inversion process, the surface segregation of hydrophilic segments of copolymer improves hydrophilicity and antifouling resistance of the membrane.⁷² Nevertheless, blending remains popular mostly due to its simplicity though finding highly compatible materials that can be blended in the

molecular level is not trivial. Another limitation of blending is that it is not limited to the surface modification and thus the bulk properties also undergo changes by this method.⁷³ Therefore, this may lead into the increased costs or adding extra resistance to the transport of species.

4 | CVD TECHNIQUES FOR THE MODIFICATION OF THIN FILMS AND MEMBRANES

4.1 | Pressure-sensitive CVD techniques

CVD modifications can be carried at different parameter settings such as pressure and energy sources and can involve a number of distinct protocols. Alternation of these parameters subsequently leads into distinguished outcomes. Considering the operational pressure as an important parameter, CVD techniques can be classified into four major categories of: atmospheric pressure CVD (AP-CVD), low pressure CVD (LP-CVD), high pressure CVD (HP-CVD) and ultrahigh vacuum CVD (UHV-CVD) which are introduced and discussed in this section.

4.1.1 | Atmospheric pressure CVD

AP-CVD is the most common variant of CVD and can produce thin films onto the surface of substrates when exposed to one or more volatile precursor at close to atmospheric pressures. The attractive features of depositions made by AP-CVD are exceptionally low diffusivity coefficient and high deposition rate. In addition, it can serve as a critical step specially for the preparation of graphene-based devices. As can be seen in Table 2, different popular substrate materials such as graphene,⁷⁴ zeolite,⁷⁵ alumina^{76,77} and silica^{78,79} have been successfully modified by this technique. Particularly, high-temperature AP-CVD processes are gaining more attention in technologies such as solid-state electronic devices, such as high quality epitaxial semiconductor films for silicon bipolar and metal oxide semiconductor transistors.⁸⁰ AP-CVD has also been recommended for surface finishing of delicate parts such as turbine blades to improve lifetime and performance and also energy storage systems.⁸¹

4.1.2 | Low pressure CVD

In contrast to AP-CVD, LP-CVD operates at lower pressures. Also, heating is applied instead of using a carrier

gas to reduce the possibility of unwanted gas phase reactions and particle contamination. This process advantageous for creating uniform thin films onto the substrates and has been widely used for surface coating of films, though only a few studies have focused on its use for the modification of separating membranes.⁸² A representative schematic of a LP-CVD system and its operation concept is illustrated in Figure 2. Recently, Lee et al.⁸³ used LP-CVD to prepare an efficient gas permeable membrane made of nanoporous single-layer graphene (NSLG). The applied pressure was 460 mTorr for the nucleation and growth to begin by which the SLG film was formed in the presence of CH₄ and H₂. Following this approach, formation of the crack which is very detrimental for the gas separation was eliminated. LP-CVD was also used by Chen et al.⁸⁴ for the formation of a SiC layer onto the alumina substrate for the purpose of oily water treatment. The deposition pressure and temperature were set to 60 Pa and 750°C, respectively, while the SiH₂Cl₂/C₂H₂ with ratio of three to one was used as a precursor and this resulted in formation of a thin coating with desirable characteristics. The advantage was considerable reduction in the time and cost of the process due to elimination of sintering. In addition, the tunability of the surface pores by formation of thin layers enabled considerable lowering of the membrane susceptibility toward fouling.

4.1.3 | High pressure CVD

HP-CVD technique takes place at elevated pressures typically above the atmospheric. This method is sometimes regarded an alternative to LP-CVD, especially for the cases which application of LP-CVD results in formation of uneven depositions.⁸⁵ Despite the common use for thin films, this technique has not been widely practiced for modification or functionalization of membranes. Just one study found in which cylindrical dead-end silica membranes fabricated by HP-CVD through feeding TMOS source from the membrane side of the reactor while oxygen was fed from the support side to promote the reaction.⁸⁶ As a result, a dense silica film was deposited and offered a hydrogen permeance of 5.0E–8 mol m⁻² s⁻¹ Pa⁻¹ at 573 K, with H₂/CH₄ and H₂/CO₂ selectivity exceeding 24,000 and 1200, respectively.

4.1.4 | Ultrahigh vacuum CVD

In UHV-CVD method, the reactor pressure is kept at extremely low levels to achieve high purity, especially when the precursors can react and generate a binding with the residual gasses. This process is often performed

TABLE 2 The specifications of various chemical vapor deposition (CVD) techniques and the governing conditions used for the modification of several thin films and membranes.

Substrate	Functional material	Precursor/reactant/carrier gas (i: initiator)	Technique	Temperature (°C)	Working pressure (Pa)	Ref.
Ti foil, Ni foam	Pt	Pt(S ₂ CNiBu ₂) ₂	AA-CVD	500	10,132.5	140
Yttrium-stabilized zirconia (YSZ)	Nickel-plated YSZ	CH ₄	AP-CVD	900	10,132.5	74
Stainless steel	Zeolite (ZSM-5)	Cr(acac) ₃ /N ₂	AP-CVD	550	11,000	75
α-Alumina and γ-alumina	Silica	TMMOS/TEOS/Ar	AP-CVD	650	10,132.5	78
α-Alumina and γ-alumina	Silica	TMOS/Ar, MTMOS/Ar, DMDMOS/Ar	AP-CVD	650	10,132.5	79
α-Alumina and γ-alumina	Silica-zirconia	TEOS/ZTBO/Ar	AP-CVD	650–700	10,132.5	76
α-Alumina and γ-alumina	Silica	VTES/Ar	AP-CVD	600	10,132.5	141
α-Alumina and γ-alumina	SiO ₂ /ZrO ₂	TEOS/ZTB/Ar	AP-CVD	650	10,132.5	77
PET	SiOx	CH-liquid/isopropanol	CCVD	–	–	142
PEN	SiN	HMDSN:N[Si(CH ₃) ₃] ₂	CCVD	100	2.67	143
α-Alumina and γ-alumina	Silica	DMDPS/N ₂	CD-CVD	600	–	144
α-Alumina and γ-alumina	Silica	HTMOS/N ₂	CD-CVD	125	–	145
α-Alumina and γ-alumina	Silica	PrTMOS, TFPrTMOS/N ₂	CD-CVD	100–270	–	146
α-Alumina and Ni-γ-Al ₂ O ₃	SiC	SCB/Ar	CD-CVD	515	–	147
α-Alumina and γ-alumina	Silica	TMOS/N ₂ , HMDSO/N ₂	CD-CVD	600	–	148
α-Alumina and γ-alumina	Silica	DMDMS/N ₂ , TMOS/N ₂	CD-CVD	–	–	149
α-Alumina and γ-alumina	Silica	DPhDMOS/N ₂ , PhTMOS/N ₂	CD-CVD	230–400	–	150
α-Alumina and γ-alumina	Silica	HTMOS/O ₂ /N ₂	CD-CVD	420–520	–	151
α-Alumina and γ-alumina	Silica	TPMS/O ₂ /N ₂	CD-CVD	600	–	152
Cu foil	Graphene	CH ₄ /H ₂ /Ar	Cold-wall CVD	1000	1066.6	153
α-Alumina and γ-alumina	Silica	APMDES/N ₂	CVD	650	1–1.5E5	154
Nylon net	<i>n</i> -(C ₅ H ₅ NO ₂)	Pyrrole-3-carboxylic acid	CVD	135	–	155
α-Alumina and γ-alumina	Silica	TEOS/ATSB, DMDMOS/O ₂ , DMDMOS/ATSB/O ₂	CVD	650, 500, 500	–	156
SSHF	CNT	C ₂ H ₄ /H ₂	CVD	700	–	157
SPPO	Propylene	–	CVD	650–700	–	158
α-Alumina, γ-alumina and ZSM-5	Carbon	Ethylene/N ₂ , <i>n</i> -hexane/N ₂	CVD	550–800	–	159
α-Alumina and ZnO	ZIF-8	2-HmIM/methanol	CVD	125	–	160

TABLE 2 (Continued)

Substrate	Functional material	Precursor/reactant/carrier gas (i: initiator)	Technique	Temperature (°C)	Working pressure (Pa)	Ref.
Mullite	CNT	CH ₄ /H ₂	CVD	600	–	161
PET	Parylene C	Parylene	CVD	25	1.3	162
Alumina	Silica-alumina	TEOS/ATSB/Ar	CVD	650	–	163
α-Alumina and γ-alumina	Silica	VTES/Ar	CVD	600	10 ⁵	141
α-Alumina and γ-alumina	Silica	VTES/Ar	CVD	600	–	164
α-Alumina–γ-alumina	Silica-zirconia	TEOS/ZTB/Ar	CVD	650	–	164
α-Alumina–γ-alumina	Silica	HTMOS/O ₂ /N ₂	CVD	450	–	165
PLGA	NMP	–	CVD	Ambient	–	166
PET	SiO _x N _y	SiH ₄ /Ar	ICP-CVD	23	0.79	167
PLLA	SiO _x	HMDSO/O ₂	ICP-CVD	25	–	168
PEN	SiN _x	TSA, N(SiH ₃) ₃ /NH ₃	ICP-CVD	28–30	66.7	169
PCL	SiO _x	HMDSO/O ₂ /Ar	ICP-PECVD	–	20	170
PP	PHDFA	HDFA i: TBP	iCVD	290	26.7	171
PVDF	PTFE	HFPO i: hydroquinone	iCVD	350	40–160	172
PAN	pDVB	DVB i: TBPO	iCVD	300	20	173
PA	4-VP-co-EGDA	4VP/EGDA i: TBPO	iCVD	220	60	174
Al ₂ O ₃ /SiO ₂ /CaCO ₃ /MgO	PPFDA	PFDA i: TBP	iCVD	220	600	175
PLA	PMAH	MAH, MAA, TBP	iCVD	200	–	176
PCTE	pDVB	DVB i: TBPO	iCVD	60	106.7	177
PCTE-pDVB	pC6PFA	C6PFA i: TBPO	iCVD	80	25.3	177
Polyester	PHFDMA	HFDMA i: tBuOOH	iCVD	210	10.7	178
PVDF	PPFDA	PFDA i: TBPO	iCVD	210	6	179
Nylon	pPFDA	PFDA i: TBPO	iCVD	–	–	180
Nylon	pDVB	DVB i: TBPO	iCVD	–	–	180
PA	HEMA-co-PFDA	HEMA/PFA i: TBPO	iCVD	210	26.66	181
PA	HEMA-co-PFDA	HEMA/PFA i: TBPO	iCVD	210	26.66	182
PTMSP	P(DVB-co-ZnTPC)	Styrene/DVB/Ar–ZnTPP/Ar i: TBPO	iPE-CVD-PECVD	250	0.5	183
Cu foil	Graphene	CH ₄ /H ₂	LP-CVD	1000	61.3	83
α-Alumina	SiC	DCS/C ₂ H ₂ /H ₂ /N ₂	LP-CVD	750	60	84
PSSF and ZSM-5	Cu	Cu(acac) ₂	MOCVD	350	10 ⁴	112

(Continues)

TABLE 2 (Continued)

Substrate	Functional material	Precursor/reactant/carrier gas (i: initiator)	Technique	Temperature (°C)	Working pressure (Pa)	Ref.
PET	a-SiN _x :H	NH ₃ /SiH ₄	MW-PECVD	45	9	98
PET	SiO _x	HMDSO/O ₂	MW-PECVD	–	25	184
AAM	CNNT	Melamine/Ar	noncatalytic CVD	520	–	185
PDMS	SiO _x C _y H _z	HMDSO/O ₂	PECVD	–	5	186
PA	PANI	Aniline/O ₂	PECVD	45	20	187
PA	AA	MMA	PECVD	60	–	188
PA	AA	AA	PECVD	60	–	189
PLA	SiO _x	HMDSO/O ₂ /Ar	PECVD	–	30	190
PEI	Silica	TEOS/O ₂ /Ar	PECVD	55	–	191
PEI	SiO _x C _y	HMDSO/TFT/N ₂	PECVD	–	–	191
PET	SiO _x	HMDSO/O ₂	PECVD	–	5	192
PET	a-SiN _x :H/ n--SiO _x N _y / h-SiO _x	SiH ₄ /NH ₃ /N ₂	PECVD	–	5.3	193
PLA	SiO _x	HMDSO/O ₂	PECVD	–	–	194
PDMS	SiN _w O _x C _y H _z	HMDSO/N ₂ /Ar	PECVD	–	–	195
PEN	SiN _x	TSA/NH ₃	PECVD	–	40	196
PET	SiO _x N _y	–	PECVD	–	–	197
PEN	Poly(HMDSO)	HMDSO/O ₂ /Ar	PECVD	–	–	198
PET	SiO _x N _y	TMS/NH ₃ /O ₂	PECVD	70	27	199
Zeolite Y	APTES	APTES/Ar/O ₂ /N ₂	PECVD	80	50	200
PSf	AA, HEMA	AA, HEMA	PECVD	–	13.3	201
PET	SiON	SiH ₄ /N ₂ O/NH ₃ /H ₂	PECVD	100	200	202
PE	SiO _x	HMDSO/O ₂	PECVD	–	15	203
Zeolite 5A	PIn	Indene	PECVD	20	30	204
PEN	SiN _x	TSA/NH ₃	PECVD	25	40	205
Silica	Nanographite	CH ₄ /H ₂	PECVD	750	–	206
PEN	Silica	TEOS/O ₂ /N ₂	PECVD	–	10,132.5	207
PEN	Silica	TEOS/O ₂ /N ₂	PECVD	–	10,132.5	208
PET	SiO _x C _y H _z	HMDSO/O ₂	PECVD	–	25	209
PET	SiO _x	HMDSO/O ₂	PECVD	–	25	209
PET	a-CH	C ₂ H ₂ /Ar	PECVD	–	–	100
α-Alumina-SiO ₂ /ZrO ₂	Silica	HMDSO/Ar	PECVD	Ambient	10,132.5	210
PEN	Silica	TEOS/O ₂ /N ₂ /Ar	PECVD	–	10,132.5	211
-	SiN _x	SiH ₄ /NH ₃ /N ₂	PECVD	85	–	212
PET	Silica	TrMS/N ₂ /O ₂	PECVD	–	10,132.5	213
PET	SiO _x	N ₂ O/SiH ₄ /Ar	R2R-PECVD	45	9	32
PET	SiN _x	NH ₃ /SiH ₄ /Ar	R2R-PECVD	45	9	32
PEN	Silica	TEOS/O ₂ /N ₂	R2R-PECVD	–	10,132.5	207
PEN	Silica	TEOS/O ₂ /N ₂	R2R-PECVD	–	10,132.5	208
PEN	Silica	TEOS/O ₂ /N ₂ /Ar	R2R-PECVD	–	10,132.5	211
PET	SiN _x	NH ₃ /SiH ₄ /Ar	R2R-PECVD	45	9	214

TABLE 2 (Continued)

Substrate	Functional material	Precursor/reactant/carrier gas (i: initiator)	Technique	Temperature (°C)	Working pressure (Pa)	Ref.
PET	SiO _x N _y	TEOS/O ₂ /N ₂	RF-PECVD	–	8	215
PET	SiN _x	HMDSN/N ₂ /Ar	RF-PECVD	Ambient	0.14	216
PVDF	HMDSO	HMDSO/O ₂	RF-PECVD	–	2.67	101
Ni foil	Graphene	Soybean oil	Thermal CVD	800	–	217
α-Alumina and γ-alumina	Silica	TMOS/O ₂	HP-CVD	600	100,000	86

Abbreviations: 2-HMIM, 2-methylimidazole; 4VP, 4-vinylpyridine; AA, acrylic acid; AAM, anodic alumina membranes; AP-CVD, atmospheric pressure chemical vapor deposition; APMDES, aminopropylmethyldiethoxysilane; APTES, 3-aminopropyltriethoxysilane; ATSB, Aluminum tri-sec-butoxide; CCVD, combustion chemical vapor deposition; CD-CVD, counter-diffusion chemical vapor deposition; CNNT, carbon nitride nanotube; CNT, carbon nanotube; DMDMOS, dimethyldimethoxysilane; DMDMS, dimethoxydimethylsilane; DMDPS, dimethoxydiphenylsilane; DPhDMOS, diphenyldimethoxysilane; DVB, divinylbenzene; EGDA, ethylene glycol diacrylate; HDFA, 1H,1H,2H,2H-heptadecafluorodecyl acrylate; HEMA, 2-hydroxyethyl methacrylate; HFDMA, 3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10-heptadecafluorodecyl methacrylate; HFPO, hexafluoropropylene oxide; HMDSN, hexamethyldisilazane; HMDSO, hexamethyldisiloxane; HTMOS, hexyltrimethoxysilane; ICO-CVD, inductively coupled plasma-chemical vapor deposition; iCVD, initiated chemical vapor deposition; iPE-CVD, initiated plasma-enhanced chemical vapor deposition; LP-CVD, low pressure chemical vapor deposition; MMA, methyl methacrylate; MOCVD, metal organic chemical vapor deposition; MTMOS, methyltrimethoxyorthosilicate; MW-PECVD, microwave plasma enhanced chemical vapor deposition; PA, polyamide; PAN, polyacrylonitrile; PANI, polyaniline; pC6PFA, poly(1H,1H,2H,2H-perfluorooctyl acrylate); PCL, polycaprolactone; PCTE, polycarbonate track etch; PDMS, polydimethylsiloxane; pDVB, poly(divinyl benzene); PE, polyester; PECVD, plasma-enhanced chemical vapor deposition; PEI, polyetherimide; PEN, polyethylene naphthalate; PET, polyethylene terephthalate; PFA, perfluorodecylacrylate; PFDA, perfluoro decylacrylate; PHDFA, poly(1H,1H,2H,2H-heptadecafluorodecyl acrylate); PhTMOS, phenyltrimethoxysilane; PIN, polyindene; PLA, polylactic acid; PLLA, poly(L-lactide); PP, polypropylene; PrTMOS, propyltrimethoxysilane; PSf, polysulfone; PSSF, paper-like stainless steel fiber; PTFE, polytetrafluoroethylene; PTMSP, poly(1-trimethylsilyl-1-propyne); PVDF, polyvinylidene fluoride; R2R-PECVD, roll-to-roll plasma-enhanced chemical vapor deposition; RF-PECVD, radio frequency plasma enhanced chemical vapor deposition; SCB, silacyclobutane; SSHF, stainless steel hollow fibre; TBPO, tert-butyl peroxide; tBuOOH, tert-butyl hydroperoxide; TEOS, tetraethoxyorthosilicate; TFPrTMOS, 3,3,3-trifluoropropyltrimethoxysilane; TMMOS, trimethylmethoxysilane; TMOS, tetramethoxyorthosilicate; TPMS, triphenylmethoxysilane; TrMS, trimethylsilane; TSA, trisilylamine; VTES, vinyltriethoxysilane; ZNTPP, meso-tetraphenylporphyrin; ZTBO, zirconiumtertbutoxide.

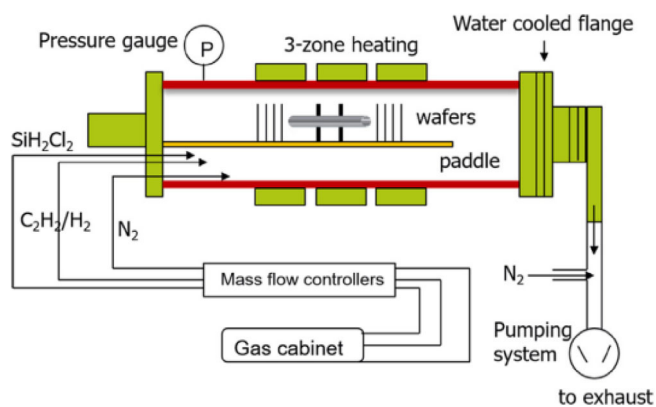


FIGURE 2 The schematic of a set-up designed for the modification of thin films and membranes via LP-CVD.⁸⁴ [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/terms-and-conditions)]

at lower temperatures compared to the conventional CVD techniques, in order to decrease the chance of dopant evaporation.⁸⁷ It should be noted that after dopant evaporation, which can happen at high temperatures, it is possible for the evaporated species to return to the surface and change the concentration of dopant. In a recent study, Byeon et al. well demonstrated the advantageous

features of using UHV-CVD compared to LP-CVD for the epitaxial growth of Si and SiGe in the absence of a carrier gas.⁸⁸

4.2 | Plasma-enhanced CVD techniques

Another alternative for the implementation of CVD is through enhancing it with the aid of plasma. During a PECVD process, the reactive species are not created by thermal fragmentation, as occurs in the most conventional CVD techniques, but rather it is accomplished within a plasma phase.⁸⁹ In principle, plasma is fed with the reactive gases and precursors and the species responsible for the deposition such as ions, radicals and neutrals are formed through the electronic collisions. PECVD processes are characterized by high versatility since precursors that are unreactive in other conditions can be activated in plasma phase. Due to the variety of possibilities, PECVD can be divided into few derivatives including atmospheric pressure plasma-enhanced CVD (AP-PECVD), direct-current plasma-enhanced CVD (DC-PECVD), initiated plasma-enhanced CVD (iPE-CVD), microwave plasma-enhanced CVD (MW-PECVD), radio-

frequency plasma-enhanced CVD (RF-PECVD), very high-frequency plasma-enhanced CVD (VHF-PECVD) and radical injection plasma-enhanced CVD (RI-PECVD) as the most attractive methods applicable to the membranes and thin films.

4.2.1 | Atmospheric pressure PECVD

As the common PECVD technique is often conducted at low pressures and there was a need to apply vacuum in the system, an atmospheric pressure plasma-enhanced CVD was introduced. This method resembles to a great extent to the low pressure PECVD, but it operates at ambient pressure which provides cost savings. This independency to vacuum also has eliminated the vacuum chambers as a size-limiting factor and simplified plasma parameters control. However, the notable weak points such as less purity and uniformity of the coating.⁹⁰

4.2.2 | Direct current PECVD

In this method, a vacuum pump is required to create a low-pressure chamber. In the DC-PECVD reactor, a DC power supply with controllable electrical current, is used as a generator of plasma and the precursors present between the anode and the cathode are decomposed for the deposition.^{91,92} In 2020, Che et al.⁹³ applied the DC-PECVD method for coating amorphous hydrogenated carbon (a-C:H) on a stainless-steel bipolar plates (BPPs) for use in proton exchange membrane fuel cells. The aim was to enhance the conductivity and the corrosion resistance of the membrane, and it was demonstrated that appropriate pressure was applied for the DC-PECVD modification, high deposition rate and consequently to achieve good corrosion resistance and performance.

4.2.3 | Initiated plasma-enhanced CVD

Initiated plasma enhanced chemical vapor deposition (iPECVD) can be used for fabrication of well-defined defect free polymeric films on different substrates with a low energy consumption. In this technique, the initiator can easily be dissociated into reactive chemical species at low plasma powers due to their weak bonds by which the plasma power is sufficiently low and just to break the weak initiator bonds. In this way, the undesired monomer fragmentation and chemical functionality lost would be avoided.⁹⁴ Fast deposition rates, high degree of functional group retention and conformal deposition are among the advantages of iPECVD. Among the research studies, fabricated thermos-

responsive poly(*N*-isopropylacrylamide) thin films using iPECVD using *tert*-butyl peroxide as an initiator along with the respective monomer.⁹⁵ The results revealed that parameters such as substrate temperature, plasma power, plasma mode and the presence of initiator has important roles in controlling the state and degree of deposition rate and wettability of the resultant films. In another study, more emphasize was devoted to the role of substrate temperature for the fabrication of poly(2-hydroxyethyl methacrylate) thin films.⁹⁶ It was demonstrated that substrate temperature not only governs the deposition rate but also the chemical structure of the deposition layer. For instance, decreasing substrate temperature led into increase in the deposition rate, whereas increasing substrate temperature decreased the water contact angle.

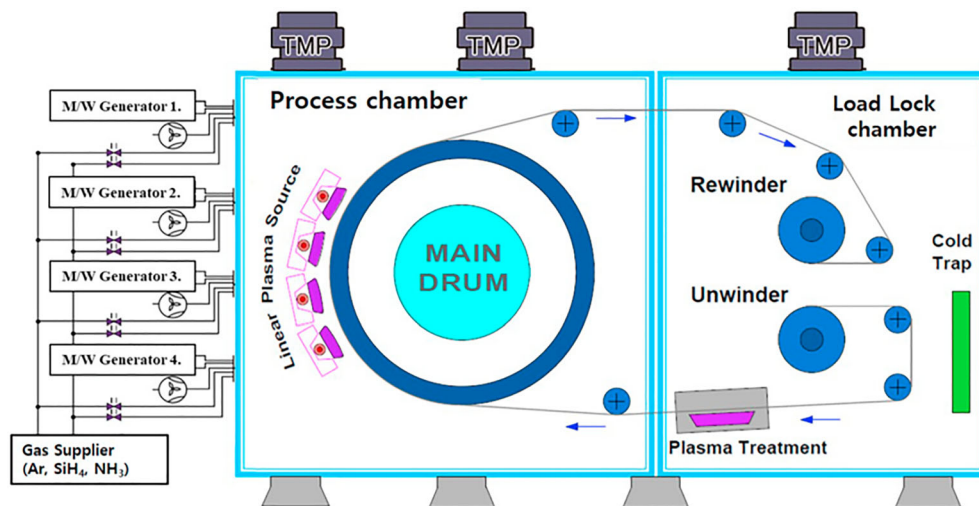
4.2.4 | Microwave PECVD

In MW-PECVD, high wavelength electromagnetic radiation is used for plasma generation.^{91,97} In 2021, Cho et al.⁹⁸ employed this technique for the modification of polyethylene terephthalate (PET) by deposition of a thin layer of hydrogenated amorphous silicon nitride (a-SiNx:H) in order to improve the barrier properties of the membrane against moisture permeation. As shown in Figure 3, the set-up comprised of a process and load lock chambers and a power of 1500 W was applied in the presence of SiH₄ and NH₃ to produce a thin uniform film. The outcome of the study showed that MW-PECVD could result in the creation of a thin film resistant against oxidation. Also, fabrication of optically clear superhydrophobic surfaces using PDMS as a sole coating material by MW-PECVD has been reported.⁹⁹ Deposited layers exhibited excellent superhydrophobic properties signified by the water contact angle up to of ~170°.

4.2.5 | Radio-frequency PECVD

In this technique (RF-PECVD), instead of DC or other power sources, a radio frequency supply is used for the generation of plasma.⁹¹ Ray et al.¹⁰⁰ adopted this method to form a thin layer of functional diamond like carbon (DLC) on PET to improve the gas impermeability of the membranes. The coating was conducted using argon and C₂H₂ as a precursor and the radio frequency was kept at 13.56 MHz. The permeability of modified membrane 10-folds less than the pristine sample which proved a successful coating. Also, RF-PECVD was examined for the surface modification of PVDF membranes by O₂ and CF₄ for membrane distillation (MD).¹⁰¹ This enabled enhancing the surface hydrophobicity up to 117° and reducing

FIGURE 3 The schematic representation of a MW-PECVD process and the steps involved for modification of thin films and membranes.⁹⁸ [Color figure can be viewed at wileyonlinelibrary.com]



the surface energy. Accordingly, the water permeation flux increased by about 28%–63% with respect to the unmodified PVDF membrane.

4.2.6 | Very high-frequency PECVD

This method is conducted at higher frequencies than RF-PECVD and thus the deposition rate is higher while the quality of the film remains outstanding.¹⁰² In different studies, this technique was used to create a gas barrier layer on an electronic device. For example, Kim et al.¹⁰³ deposited a SiN_x coating onto the surface of soda-lime glass and PET by VHF-PECVD at a very high frequency of 162 MHz to prevent moisture and oxygen permeation into flexible organic electronic devices. Also, in a recent study, the effect of power on crystallinity and optoelectronic properties of silicon thin films grown by this process was investigated.¹⁰⁴ They concluded that using an optimized VHF power for generation of high-density plasma with low energetic ions results in deposition of high crystalline contents with good optoelectronic properties for solar cell applications. Based on an extensive literature survey, no study could be found on the utilization of this technique for manipulation of separating membranes.

4.2.7 | Radical injection PECVD

In this technique (RI-PECVD), mostly H radicals are created on the surface with the aid of microwave radiation.^{105,106} This method has rarely been used for the introduction of coating on the surface though recently has attracted attention especially for the synthesis of carbon nanowalls (CNWs) on the surface of nanoporous alumina membranes.¹⁰⁷ The results revealed that not only the synthesis was successful, but also the pore size and thickness of

substrate played great roles on the height and structural morphology of the resultant CNWs. Therefore, the best configuration could be attained by the proper selection of these parameters. It was also shown that the thinner walls possessing lower number of graphene layers could be obtained on highly porous alumina substrates and which was attributed to the higher rate of vertical growth.

4.3 | Aerosol-assisted CVD

In this technique, precursors are born by gasses in the form of aerosol droplets at an ambient pressure. In addition to being economical, one of the advantages of this method is that nonvolatile precursors can be used to modify the surface whereas in conventional CVD, precursors are required to be heated and converted to the vapor phase, which increases the chance of thermal decomposition.¹⁰⁸ In heterogeneous AA-CVD process, the aerosol is sprayed on the membrane surface to produce an ultrathin and uniform layer through the material adsorption and decomposition on the surface. On the other hand, in homogenous AA-CVD, the aerosol droplets enter the hot gas phase and consequently, the decomposition takes place at the gas phase through an exothermic reaction.

4.4 | Laser-assisted CVD

This technique, also known as laser-induced CVD, has many similarities with PECVD in which a focused laser beam is used to locally provide the required heat for the decomposition of precursor gasses. In LCVD, the deposition rate, can be higher than other techniques of CVD though this depends on the laser power density.¹⁰⁹ Although his method is widely used for surface coating of thin films, it has not been

investigated for membrane separation processes. Just one study was found in which LCVD was used for repairing the contrast of X-ray masks by deposition of rhenium, gold and platinum on the surface of silicone membranes.¹¹⁰

4.5 | Metal-organic CVD

In this technique, organometallic precursors are used for deposition of amorphous, epitaxial, and polycrystalline thin films. In brief, organometallic precursors are compounds with carbon-metal covalent bonds, which require lower temperatures for decomposition, and this distinguishes them from the conventional precursors. Although the high cost of precursors is a disadvantage, MOCVD has many benefits such as feasibility of deposition on relatively large substrate surfaces and at higher deposition rates.^{17,111} Diverse precursors such as $\text{Cu}(\text{acac})_2$, $\text{Mo}(\text{CO})_6$, $\text{C}_2\text{H}_6\text{S}_2$, $\text{Ag}(\text{OCC}_2\text{F}_5)$ and $(\text{C}_2\text{H}_5)_2\text{S}$ have been used by this method.^{112–115} For instance, Park et al. used electron cyclotron resonance MOCVD to coat the surface of STS316 by fluorine-doped tin oxide ($\text{SnO}_x\text{:F-FTO}$) for promoting the contact and corrosion resistance bipolar plates.¹¹⁶ Tin and fluorine precursors flowed to the deposition chamber with the help of argon carrier gas. The outcomes contributed to the enhancement of interfacial contact resistance, corrosion resistance, power density, and cell voltage stability of bipolar plates for their use in polymer electrolyte membrane fuel cell devices.

4.6 | Hot-filament CVD

HFCVD is a simple and economical technique in which a metallic filament like tungsten, tantalum, molybdenum, and rhenium is heated to about 2000°C or more and in the presence of hydrogen and a hydrocarbon. The reaction results in the splitting of the hydrocarbon molecules for the generation of reactive precursors and leads to the deposition of nanoparticles onto surface of substrate.^{117,118} HFCVD is mostly used for coating carbon-based nanomaterials and applying a fine coating of diamond nanoparticles on the membrane surfaces. The HFCVD process should be conducted at high temperatures to obtain a high-quality deposition. However, as can be observed in Table 1, there still are studies on utilizing this technique at lower temperatures. In some of the various studies, such as those undertaken by Kim,^{119,120} Zhou,¹²¹ and Park,¹²² diamond nanoparticles were synthesized using HFCVD reactors. In the studies lead by Kim and colleagues, the temperature of filament reactor ranged between 2000 and 2100°C while the pressure was kept at 20 Torr.

4.7 | Oxidative CVD

This method has emerged as an innovative route for the synthesis of conductive polymer films with elevated conductivity values and provides advantages over the conventional method of polymerization of vapor phase monomers in the presence of oxidizing agents.^{123,124} Particularly, OCVD can result in deposition of uniform patterned polymer films with controllable thickness onto the surface of several substrates regardless of the morphology and functionality. At the same time, it allows maintaining the inherent characteristics of surfaces such as mechanical stability and breathability, which are essential for diverse applications including photovoltaic devices and sensors.^{125–128} Efforts have been made on further tuning and extension of this techniques such as using water to assist the formation of nanostructures owing to its ability to act as a proton scavenger to promote decomposition of oxidant.¹²⁹ Like other methods, process parameters can be used viable tools in order to yield structures with desirable characteristics via OCVD.^{130,131} The fundamental and governing mechanisms of this technique have also been recently explained including the applications.¹³² Overall, an expanding growth is anticipated for this techniques.¹³³

4.8 | Counter diffusion CVD

In the CDCVD technique, as shown in Figure 4, while the precursor is supplied to the outer side of the porous substrate, the oxidant is simultaneously supplied to the inner side. The reaction thus occurs due to the diffusion of precursor and oxidant at opposite directions and the layer is constructed in the substrate in the form of deposits within the pores. Deposition reaction ceases automatically once the membrane is

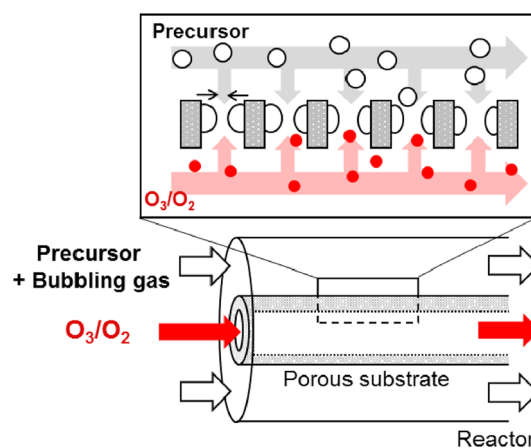


FIGURE 4 The mechanism of counter diffusion of precursor and oxidant in a CDCVD process.¹³⁴ [Color figure can be viewed at wileyonlinelibrary.com]

fully formed.¹³⁴ This method has been widely used for the preparation of silica membranes with molecular sieving as the main mechanism of transport.^{135–137}

4.9 | Initiated CVD

iCVD is one of the most attractive variations of CVD in which a precursor is introduced to the CVD chamber at low pressures and relies on the use of a radical initiator that can be thermally activated at low temperatures and preserving the functionality of the precursor.^{138,139} A free-radical polymerization occurs between the radicals formed by initiator decomposition and monomer species.¹⁶ During the deposition, substrate is kept at room temperature which is advantageous in utilization of all kinds of substrates including polymeric membranes. Table 2 provides an overview of the extent of investigations on the employment of different CVD modification techniques for thin films and membranes by highlighting the key characteristics, materials involved as well as the controlled conditions.

5 | MATERIAL SELECTION FOR CVD PROCESSES

5.1 | Substrate materials

According to the data in Table 1, a large variety of materials have been used as substrate in CVD modification techniques. Since the type and nature of material play crucial roles, the most widely used materials in the form of membrane and thin film are discussed by highlighting their specific characteristics.

5.1.1 | Ceramic substrates

Ceramic substrates made of selected oxide materials such as alumina, silica, zirconia, and titania as well as few others like silicon carbide, zeolites, microporous glasses are the most prevalent materials used for the fabrication of thin films and membranes. Among the advantageous features of ceramic substrates are the high mechanical strength, superior thermal and chemical stability, corrosion resistance, stability at a high range of pH and durability.^{218–220}

Alumina

One of the most popular ceramic substrates for applying a thin CVD coating is alumina. Alumina or aluminum oxide (Al_2O_3) has all the distinct advantages of a good ceramic membrane and can be prepared using sol-gel

method, chemical precipitation, hydrothermal techniques and microemulsion.²²¹ Firstly, one or more porous layers of α -alumina are prepared to function as support and then the final layer is coated by an active nonporous alumina layer of γ -alumina. The γ -alumina is thus considered to act as the intermediate layer on which the CVD is performed. For instance, Nishida et al.¹⁴⁸ developed a membrane made of two layers of α -alumina followed by an intermediate layer of γ -alumina. They used CDCVD to deposit an amorphous silica layer in the pores of the alumina membrane to render a high hydrogen permeability. These types of silica coated ceramic membranes are reasonable alternatives for low permeable metal membranes for hydrogen purification.

Since CVD processes are often carried out at high temperatures, alumina membranes are of high interest due to their high tolerance. The CVD-coated alumina membranes have shown promising performance for applications such as gas separation⁷⁹ and oily water treatment.⁸⁴ However, their use in some processes like MD, where a hydrophobic membrane is desirable, has not been successful mainly due to the hydrophilic nature. Moreover, ceramic membranes generally have high costs and higher thermal conductivity than polymeric ones, which has hampered their use in MD which needs low thermal conductivity characteristics.²²²

Zeolitic

Zeolites have mostly been used for the preparation of catalyst substrates while there are some studies in which zeolites have been employed as a membrane material. Zeolitic membranes offer dual functions simultaneously including pores for permeation and the catalytic activity. The prominent applications are dehydration and gas separation, and are known for ease of cleaning and high resistance against corrosion.²²³ However, they are mostly used as molecular sieve membranes rather than serving as the porous support. There are only a few studies in which a zeolite support is modified by CVD for membrane separation. For instance, Kyaw et al.²⁰⁴ successfully deposited polyindene (PIIn) onto the surface of a commercial zeolite 5A via PECVD at low temperature for the purpose of hydrogen separation from its mixtures with CO_2 and N_2 . A good interaction was found between PIIn and the substrate with full coverage and no cracks. In addition, the thickness of PIIn layer reached 20 μm after 1.5 h of deposition. Also, Zhu et al.²²⁴ fabricated a methyl-diethoxysilane (MDES)-coated MFI-type zeolite membrane by using CVD. The aim was to reduce the pore size to enhance the separation of H_2 and He from their mixtures with CO_2 . A notable outcome was demonstration of the role of substrate quality on the deposition performance and separation factor of the resultant membranes.

Other ceramic substrates

Alumina membranes, thanks to their benefits, are widely used as substrate for CVD processes, far more than any other ceramics. Faucheux et al.²²⁵ performed an analysis on the porous zirconia as a substrate for the growth of a thin film by MOCVD for preparation of an oxygen ionic conducting membrane. Zirconia or zirconium oxide with the chemical formula of ZrO_2 can tolerate high temperatures and compression resistance up to about 2000 MPa.²²⁶ Ceramic membrane can also be produced by titania or titanium dioxide (TiO_2). Recently, Khoo et al.²²⁷ developed titania nanotubes (TNTs) and coated the surface with MMA layer by PECVD which improved the dispersibility of TNTs in the solvent. Eventual incorporation of modified TNTs in a polyimide matrix revealed offering improved antifouling and antibacterial properties of the resultant RO membranes. Another study focused on coating of CNTs on the surface of a porous silicon carbide (SiC) ceramic support via CVD aiming to remove fine particles from polluted air.²²⁸ The innovative aspect was formation of a one-dimensional nanostructure with controllable in situ growth rate. Silica or silicon dioxide (SiO_2) is another famous ceramic membrane which is mostly used as a modifying agent rather than as a support. In another investigation, Cun et al.¹¹⁵ employed SiO_2 support and deposited monolayer MoS_2 by MOCVD at 850°C which resulted in a membrane suitable for different applications such as desalination and power generation.

5.1.2 | Polymeric substrates

Polymeric substrates offer many benefits such as affordability, ease of processability, high performance and selectivity. Polymers in general can be classified to diverse groups considering their source, structure, and the molecular forces existing in the repeating unit. They are also more flexible than ceramic substrates, typically less expensive and often limited fragility. The most prevailing polymeric substrate used for CVD process are discussed in the following sections.

PET

This engineering polymer with the chemical formula of $(C_{10}H_8O_4)_n$ and the melting point of about 260°C is used as a gas separation and barrier membranes. PET is a saturated thermoplastic polyester with availability in both amorphous and semicrystalline morphology.²²⁹ Semicrystalline PET is characterized by its high thermal, chemical and mechanical stability, clarity, durability, and flexibility while the amorphous PET possesses the same properties but with a less hardness and a higher flexibility.

These desirable characteristics along with the relatively low cost have enabled widespread use of PET especially in food packaging and drink bottles.^{230–233} As can be seen in Table 1, there are several studies on the use of PET substrates for CVD, particularly to enhance oxygen and water vapor barrier properties. Specifically, silica and silicon-based coatings have been applied by CVD which effectively improved the impermeability by more than 90%.^{142,167,192,215}

PEN

Polyethylene naphthalate (PEN) with chemical formula of $(C_{14}H_{10}O_4)_n$ is a thermoplastic polyester with strong chemical, mechanical and thermal properties.²³¹ It has strong gas barrier properties, especially when its surface is modified by silica derivatives. Different CVD techniques such as PECVD, C-CVD and R2R-PECVD have been used to introduce SiN_x and SiO_x on the surface for attaining water vapor transmission rates (WVTR) as low as $3E-3$, $1.31E-6$, and $6.9E-4$ g day⁻¹ m⁻², respectively.^{143,196,211}

PA

Polyamides (PA) such as nylons are among the thermoplastic high-performance polymers with high mechanical strength, chemical stability, and durability with applications in different industries. In most of the commercial nanofiltration (NF) membranes, often a very thin selective layer of PA exists on a substrate of a cheaper material. Many researchers tried to manipulate the surface features of the PA to improve antifouling properties. Shafi et al. in successive attempts was based on the use of iCVD to fulfil this objective and worth attention in this field.^{174,181,234} In their latest study, a 4-VP-co-EGDA coating was deposited on the surface which reduced the fouling by 99.5% with negligible impact on the performance. Similar trends were observed in other works carried using PECVD.^{187–189}

PLA

This as a viable gas barrier substrate with the chemical formula of $(C_3H_4O_2)_n$ and melting temperature of 130–180°C. PLA is a biocompatible and biodegradable thermoplastic aliphatic polyester widely used for packaging and medical applications.²³⁵ Unlike other CVD modified membranes, the silica coated PLA does not show acceptable permeation resistance. For example, WVTR of PECVD modified PLA has offered high permeance of 48–205 g day⁻¹ m⁻² which is not comparable to modified PEN and PET membranes.^{190,194}

PVDF

Polyvinylidene fluoride (PVDF) with melting temperature of 165–175°C and chemical formula of $-(C_2H_2F_2)_n-$

has been used as a substrate in different applications.^{236,237} PVDF is a semicrystalline fluoropolymer with high chemical resistance and a reasonable hydrophobicity.^{238,239} In a recent study, a CVD coating was created on the surface of Ni substrates.²¹⁷ Subsequently, porous poly(methyl methacrylate) (PMMA) binder was used to transfer the coating to the PVDF surface. It is also possible for direct deposition onto the surface of PVDF substrate. Subramaniam et al.²⁴⁰ applied iCVD with the aim of depositing HPMA onto the surface of a PVDF membrane to obtain a hydrophilic hollow fiber membrane. The modified membrane had a contact angle of 54.5° that was lower than that of the pristine membrane.

Other polymeric substrates

There are many other materials used as the substrate for CVD though with limited references to be discussed herein. These include PDMS, polycaprolactone (PCL) and polyethylene (PE) as gas separation membranes and polyethylenimine (PEI), polypropylene (PP), polyacrylonitrile (PAN), polytetrafluoroethylene (PTFE), polycarbonate (PC) and PSf for liquid separations and water purification systems.

5.2 | Modifying materials

The main aim in CVD processes is to modify the surface by introducing functional materials with specific characteristics like hydrophilicity, biocompatibility. Hence, the properties of the modifying agent play a critical role in a quality of process. In this part, the most popular modifying agents that have been used in CVD modification of membranes and thin films are discussed in tandem with elaborating on their prominent features.

5.2.1 | Carbon-based nanomaterials

Carbon-based nanomaterials (CBNs) are considered as the group of nanoparticles in which carbon is the main element. Carbon, due to its ability to forge bonds with nearby elements, can form various structures each with diverse properties. As a consequence, CBNs including graphite, graphene and its derivatives, CNTs, diamond and fullerene have attracted high attention compared to other nanoparticles.^{241–243} Particularly, CBNs are used for the modification of membranes and thin films through different techniques like CVD. In the recent years, several studies in high-impact journals can be found focusing on the assessment of CBN-modified membranes for different purposes.

CNTs

CNTs are among the most applicable group of this family employed for the fabrication of membranes. Besides, several studies have been devoted to the modification of membranes by this type of nanomaterials of which many conducted by CVD processes. CNTs, discovered in 1991, possess hollow and tubular walls made of graphene with a few nanometers in diameter and even more than a few millimeters in length. CNTs can be prepared in different geometries including single-wall carbon nanotubes (SWCNTs), double-wall carbon nanotubes (DWCNTs) and multi-wall carbon nanotubes (MWCNTs). CNTs, in general, have immense tensile strength and stiffness while they have other significant features such as thermal and electrical conductivity, large surface area and acceptable biocompatibility.^{244–246}

Graphene

Graphene is a 2D material with many advantages like biocompatibility, mechanical stability while possessing other favorable features of CNTs.^{247,248} One of the noticeable differences of graphene and CNT is the amorphous structure which can be analyzed using Raman spectroscopy. By making a comparison between the results of CNT and graphene coated membranes, it was observed that the I_D/I_G of CNT coating, which is an indicative representation of the ratio of structural defects, was around 1. This was higher than that of graphene coating that ranges between 0 and 0.6^{153,161,217} The PECVD nanographitic membrane prepared by Fishlock et al.²⁰⁶ had an I_D/I_G ratio of 1.79. Despite the attractive features of graphene and essentially other 2D structures, there have been problems associated to isomer cataloguing caused by the presence of extended defects or nanopores.²⁴⁹ Although practical solutions have been proposed to address this issue by identification of most probable isomers, still require special attention since they can change the transport, electronic and magnetic properties of the final product, especially if intended for separation of tiny molecules based on size sieving.

5.2.2 | Silicon-based materials

Silicon derivatives such as silica are highly popular for CVD coating of membranes. Silica and functionalized silica membranes are chemically and thermally stable and thus are highly recommended for use in hydrogen production. The chemical structure of deposited silicon-based materials depends on a few parameters especially the precursor, gas content ratio and deposition condition. Cho et al.⁹⁸ changed the NH_3/SiH_4 gas ratio from 0.75 to 9 to achieve the amorphous SiN_x coatings with N/Si

ratios of 0.37 to 1.34. Also, Park et al.²⁰² changed the ratio of SiH₄:N₂O:NH₃:H₂ from 30:30:120:0 to 30:30:120:1000 which resulted in formation of H:SiO_xN_y films with different H₂ content rendering different performance and features to the final film. Likewise, other precursors such as HMDSO have also been evaluated for deposition of silica membranes. An interesting work was performed by Kleins et al.¹⁸⁶ who examined the O₂:HMDSO flow rates of 0:1, 1:1, 2:1, and 5:1 by which could form silica structures of SiO_{1.0}C_{1.9}H_x, SiO_{1.4}C_{1.3}H_x, SiO_{1.8}C_{1.1}H_x, and SiO₂C_{0.9}H_x, respectively. This demonstrated that, increasing the oxygen content had a direct relation with oxygen incorporation in the coating and carbon reduction due to the appearance of gases such as CO₂, CO, and H₂O.

5.3 | Precursor materials

One of the most critical factors in CVD is the type and nature of the precursors employed in the process, especially considering the safety aspects.²⁵⁰ An interesting review in 2006 provided useful insights on the recent advances in the design and development of CVD precursors including ligand systems for the metal-organic CVD systems.²¹

5.3.1 | Silicon-based precursors

There are a number of precursors that are used for the deposition of silica and its derivatives on a membrane substrate. Some of the important precursors include dimethoxydiphenylsilane (DMDPS or DPDMS or DPhD MOS),¹⁴⁴ silane mixtures,^{32,193} hexamethyldisiloxane (HMDSO),¹⁸⁶ hexyltrimethoxysilane (HTMOS),¹⁴⁵ 3-aminopropylmethyl diethoxysilane (APMDES),¹⁵⁴ tetraethyl orthosilicate (TEOS),¹⁹¹ trisilylamine (TSA),¹⁹⁶ CH-liquid/isopropanol mixture,¹⁴² tetramethylsilane (TMS),¹⁹⁹ trimethoxypropylsilane (PrTMOS),¹⁴⁶ 3,3,3-trifluoropropyltrimethoxysilane (TFPrTMOS),¹⁴⁶ dimethyldimethoxysilane (DMDMOS),¹⁵⁶ silacyclobutane (SCB),¹⁴⁷ dichlorosilane (DCS),⁸⁴ methyltrimethoxysilane (MTMOS),⁷⁹ tetramethyl orthosilicate (TMOS),⁷⁹ methoxytrimethylsilane (TMMOS),⁷⁸ hexamethyldisilazane (HMDSN),²¹⁶ phenyltrimethoxysilane (PhTMOS or PTMS),¹⁵⁰ 3-Aminopropyltriethoxysilane (APTES),²⁵¹ vinyltriethoxysilane (VTES),¹⁴¹ triphenylmethoxysilane (TPMS) or methoxy(triphenyl)silane²⁵² and trimethylsilane (TrMS).²¹³ The prominent properties and characteristics of these precursors are summarized in Table 3.

As can be seen from the data in Table 3, a wide range of precursors are used for the deposition of silicon-based materials each with a different outcome. In 2021, Myagmarjav et al.¹⁴⁵ compared the hydrogen permeation

properties of silica-deposited membranes obtained using different precursors and techniques. In this comparison, the highest performance belonged to HMDSO, DMDPS, and TPMS while the lowest were for MTMOS and TMOS. Despite the value of this study in highlighting the differences, it may not be fully trusted as reliable measure since the CVD processes and parameters were also different which certainly had influence. In another attempt, Messaoud et al.²⁵³ reported that the coating made by PTMS with secondary amine (e.g., MAPTMS) with a low boiling point offered higher performance than coating with primary amine (e.g., APTMS) and PTMS with no amines. An another investigation, Suzuki et al.²⁵¹ mixed TEOS with APTES at different concentration and found that the optimal performance can be achieved with 25% TEOS to APTES ratio while the permeability of pure APTES is still higher due to its very low deposition rate. Similarly, Nishida et al.¹⁴⁸ compared HMDSO with TMOS and reported that although HMDSO-based coating exhibited a higher permeability, the selectivity of TMOS-based coating was 44 times higher. Akamatsu et al.¹⁴⁹ showed that the use of DMDMS precursor offered a higher performance than TMOS. Furthermore, the deposition rate of TMOS-based coating was much higher owing to the higher atomic ratio of Si at longer depositions. The above exemplary cases along with many other studies that have compared different precursors reveal clearly that a careful selection of precursor should be regarded as an essential factor for obtaining a coating with desirable characteristics.

5.3.2 | Mixed ceramic precursors

There are also some studies on the deposition of hybrid materials onto the surface using mixed precursors. Akbari et al.⁷⁶ used two precursors of TEOS and zirconiumtertbutoxide (ZTBO) to deposit a 20-nm silica-zirconia hybrid coating at high temperatures onto an alumina surface. The final membrane showed higher durability and hydrothermal stability compared to the silica membranes. Ahn et al.⁷⁷ used the same precursors, but in different concentrations and demonstrated that the reactivity of zirconia precursors was lower than that of silica, indicating the need for more deposition times. They recommended that the best membrane obtained with the ZTB/TEOS molar ratio of 0.1. A study lead by Kageyama et al.¹⁶³ revealed that the hybrid silica-alumina coating prepared by using aluminum tri-sec-butoxide (ATSB) (as an alumina precursor) and TEOS (as a silica precursor) improved durability of membranes for sensitive applications such as membrane reactors and hydrogen production.

TABLE 3 Some of the prominent properties and characteristics of silicon-based precursors used for the chemical vapor deposition (CVD) modification of membranes and thin films.

Precursor	Chemical formula	Boiling temperature (°C) (@ 1 atm)	Vapor pressure (mmHg) (@25°C)	Deposited material(s)	CVD temperature range (°C)	Cost (100 mL/g) (USD)	Number of publications
TPMS	C ₁₉ H ₁₈ OSi	328	Very low	SiO ₂	600	–	3
DMDPS (DPDMS)	C ₁₄ H ₁₆ O ₂ Si	287	Very low	SiO ₂	600	16.7	5
APTES	C ₁₂ H ₃₀ N ₂ O ₃ Si	321	Very low	–	–	–	26
HTMOS	C ₉ H ₂₂ O ₃ Si	168	2.1	SiO ₂	125–520	63.7	6
PhTMOS (PTMS)	C ₉ H ₁₄ O ₃ Si	186	0.9	SiO ₂	230–400	39.3	6
TEOS	C ₈ H ₂₀ O ₄ Si	166	2.5	SiO ₂ , SiO _x N _y	55, 500–700	2.5	317
APMDES	C ₈ H ₂₁ NO ₂ Si	214	0.2	SiO ₂	650	25.9	2
VTES	C ₈ H ₁₈ O ₃ Si	161	3.1	SiO ₂	600	16.7	6
HMDSN	C ₆ H ₁₉ NSi ₂	126	11.9	SiO _x , SiN	Room, 100	9.5	77
HMDSO	C ₆ H ₁₈ OSi ₂	101	41.4	SiO _x C _y H _z , SiO _x C _y , SiO _x , SiN _w O _x C _y H, SiO ₂ , SiO _x N _y	600, 25	10.5	116
TFPrTMOS	C ₆ H ₁₃ F ₃ O ₃ Si	124	15.4	SiO ₂	100–270	800	3
PrTMOS	C ₆ H ₁₆ O ₃ Si	142	7.1	SiO ₂	100–270	18.2	2
TMOS	C ₄ H ₁₂ O ₄ Si	121	17.7	SiO ₂	600, 650	18.2	41
MTMOS	C ₄ H ₁₂ O ₃ Si	103	38.8	SiO ₂	650	6.2	22
DMDMOS (DMDMS)	C ₄ H ₁₂ O ₂ Si	82	89.0	SiO ₂	500–650	18.2	13
TMMOS	C ₄ H ₁₂ OSi	58	230.3	SiO ₂	650	124.6	7
TMS	C ₄ H ₁₂ Si	26–28	718	SiO _x N _y	70	352.9	115
TrMS	C ₃ H ₁₀ Si	7	NA	SiO ₂	–	–	35
SCB	C ₃ H ₈ Si	29.8	65	SiC	550	–	4
DCS	Cl ₂ H ₂ Si	8	1254 (20°C)	SiC	750	–	102
TSA	H ₉ NSi ₃	52	NA	SiN _x	25–30	–	6
Silane	H ₄ Si	–112	NA	SiO _x , SiN _x , a-SiN _x , n-SiO _x N _y , h-SiO _x , SiON, SiO _x N _y	45–100	–	High

Abbreviations: APMDES, aminopropylmethyldiethoxysilane; APTES, 3-aminopropyltriethoxysilane; DCS, dichlorosilane; DMDMOS, dimethyldimethoxysilane; DMDPS, dimethoxydiphenylsilane; HMDSN, hexamethyldisilazane; HMDSO, hexamethyldisiloxane; HTMOS, hexyltrimethoxysilane; MTMOS, methyltrimethoxyorthosilicate; PhTMOS, phenyltrimethoxysilane; PrTMOS, propyltrimethoxysilane; SCB, silacyclobutane; TEOS, tetraethoxyorthosilicate; TFPrTMOS, 3,3,3-trifluoropropyltrimethoxysilane; TMMOS, trimethylmethoxysilane; TMOS, tetramethoxyorthosilicate; TMS, tetramethylsilane; TPMS, triphenylmethoxysilane; TrMS, trimethylsilane; TSA, trisilylamine; VTES, vinyltriethoxysilane.

Source: www.chemsrc.com.

5.3.3 | Carbon precursors

Essentially, carbon precursors can be divided into three main general categories based on the phase namely solid, liquid, and gas precursors. PMMA (C₅H₈O₂)_n, sucrose (C₁₂H₂₂O₁₁), fluorene (C₁₃H₁₀), polystyrene (C₈H₈)_n, thiocamphor (C₁₀H₁₆S), camphor (C₁₀H₁₆O), waste plastic, amorphous carbon, asphalt, hexabenzocoronene (C₄₈H₂₄), coronene (C₄₂H₁₈), p-terphenyl

(C₁₈H₁₄), hexachlorobenzene (C₆Cl₆), melamine (C₃H₆N₆) and some food and plants are all solid precursors. On the other hand, ethanol (C₂H₅OH), hexane (C₆H₁₄), pyridine (C₅H₅N), methanol (CH₃OH), 1-propanol (C₂H₅OH), pentane (C₅H₁₂), benzene (C₆H₆), soybean oil, cyclohexane (C₆H₁₂), palm oil and waste chicken fat are among the liquid precursors. Some of the notable gas precursors are methane (CH₄), ethylene (C₂H₄) and propene (C₃H₆).

All this variety of precursors have been used for the deposition of carbon materials like graphene, CNTs, graphite, fullerenes, carbon, and diamond on the surfaces. The number of studies on the deposition of carbon-based materials on membranes by CVD for the purpose of performance and characteristics improvement is not high. In addition, they have mostly been conducted for the modification of MD systems. Nevertheless, an interesting review is available on the graphene materials synthesized by CVD with various carbon precursors.²⁵⁴

6 | CVD PROCESS PARAMETERS SELECTION AND CONTROL

Membranes are modified and functionalized to achieve a higher performance or improved characteristics. For each application, CVD modification changes essential properties such as the contact angle, membrane thickness, coating density, surface roughness, membrane porosity and pore diameter. As discussed in the previous sections, changing CVD parameters can exert great effects on the properties including performance indices such as permeability and selectivity. This necessitates having an optimization approach as an essential asset. This section is devoted to the various aspects of parameter selection and control relying on the experimental results reported in the literature.

6.1 | Deposition time

The impact and influence of deposition time has been investigated in several studies. Figure 5 demonstrates the effect of deposition time on permeability, selectivity and rejection of different systems. As it can be observed from Figure 5a, hydrogen permeance of the membranes decreased from 20% to 90% for every 30 min increase in deposition time. Quite different trends could be observed in the case of WVTR and oxygen transmission rate (OTR; Figure 5c), pure water flux through UF membranes (Figure 5d) and CO₂ separation membranes (Figure 5 (e)). Meanwhile, Figure 5 (b) and (e) indicate that their selectivity increased upon increasing the CVD deposition time. These observations clearly reveal that deposition time can to large extend influence the flux and selectivity of the resultant membranes. It is worthy of noting that the results of Kato et al.⁷⁹ in Figure 5a revealed that when deposition time was extended to more than a few hours, the permeance graph reached a plateau with its minimum value. On the other hand, according to Figure 5d, UF

membranes experienced a decrease in both flux and rejection through deposition time increase although the selectivity was still much higher than the neat membranes. Overall, it may be concluded that variation in deposition time in case of membranes does not necessarily result in enhancement in the separation performance and this necessitates conducting a careful optimization to identify the best window of operations for obtaining desirable outcomes.

The changes in the transport and separation properties of membranes are related to the characteristics of the deposition. Figure 6 clearly confirms this by demonstrating the interdependency of the coating thickness, pore size and contact angle to the deposition time for some of the exemplary samples. Coatings were conducted at deposition rates of 0.004 to 2.2 nm/s. According to Figure 6a, increase in deposition time greatly influenced the thickness of depositions and even multi-folds. The slight difference in the intensity of changes was owing to other parameters such as the type of precursor, gas ratio, flow rate and temperature but obviously the trend is consistent for all. It is generally accepted that one of the common consequences of increase in thickness is increase in the resistance for the transport which corresponds to the reduction in permeation or flux, whichever applicable. The other major effect of deposition time is on the coating porosity and pore size with unavoidable impacts on the permeability and selectivity or rejection of membranes. Chen et al.⁸⁴ assessed the effect of deposition time on the pore size of depositions on the membranes and the findings are shown in Figure 6b. As can be seen, increasing the CVD deposition time resulted in formation of coating with smaller pore size, which certainly affects the spaces available for the transport of molecules. Often, the changes in the pore size also includes the surface pores and thus the surface roughness. Figure 7 shows the changes in the surface morphology of membranes upon variation in the CVD deposition time upon which not only the changes in pore size but also in thickness were noticeable.¹⁹² Figure 6 (c) exhibits the effect of deposition time on contact angle. In an investigation, Said et al.²⁰¹ examined the effect of deposition time on membrane contact angle and the results showed a steady decline from 55° to 33° by raising deposition time from 15s to 90s, respectively. In fact, increasing the deposition time led to the concentration rise of the deposited material consisting of OH hydrophilic groups. This was at the expense of water permeance that decreased from 42 to 10 L m⁻² h bar.

In general, based on the examinations, it may be concluded that upon increase in deposition time, contact

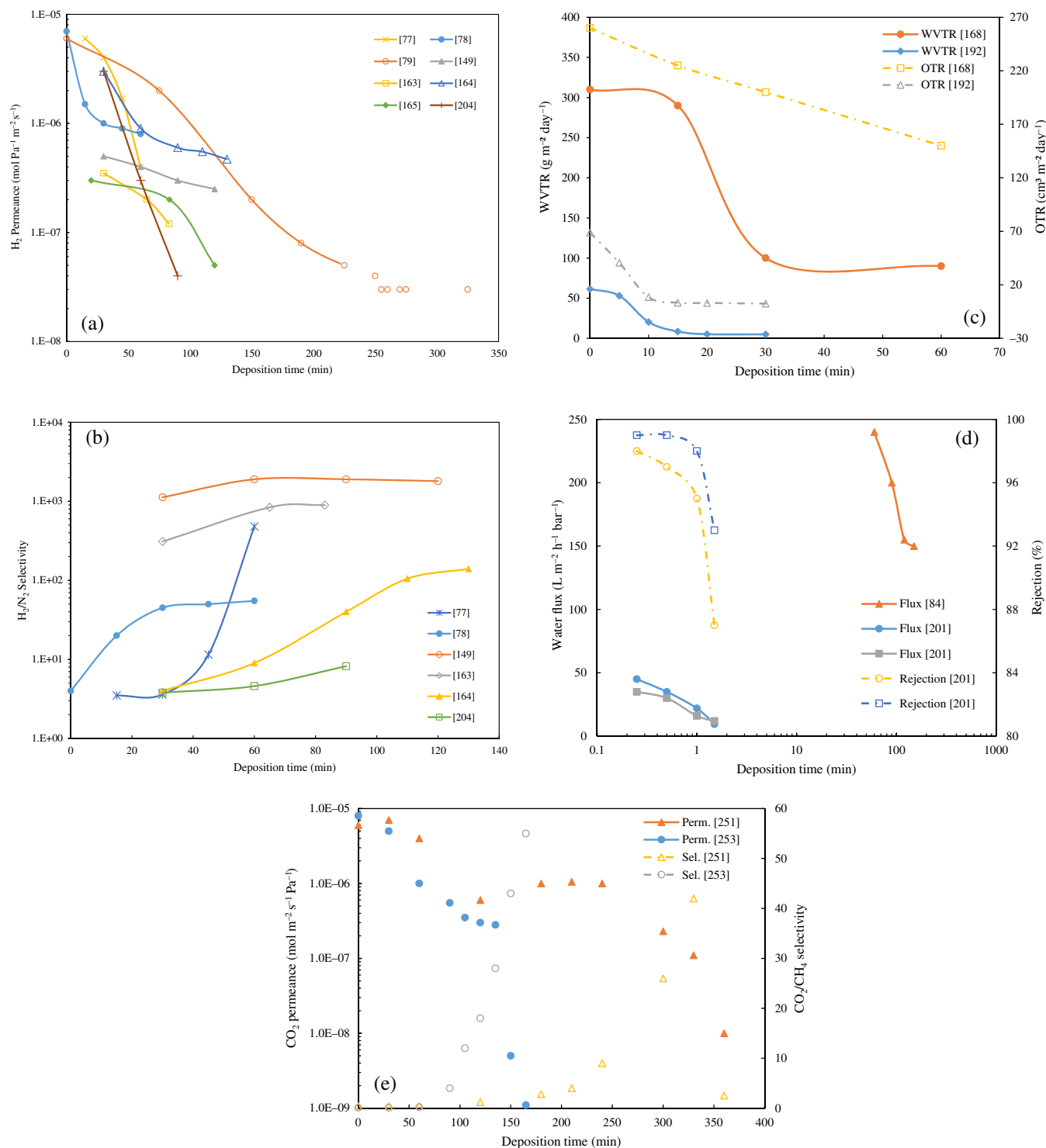


FIGURE 5 Performance-deposition time trends of different systems. (a) H₂ permeance, (b) H₂/N₂ selectivity, (c) water vapor transmission rate (WVTR) and oxygen transmission rate (OTR), (d) water flux and rejection of UF membranes, and (e) CO₂ selective membranes. ^{77-79,84,141,149,163,165,168,192,201,204,251,253} [Color figure can be viewed at wileyonlinelibrary.com]

angle experiences a rise in case of hydrophobic PHDFA and a fall in case of hydrophilic PANI, AA and APTES. It is also shown that in some cases, hydrophilicity has a direct relation with fouling reduction. Khoo et al.¹⁸⁷

explored the influence of the deposition time on hydrophilicity and demonstrated that it directly affected hydrophilicity of membranes and consequently the antifouling properties.

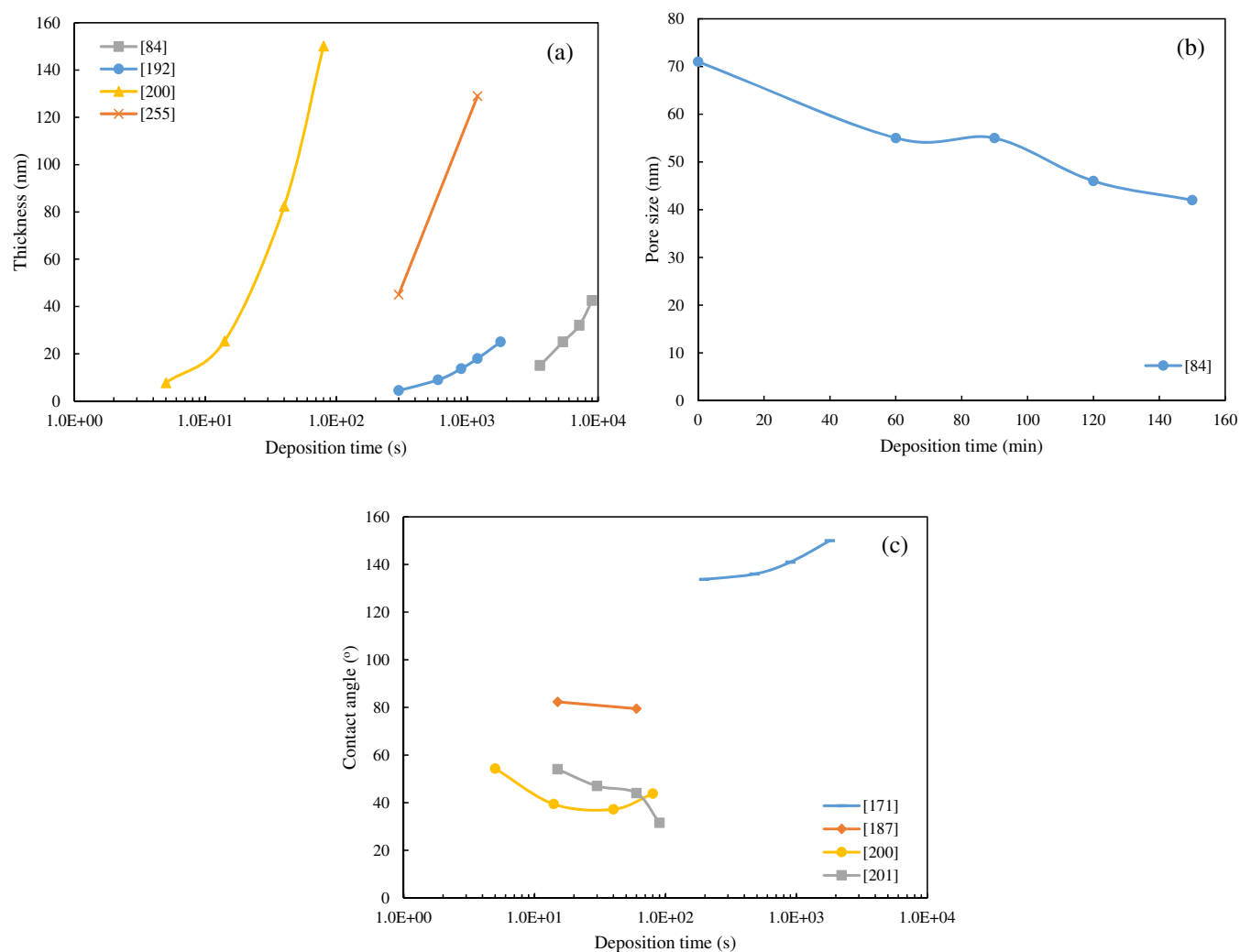


FIGURE 6 The influence of CVD deposition time on three key characteristics of the coating: (a) coating thickness, (b) pore size, and (c) surface contact angle.^{84,171,187,192,200,201,255} [Color figure can be viewed at wileyonlinelibrary.com]

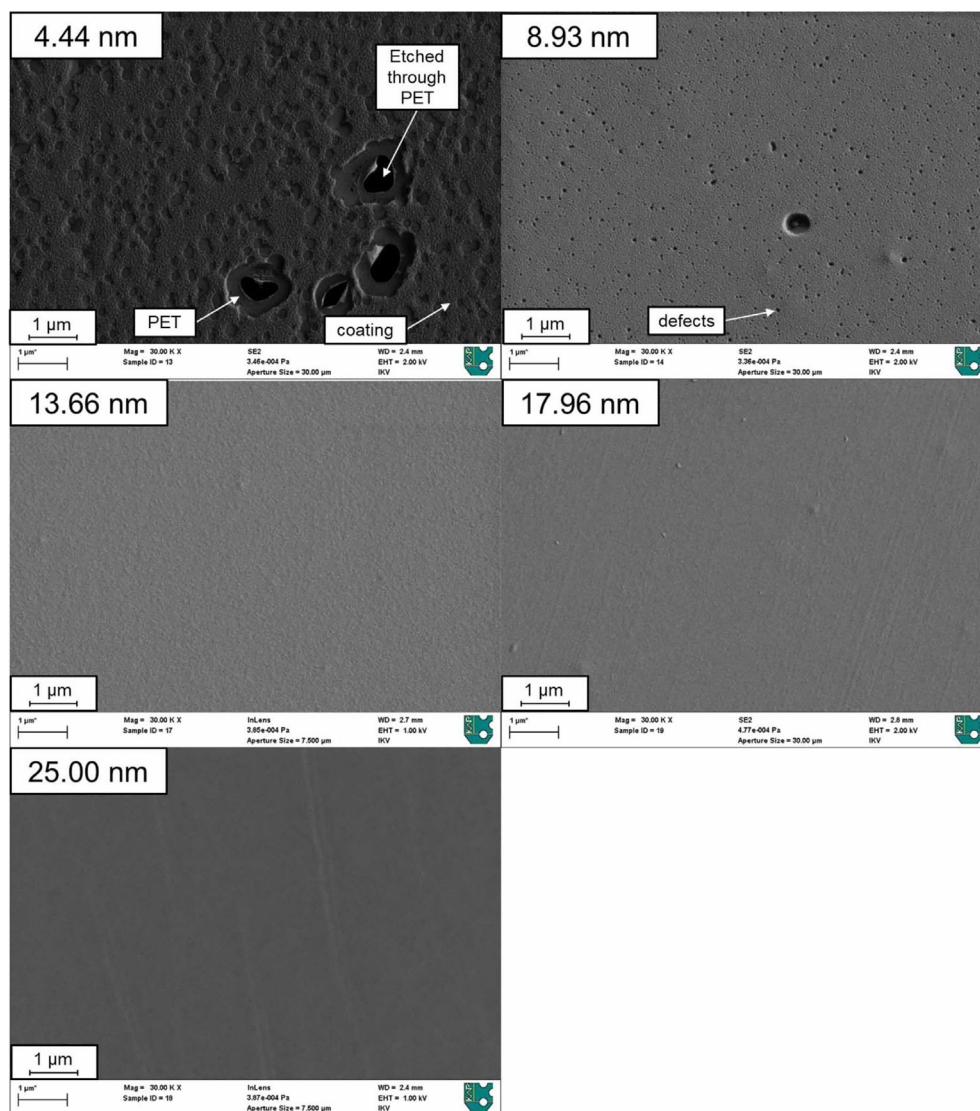
6.2 | Deposition temperature

Another parameter of high importance in CVD process is temperature. Figure 8 demonstrates the effect of deposition temperature on the permeance of a number of membranes. It is evident that deposition temperature caused different trends though the extent varied depending on the type of precursor, size of the functional groups as well as the decomposition temperature. It can also be observed that the gas permeance of some membranes declined and then increased again when temperature was further increased. Yoshiura et al.¹⁴⁶ attributed this trend to the interactions between deposition and decomposition rates at higher temperatures. In their investigation, it was noted that increase in deposition temperature from 175°C to 200°C led to reduction in mean pore diameter from 1.5 to 0.5 nm and consequently 15% increase in rejection as well as 60% drop in

permeance. While further increase in temperature to 250°C had no effect on the size of pores. It was also noted that exceeding a threshold temperature contributed to the oxidative removal of organic functional groups and resulted in the formation of large pores. Therefore, it can be realized that optimization of deposition temperature can be essential for obtaining desirable morphology and microstructure as well as performance in the resultant membranes and thin films, especially if used for molecular separations. In another research, Myagmarjav et al.¹⁵¹ suggested that when the CVD deposition temperature exceeded a certain value, the thermal decomposition rate increased and eventually left no precursor inside the CVD chamber.

In addition to the experimental works, modeling and simulation has also been employed as powerful tools to enable prediction of the effect of temperature. This has been conducted in the case of transition metal

FIGURE 7 Evolution of membrane surface morphology upon implementation of different deposition times in CVD deposition of SiO_x on PET.¹⁹² [Color figure can be viewed at wileyonlinelibrary.com]



dichalcogenides (TMDs) which are a class of materials with growing interests due to their unusual electrical, optical, and mechanical properties. The three-atom thick unit cell of TMDs is created by a layer of transition metal atoms sandwiched between two layers of chalcogen atoms. Govind Rajan et. al. presented a stochastic kinetic model for the growth of TMD monolayers in a CVD process.²⁵⁶ The model relied on the intrinsic bond energies for the prediction of the variation in shape and size of the grown MoS_2 crystals from triangular to hexagonal due to the local stoichiometry in the CVD reactor. They demonstrated existence of a good match between the analytical theory and simulation data in the temperature range of 600–750°C.

6.3 | Deposition pressure

Deposition pressure is another important CVD parameter that surprisingly has been investigated randomly. As

discussed in the previous sections, this might be due to the fact that essentially CVD derivative techniques have emerged to suit different pressure ranges and thus, each process works at certain range of associated pressure. Nevertheless, in a study, Ghaleni et al.¹⁷² studied the effect of deposition pressure on membrane contact angle. They came into the conclusion that increasing the pressure during the iCVD coating can have a moderate effect on the contact angle of hydrophobic PTFE-modified PVDF membrane evidenced by its ~20% increase upon changes in pressure from 300 to 1200 mTorr.

6.4 | Plasma power

In PECVD processes, plasma power can also have a dramatic impact on the quality and extent of CVD process and the resultant depositions. Figure 9a presents the results of investigations concerning the effect of plasma power on He permeance and WVTR for some of the

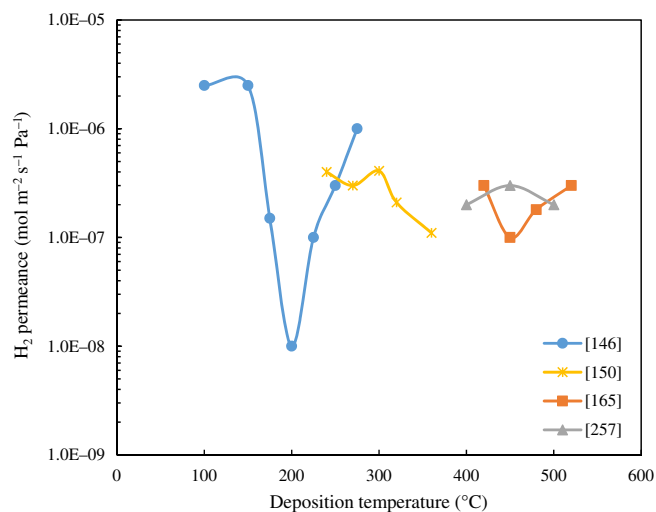


FIGURE 8 The effect of deposition temperature on the hydrogen permeance of a few CVD processed membranes.^{146,150,165,257} [Color figure can be viewed at wileyonlinelibrary.com]

exemplary cases. A general conclusion that may be obtained is that increasing the plasma power has negative impact on the transport and permeance. However, there was also a case in which a contradictory increasing effect can be seen. Bang et al.¹⁶⁷ investigated the effect of plasma power on the surface density and showed that increasing the plasma power from 500 to 900 W enhanced the coating density by 30% and attributed the decrease in permeability to this change. It is worth noting that plasma power and surface density often have a direct relation with the deposition rate.

Figure 9b shows the effect of plasma power on the deposition rate for three coated membranes covering a relatively wide range of plasma power. It may be seen that increase in plasma power contributed positively to the deposition rate, though the amount of increase was different. However, there exists also reports on the contrary in which increasing the plasma power resulted in decline of deposition rate and increase of permeability as shown in the same figure.²⁵⁸ Research study by Kleins et al.¹⁸⁶ also revealed that increasing the plasma power influenced the permeability of different gasses in different ways. While increasing the power from 1000 to 3000 W, they observed that helium permeance decreased, whereas nitrogen permeance increased and in the case of CO₂, permeance could follow a decrease or an increase depending on the CVD gas concentration. They explained that at higher plasma powers, more agglomeration occurred on the surface of membranes which resulted in a rougher surface. Figure 10 shows the effect of plasma power on the surface morphology and roughness.¹⁸⁶ The results indicated that upon three folds increase in plasma power, the mean square roughness of the surface raised

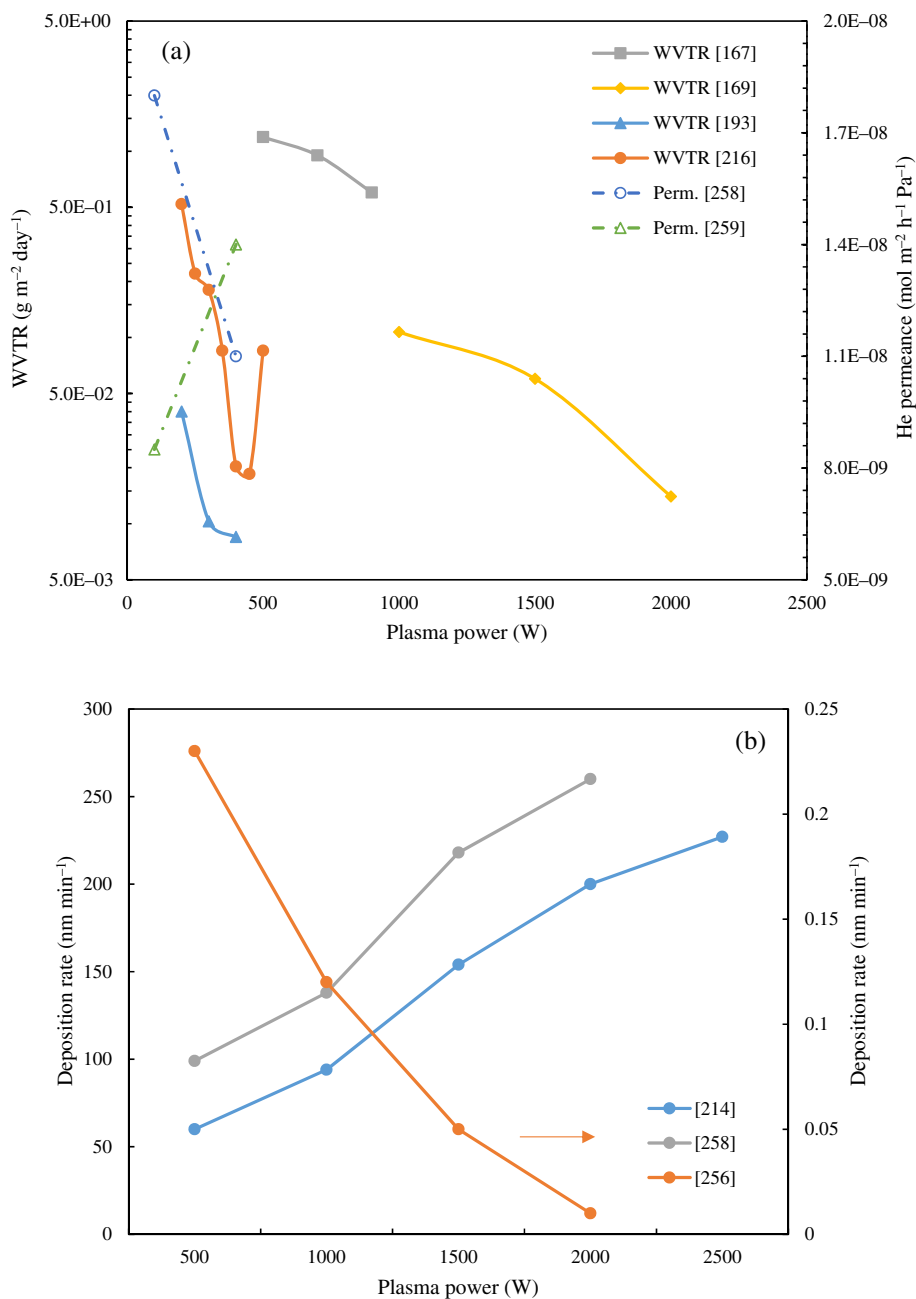
from 0.4 to 3.5 nm. This may also have resulted in creation of larger free volumes which further promotes the transport of small and large molecules.

It is known that raising the plasma power during the PECVD process causes fragmentation of gas molecules. Therefore, the particle collision leads to the formation of reactive species which is followed by the condensation of reactive particles on the surface and resulting in agglomeration. These collisions also can lead to volume polymerization and creation of strongly cross-linked and amorphous coatings. It should be noted that increasing membrane roughness can also affect the contact angle of membranes. In fact, roughness improvement can intensify hydrophilicity or hydrophobicity of surface. In case of dense membranes, where the transport mechanism is solution-diffusion, this contact angle alteration can have an influence on the gas-membrane affinity and membrane permeability.

6.5 | Gas composition and flow rate

The composition of the gas and its flow rate are other parameters that play roles on the performance and properties of process and CVD deposition. Part of the effects on the coating structure was discussed in the previous sections. By gathering information from different prior studies and analysis of the data, no general correlation could be established between gas composition and flow rate and the performance of the resultant membranes. This is because depending on the type of precursor, reactant gas, carrier gas and gas ratios, different results have been obtained. Among the notable ones, Oh et al.²¹² changed the NH₃:SiH₄ from 0.8 to 3.2 and showed that WVTR did not change significantly while Cho et al.²¹⁴ reported that at the ratios of 2, 3, 5, 7, and 9, WVTR decreased to 0.0078, 0.0073, 0.03, 0.8 and 1.4 g m⁻² day⁻¹, respectively. These values were not in accordance with the density of the coating which dropped from 2.21 to 1.89 g cm⁻³. In another study, Kleins et al.¹⁸⁶ changed the plasma power along with the HMDSO:O₂ gas ratio and yet no clear trend was detected, though the best results achieved by using pure HMDSO. In deposition of SiO_xN_y onto a substrate, Shahpanah et al.²¹⁵ kept O₂ and TEOS flow rates constant at 150 and 3 sccm, respectively, while changing N₂ flow rate from 0 to 150. The results showed that the deposition rate declined gradually to 70% because of increase in N₂ ratio. Besides, surface roughness increased from 1.2 to 2.6 nm with improvement on the overall surface hydrophilicity. By adjusting N₂ flow rate within the investigation range, they could obtain an oxygen permeance of 0.08 mL cm⁻² day⁻¹ bar⁻¹ at 90 sccm which was much (~99%) lower than what were obtained at N₂ flow rates of 0, 30 and 150 sccm. Similarly, Moritoki et al.²¹³ used

FIGURE 9 The effect of plasma power on (a) He permeance and water vapor transmission rate (WVTR), and (b) deposition rate. [167,169,193,214,216,258,259](#) [Color figure can be viewed at wileyonlinelibrary.com]



manipulation of oxygen/TrMS ratio and oxygen flow rate as a viable means to optimize the oxygen barrier properties of the intended membrane.

Based on some findings, a relation between flow rate and deposition time has been identified. In other words, when the gas flow rate is higher, total residence time of reactants is lower. Accordingly, reactants have less time for deposition onto the surface, which means more deposition time is required to achieve a desired level of coating. Nonetheless, increasing the flow rate leads to the velocity enhancement of gas and improving mass transfer rate according to the Navier–Stokes and mass continuity equations. In a study carried out Kato et al.,⁷⁹ increasing the residence time from 0.4 to 0.8 and 1.3 s led to the change in CVD time from 600 to 700 and 250 min in

order to achieve an equivalent nitrogen permeance. Likewise, Myagmarjav et al.¹⁶⁵ showed that increasing the velocity of N₂ as a carrier gas resulted in formation of a peak in selectivity-velocity graph. Both these studies highlight the necessity of residence time optimization.

6.6 | Substrate temperature

Substrate temperature is considered as an important parameter for altering the deposition rate through controlling the surface reaction rates and sorption mechanisms. Only a few studies on CVD-coated membranes have been devoted to the investigation of the effect of substrate temperature on membrane performance.

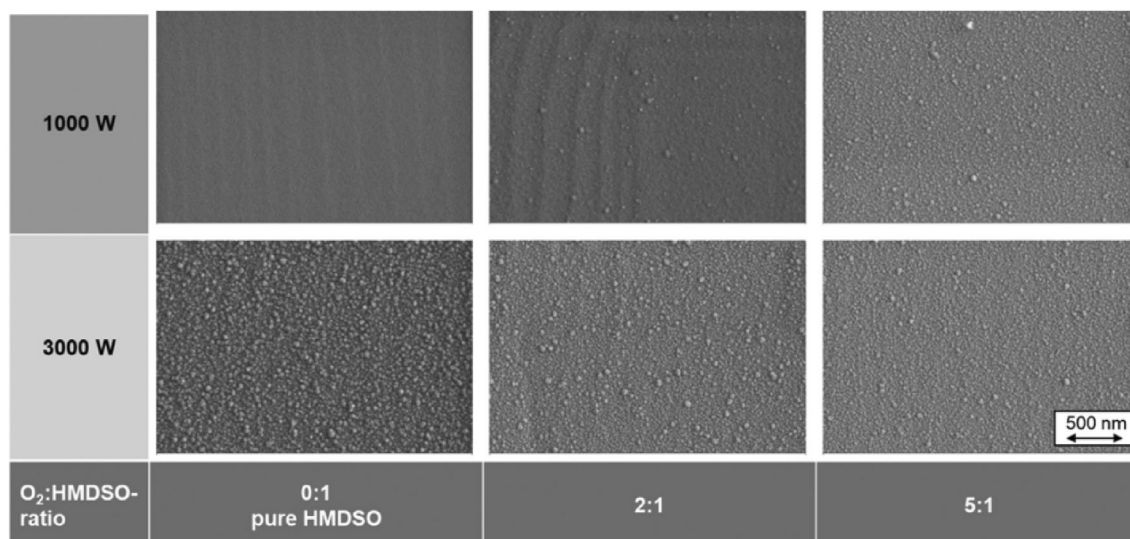


FIGURE 10 Effect of plasma power on the surface morphology of CVD depositions at three different O_2 :HMDSO precursor ratios.¹⁸⁶

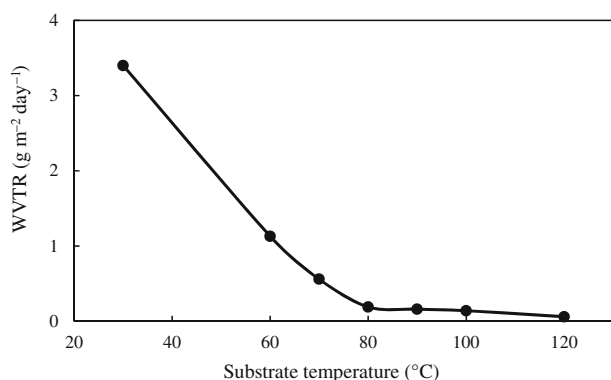


FIGURE 11 The impact of substrate temperature on the water vapor transmission rate (WVTR) of SiO_xN_y -coated PET membrane.¹⁹⁹

Figure 11 shows the results of the study conducted by Fu et al.¹⁹⁹ revealing the effect of substrate temperature on WVTR of a SiO_xN_y -coated PET membrane. It was demonstrated that a fourfold increase in substrate temperature brought about $\sim 98\%$ decline in WVTR. Further details on the consequences of substrate temperature on deposition characteristics can be found in the extensive review by Ozaydin-Ince et al.²²

7 | PROGRESS IN APPLICATIONS OF CVD-BASED THIN FILMS AND MEMBRANES

7.1 | Desalination and water treatment

Desalination and water treatment processes are essential tools for addressing the ever-growing demands for water.

Aside to the capability of these methods for providing fresh water for human and livestock consumptions, they are also great assets in supplying the water needed for industrial, agricultural, municipal purposes that do not necessarily require drinkable quality.^{260–262} Despite the great helps that these approaches provide, still some challenges need to be solved including brine management of desalination plants,²⁶³ issues associated with contaminations²⁶⁴ and complexity in elimination of certain species.²⁶⁵

From the diverse ranges of technologies available to desalination and water treatment, membrane separation processes have gained popularity due to offering a higher energy efficiency, modular structure, simplicity and ease of operation, high performance, and yet often lower costs.²⁶⁶ Expectedly, like any process, despite the great benefits, membranes processes also suffer from few aspects, including fouling, degradation, susceptibility toward certain elements, and need for careful operational control. Membrane elements, constitute the heart of any membrane plant which are made of thin films. Essentially, any improvement in the physicochemical characteristics of the membrane surface can result in great savings and advantages in the application especially for handling water feeds. In this part, the prevailing trends in applications of CVD modification techniques for development of high-performance membranes applicable to desalination and water treatments are discussed.

7.1.1 | Membrane distillation

MD is recognized due to the great energy savings that it can provide for the treatment of water contaminated

streams since they can also operate based on the waste heat. Furthermore, due to a lower energy demand, majority of renewable energies such as solar and geothermal sources can be easily integrated to the MD process and add to its environmental friendliness features. Moreover, as the operating pressure in MD is lower than that of other pressure-driven membrane processes such as NF and this itself reduces the probability of fouling by a considerable extent.

In MD, the feed is heated below its boiling point, and this creates enough vapor pressure to stimulate the transport of more volatile molecules for passing through the membrane. In other words, partial pressure gradient, which is the result of temperature difference, is the major driving force for MD process. A key factor in the design of a MD is that the membrane should be hydrophobic to prevent the intrusion of feed ingredients in the liquid form. Moreover, the membrane should be microporous enough to be highly permeable for the vapor phase. Although MD membranes have shown promising performance, some of the features such as thermal resistance of the materials used so far requires further improvements.^{267–269} One of the effective methods for making breakthroughs is through surface modification where CVD methods have had and still will have great opportunities. For instance, one of the methods of membrane surface hydrophobicity enhancement is deposition of a super hydrophobic layer and several experiences on the use of CVD methods for this purpose exist.

In a number of studies, CVD method have been used to modify the surface of the MD membrane for desalination and wastewater treatment. In one study, Cong et al.¹⁷⁵ in 2019 examined an approach to increase the hydrophobicity of porous ceramic tubes by increasing the fluorine content of the surface through iCVD. They realized that after modification, the chance of pore wetting decreased and the permeate flux of the membrane slightly increased. In another attempt, Si et al.¹⁵⁷ developed a stainless steel-based carbon nanotube membrane by CVD to promote the hydrophobicity of the membrane surface evidenced by 50° increase in the contact angle. Table 4 shows an overview of the research works carried out in the utilization of CVD methods for the surface modification of MD membranes including the major performance values before and after the modification. From the data, it can be noted that various CVD modifications have been able to effectively enhance membrane hydrophobicity and consequently reduce the chance of pore wetting. However, it should be noted that surface characteristics and performance of membranes are largely dependent on the type and nature of material being deposited onto the surface. Besides, the quality of coating is governed by the modification technique, deposition time and the substrate properties among other factors.

The other significance of selecting a proper modification technology lies in the stability during operation. For industrial MD systems, the permeability, rejection, and hydrophobicity of the membranes should remain unchanged for a prolonged period of time. Nevertheless, always slight declines in associated to other factors such as fouling are inevitable. Figure 12 shows the performance change as a function of duration of operation in some publications. It can be observed that after a long time and reaching steady state condition, membrane performance has not declined significantly in most cases. This may be regarded as a good indication of the stability of CVD depositions for MD membranes.

7.1.2 | Reverse osmosis

RO membranes are most widely used in desalination plants for extracting fresh water out of seawater by rejection of ions. In this process, high pressure is exerted on the saline water to overcome the osmotic pressure upon which the water molecules pass through the semi-permeable membrane.²⁷³ This process is more established than other techniques of desalination for large scale applications though challenges associated to the large energy consumption per unit volume of the produced water has recently diverted attentions to other more energy-efficient membrane-based methods.^{274–277}

Since RO membranes are prone to organic fouling, bio-fouling, and scaling, the surface of such membranes must be modified by appropriate techniques among which CVD techniques are attractive due to providing a high-quality coating. Therefore, several studies have been conducted in this field. Table 5 provides an overview of the characteristics and performance of several RO membranes modified by CVD methods to improve the surface characteristics for desalination applications. In most cases, a modest drop or increase in rejection is noticeable while the effect of deposition on the water flux could be considerable. Beside the experimental trials on the laboratory synthesized materials, a number of studies have been devoted to the CVD modification of commercial RO membranes. For example, Ozaydin-Ince et al.²⁷⁸ modified the surface of a commercial PA TFC membrane with iCVD without causing damage to the membrane active layer. In their study, they successfully deposited HEMA-co-PFA which proved to reduce the microbial fouling at the membrane surface. A similar trend was reported by Matin et al. in case of modification of three commercial RO membranes.²⁷⁶

Also, since occurrence of fouling and biofouling onto the surface of RO membranes can adversely affect membrane performance, specific measures must be in place to mitigate such phenomena or to reduce the propensity.

TABLE 4 The characteristics and performance of a few chemical vapor deposition (CVD)-modified membranes utilized for membrane distillation (MD) applications.

Substrate	Coating material	Technique	Achieved contact angle (°)	Water flux upon modification		Rejection upon modification (%)		Ref.
				Before	After	Before	After	
PTFE	Graphene	CVD	–	18–24	25 ^a	97–99.9	99.9	217
PVDF	Graphene	CVD	–	25–140	21–22 ^a	60–99.9	99.9	217
PP	PHDFA	CVD	130–150	4.5	5 ^b	99.70	99.99	171
SS	CNT	CVD	171	–	13.8 ^a	–	99.8	157
PVDF	PTFE	iCVD	150–170	–	20–32 ^a	–	99.9	172
PAN	pDVB	iCVD	122–149	–	6–11 ^a	–	100%	173
–	PPFDA	iCVD	130–160	–	1.4 ^b	–	>99.98	175
PCTE	pDVB-pC6PFA	iCVD	110–135	–	1.36E–6 ^c	–	99.98	177
Nylon	pDVB	iCVD	96	–	8 ^a	–	99.99	180
PVDF	HMDSO	RF-PECVD	117	20.4	33.2 ^b	–	–	101
SS mesh	CNT	CVD	163	–	10 ^b	–	>95	270
PA6(3)T	PPFDA	iCVD	131–151	–	2–11 ^b	–	99.98	271
–	CNT	CVD	118	–	5.5 ^b	–	97.5	272

Abbreviations: CNT, carbon nanotube; HMDSO, hexamethyldisiloxane; iCVD, initiated chemical vapor deposition; PA6(3)T, poly(trimethyl hexamethylene terephthalamide); PAN, polyacrylonitrile; pC6PFA, poly(1H,1H,2H,2H-perfluorooctyl acrylate); PCTE, polycarbonate track etch; pDVB, poly(divinyl benzene); pDVB, poly(divinyl benzene); PHDFA, poly(1H,1H,2H,2H-heptadecafluorodecyl acrylate); PP, polypropylene; PPFDA, poly(perfluorodecylacrylate); PTFE, polytetrafluoroethylene; PVDF, polyvinylidene fluoride; RF-PECVD, radio frequency plasma enhanced chemical vapor deposition; SS, stainless steel.

^aL m⁻² h⁻¹.

^bkg m⁻² h⁻¹.

^ckg m⁻² h⁻¹ Pa⁻¹.

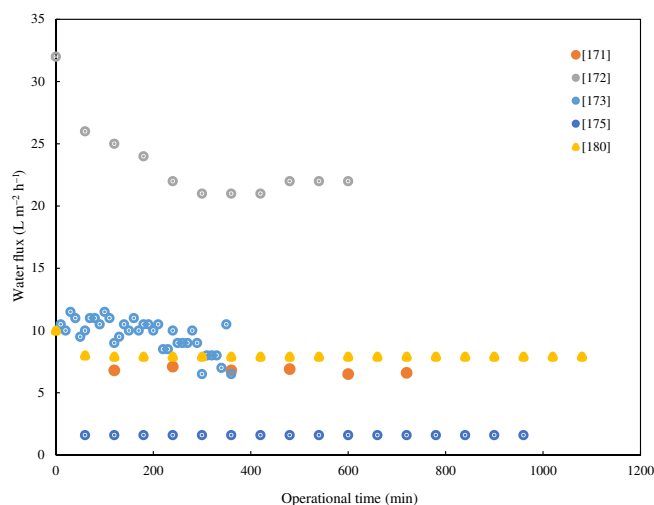


FIGURE 12 The state of decline in water flux during the operation as an indication of stability of deposition for a few CVD-modified MD membranes.^{171–173,175,180} [Color figure can be viewed at wileyonlinelibrary.com]

Figure 13 shows the trend of changes in the normalized flux of some neat and modified membranes for an extended operation time. The values have been obtained by taking the ratio of flux in the presence (J) and absence

of fouling agent (J_0) in the feed. As can be seen, the slopes of modified membranes are larger than the neat membranes, which suggest that the flux of neat membranes in the course of time decreases more rapidly compared to the modified ones due to the larger fouling.

7.1.3 | Nanofiltration

NF membranes are of particular interest for the removal of ions from water streams in applications such as hardness reduction and elimination of corrosive and valuable metallic ions from industrial wastewater streams. NF membranes have a large flux due to having large pores compared to RO membranes. In addition, they require less operational pressure to perform the separation.^{285,286} State of the art NF membranes possess a higher permeability which is a result of the formation of an ultrathin selective layer on a microporous membrane.^{287–289} However, there are still some challenges such as membrane fouling which impairs achieving higher performance values.²⁹⁰ Various surface modification and functionalization methods have shown promising results in advancement of these features including polymeric and ceramic membranes. Table 6 provides some of

TABLE 5 The characteristics and performance of several chemical vapor deposition (CVD)-modified reverse osmosis (RO) membranes used for desalination applications.

Substrate	Coating material	Modification technique	Water flux upon modification		Rejection upon modification (%)		Fouling improvement (%)	Ref.
			Before	After	Before	After		
PA	PANI	PECVD	8.31	5.6–2.8 ^a	91.38	92.3–93.2	–	187
PA/TNT	AA	PECVD	–	49.5 ^b	98.7	99.5	–	188
PA/TNT	AA	PECVD	52.5	49.5 ^b	97.6	98.5	>40	189
PA	p-4VP-co-EGDA	iCVD	44.7	36.4 ^b	96.1	97.6	99.5	174
PES	MoS ₂	CVD	2735	322.7 ^a	–	>99.99	–	279
Alumina	Silica	CD-CVD	–	5.8 ^c	–	81 (H ₂ SO ₄)	–	150
PA	HEMA-co-PFDA	iCVD	126.3	116 ^b	98.9	99.1	–	234
PSf-PA	HEMA-co-PFDA	iCVD	120	115 ^b	–	–	–	182
PSf-PA	HEMA-co-PFDA	iCVD	110	95 ^b	–	–	–	182
PA	p(4-VP-co-EGDA)	iCVD	–	–	–	–	97–98.1	280
PA	p(4-VP-co-EGDA)	iCVD	45.6	37.7 ^b	96	97.9	96.5–98	234
PSf-PA	P4VP	iCVD	30	20 ^b	>90	>90	≈90	281
PS-PSf-PA	HEMA-co-PFDA	iCVD	37	34 ^b	99.5	99.3	–	276
PS-PSf-PA	HEMA-co-PFDA	iCVD	25	22.5 ^b	99.2	99.4	–	276
PS-PSf-PA	HEMA-co-PFDA	iCVD	47	42 ^b	99.3	99.7	–	276
PA	HEMA-co-PFDA	iCVD	120 ^b	–	99.5	–	95	282
PA	HEMA-co-PFA	iCVD	170	80–153 ^a	–	98	–	278
PSf-PA	PDE	iCVD	109.8	91.1 ^b	97	95	–	283
PA	HEMA/PFA	iCVD	38	22 ^b	–	–	–	284
PA	HEMA/PFA	iCVD	50	40 ^b	–	–	–	284
PA	HEMA/PFA	iCVD	120	105 ^b	–	–	–	284

Abbreviations: 4NP, 4-vinylpyridine; AA, acrylic acid; CD-CVD, counter-diffusion chemical vapor deposition; EGDA, ethylene glycol diacrylate; HEMA, 2-hydroxyethyl methacrylate; iCVD, initiated chemical vapor deposition; PA, polyamide; PANI, polyaniline; PDE, poly(2-(dimethylamino)ethyl methacrylate-co-ethylene glycol dimethacrylate); PECVD, plasma-enhanced chemical vapor deposition; PES, polyethersulfone; PFA, perfluorodecylacrylate; PFDA, perfluoro decylacrylate; PS, polystyrene; PSf, polysulfone.

^aL m⁻² h⁻¹ bar⁻¹.

^bL m⁻² h⁻¹.

^ckg m⁻² h⁻¹.

the specifications and characteristics of CVD-modified NF membranes studied in recent years. Considering the other emerging areas of applications of NF membranes including separation of organic solvents, treatment of bio and pharmaceutical streams, and food and beverage industrial process, CVD processes may gain further attention for boosting the properties of the existing NF membranes.

7.1.4 | Ultrafiltration

UF membranes are favorable for separation of micrometer-sized species including proteins, bacteria, biological solutions and microorganisms in addition to serving as a pretreatment unit for desalination and water treatment membranes.²⁹² UF processes, in comparison

with other techniques, have many advantages such as requiring low operational pressure, low cost, and high flux due to the presence of relatively large pores in their structure.^{293,294} The mechanisms of separation in UF membranes are screening or in-depth filtrations which largely depend on the type of membrane structure.

Despite the merits of UF membranes, the major challenge is still fouling which negatively influence the membrane performance.^{201,295–297} Considering its importance, several studies have been devoted to the surface modification and functionalization of diverse organic and inorganic UF membranes to reduce the tendency for fouling. Table 7 provides a summary of some of the recent works in the field by showing the characteristic changes upon application of CVD modification. It can be noticed that in all cases, rejection and anti-fouling properties of the

membranes improved though at the expense of water permeation.

7.1.5 | Electrodialysis

Electrodialysis (ED) is another method of seawater and mostly used for desalination of brackish waters. In contrast to other membrane-based desalination systems, which are dependent on the pressure, concentration or temperature difference, water purification in ED is

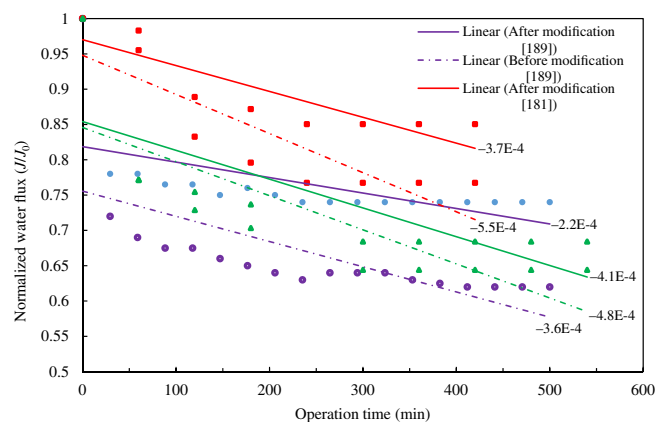


FIGURE 13 The trend of changes in the normalized flux for a few neat and CVD modified RO membranes after an extended period of operation. For clarity, linear regressions are plotted with corresponding slopes.^{181,182,189} [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 6 The characteristics and performance of chemical vapor deposition (CVD)-modified nanofiltration (NF) membranes for water treatment and removal of contaminants.

Substrate	Modifying material	Objective	Technique	Water flux upon modification		Rejection upon modification (%)		Ref.
				Before	After	Before	After	
α - γ Alumina	Silica	NaCl separation	CD-CVD	–	$3.06\text{E}-10^{\text{a}}$	–	89.5	146
α - γ Alumina	Silica	Na_2SO_4 separation	CD-CVD	–	$3.06\text{E}-10^{\text{a}}$	–	91	146
α - γ Alumina	Silica	MgCl_2 separation	CD-CVD	–	$3.06\text{E}-10^{\text{a}}$	–	95.8	146
α - γ Alumina	Silica	MgSO_4 separation	CD-CVD	–	$3.06\text{E}-10^{\text{a}}$	–	98.2	146
PP-PEEK	–	styrene oligomers	PECVD	1.5	$1.3\text{--}1.7^{\text{b}}$	60–100	85–100	255
PEI	–	styrene oligomers	PECVD	111.6	9.6^{b}	low	≈ 100	255
PAN	–	styrene oligomers	PECVD	163.3	3.7^{b}	low	≈ 100	255
–	Poly- <i>p</i> -xylene	Rose Bengal	CVD	–	30.5^{c}	–	99	291
–	Poly- <i>p</i> -xylene	Methyl Orange	CVD	–	30.5^{c}	–	87	291

Abbreviations: CD-CVD, counter-diffusion chemical vapor deposition; PAN, polyacrylonitrile; PECVD, plasma-enhanced chemical vapor deposition; PEEK, poly(etheretherketone); PEI, polyesteramide; PP, polypropylene.

^a $\text{mol m}^{-2} \text{s}^{-1} \text{Pa}^{-1}$.

^b $\text{L m}^{-2} \text{h}^{-1} \text{bar}^{-1}$.

^c $\text{L m}^{-2} \text{h}^{-1} \text{MPa}^{-1}$.

achieved with the aid of an electric field. As can be seen in Figure 14, cations present in the water migrate toward the cathode while anions move toward anode. The transport in ED systems is regulated by cation-exchange membranes (CEMs) and anion-exchange membranes (AEM) which their role is to facilitate the transport of cations and anions, respectively. In other words, CEMs are impermeable to anions and AEMs are impermeable for cations. The combined use of AEMs and CEMs creates the opportunity for the splitting of the feed stream into two separate streams of an ion-free as the product and an ion-rich, which serves as the retentate.²⁹⁸ Only limited studies could be found on the modification of ion-exchange membranes by CVD for use in ED. In 2002, Roualdes et al.²⁹⁹ modified PVDF membranes by aminosiloxane groups using PECVD to investigate its capacity as anion-exchange membrane for Cr transport. Also, Vallois et al.³⁰⁰ used PECVD technique for deposition of polyethylene imine (PEI) on Nafion and sulfonated polyimide (SPI) to improve $\text{H}^+/\text{Cu}^{2+}$ separation performance.

7.2 | Energy and environmental applications

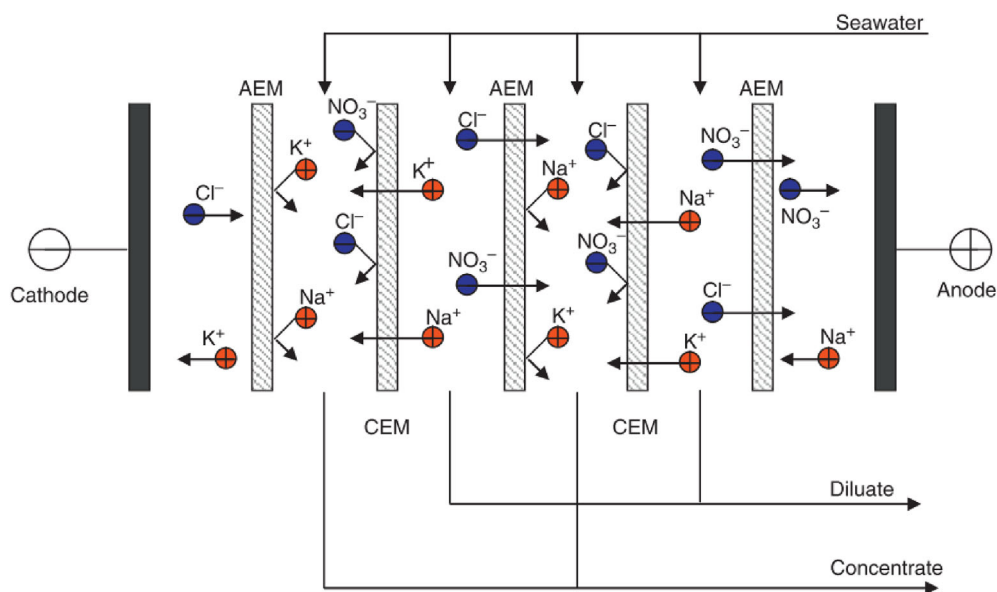
Global energy supply is heavily dependent on conventional fossil fuels such as coal, oil, and gas. However, these resources are extremely limited and have caused severe damage to the environment by expediting global warming as well as producing liquid and solid wastes.

TABLE 7 The characteristics and performance of chemical vapor deposition (CVD)-modified ultrafiltration (UF) membranes for water treatment and removal of contaminants.

Substrate	Modifying material	Objective	Modification technique	Water permeance upon modification ($L m^{-2} h^{-1} bar^{-1}$)		Rejection upon modification (%)		Fouling improvement FRR (%)	Ref.
				Before	After	Before	After		
PSf	AA	BSA rejection	PECVD	156	42	69.7	97.5	48	201
PSf	HEMA	BSA rejection	PECVD	156	35	69.7	98.5	29	201
PSf	AA	Pepsin rejection	PECVD	156	42	72.4	83.9	52	201
PSf	HEMA	Pepsin rejection	PECVD	156	35	72.4	98.5	29	201
Alumina	SiC	Oily water treatment	LP-CVD	350	157	–	–	75	84
Mullite	CNT	Oily water treatment	CVD	–	12.8–15.7	–	99.99	–	161

Abbreviations: AA, acrylic acid; BSA, bovine serum albumin; CNT, carbon nanotube; HEMA, 2-hydroxyethyl methacrylate; LP-CVD, low pressure chemical vapor deposition; PECVD, plasma-enhanced chemical vapor deposition; PSf, polysulfone.

FIGURE 14 The schematic illustration of an electrodialysis process.²⁹⁸ [Color figure can be viewed at wileyonlinelibrary.com]



Rising demand for the replacement of fossil fuels by green and renewable resources has resulted in the development of various technologies.

Membrane separation processes are among the enabler methods that support promotion of clean energy production such as hydrogen, biofuels, biogas.³⁰¹ Membranes have also shown promising features for energy storage and conversion.^{302–306} Part of the achievements in the membranes are due to the progresses made by the modifications that rendered higher performance and surface characteristics. In this section, applications of CVD techniques for modification and functionalization of membranes and thin films used in energy production, efficiency, and storage are discussed.

7.2.1 | Pervaporation

In pervaporation, components of a liquid mixtures are separated based on the relative boiling points and the affinity of ingredients for the transport through the membrane in the vapor phase.^{307,308} This method is highly competitive in terms of energy saving and efficiency compared to alternative techniques such as distillation and has been widely used for dehydration of organic solvents and alcohols, separation of organic-organic mixtures as well as removal of volatile compounds from wastewaters.^{309,310} In development of membranes for pervaporation, the strategy depends on which component transports faster. For instance, it is often desirable to preferentially remove water from a mixture,

which makes it highly desirable to introduce hydrophilicity features into membrane and especially at its surface to promote the transport. This is where CVD techniques can offer great advantages of improving the hydrophilic properties but at the same time not adding the resistance due to the possibility of making tiny layer depositions.

So far only limited number of studies have been devoted to this subject. In a study, Ngamou et al.³¹¹ deposited a thin layer of silica onto the surface of a polyamide-imide membrane to create a selective and yet permeable surface using expanding thermal plasma CVD (ETP-CVD) method which brought about desirable characteristics for improved retention of organic bridges. The defect-free film offered pervaporation separation performances comparable to those of conventional ceramic supported membranes for of an *n*-butanol–water mixture. The water flux was in modified membranes was ~ 1.8 kg m⁻² h⁻¹ and separation factor exceeded 1100.

In another study, multilayered mixed matrix pervaporation membranes were synthesized based on PVA and PES comprising a functional layer of MWCNTs at the outermost surface deposited by thermal CVD process.³¹² Further modifications were made by incorporating carboxyl functional groups on MWCNTs followed by the synthesis of titanium oxide (TiO₂) nanocrystals on them. This approach resulted in improved hydrophilicity, surface roughness and crosslinking of the membranes compared to the neat sample. However, the results revealed that deposition and modification had negative impacts on the permeation flux which is undesirable and could have been controlled. Matsuyama et al. conducted an investigation on fabrication of a benzene-permselective silica hybrid membrane using CDCVD utilizing PrTMOS (propyltrimethoxysilane) and O₃ as reactants.³¹³ They demonstrated that deposition temperatures and ozone flow rate were important parameters in controlling the properties of the resultant membrane. For instance, Thus, the pore size of the membranes increased with increasing the deposition temperature up to 270°C. It was reported that the maximum benzene selectivity over cyclohexane was 113 with the total flux of 2.2E-4 kg m⁻² h⁻¹ through the membrane deposited at 320°C at an ozone flow rate of 0.4 L.min⁻¹. Considering the attractive features of CVD for tuning pervaporation membranes, it is expected that still more rooms are available for the scientists and researchers for making further progresses.

7.2.2 | Hydrogen production and purification

Hydrogen is a single-proton molecule that strongly reacts with oxygen with a considerable amount of energy

released. In the past decades, excessive consumption of fossil fuels has had significant environmental impact along with acceleration of global warming. Accordingly, hydrogen was recognized as one of the alternative sources of energy as a clean fuel. It continues drawing great attention and several countries are rapidly implementing and further advancing the concept of hydrogen economy.

Hydrogen can be produced by employing various techniques among which steam reforming of natural gas accounts for almost 50% of the share of total hydrogen productions.³¹⁴ The process involves heating of methane along with steam in the presence of a catalyst, which results in production of hydrogen and carbon monoxide as the major components and a relatively small amount of carbon dioxide. The process is then followed by a water-gas shift reaction involving the catalytic conversion of carbon monoxide and steam to produce more hydrogen and carbon dioxide. Under these circumstances, membrane separation is utilized, aside from other alternative methods, for the removal of CO₂ and other impurities from the product stream to obtain high purity H₂.³¹⁵

CVD is one of the attractive techniques used especially for the fabrication of hydrogen selective membranes based on silica and palladium. According to the prevailing procedures, often γ -alumina is coated onto the surface of a porous α -alumina by sol-gel to serve as an intermediate layer. Afterward, a thin selective layer is deposited by employing an appropriate CVD technique to form the final membrane. It is claimed that among the alternative procedures for fabrication of such membranes, CVD provide more reliable and selective structures for hydrogen separation.^{78,148}

In the oil reforming or coal gasification, which are alternative methods for hydrogen production, some other chemical compounds are generated besides hydrogen.^{316,317} For example, possibly methyl cyclohexane is converted to toluene and hydrogen which adds to the complexity of the process since hydrogen then needs to be separated from its mixtures with toluene. It has been demonstrated that CVD membranes can also be used to handle such separation efficiently.³¹⁸ For instance, Seshimo et al.¹⁴⁴ reported successful fabrication of silica membranes for hydrogen separation from its mixture with methylcyclohexane and toluene. SF₆ was used instead of toluene due to sharing the same kinetic diameter and the results revealed H₂/SF₆ selectivity of 120,00 (at 300°C) for the silica membranes fabricated by CDCVD.

Porous graphene membranes with sub-nanometer pores have attracted attention among the promising candidates for the separation and purification of several gas mixtures including hydrogen.^{319,320} Therefore, several studies have been conducted on this topic over the past years. In one of the investigations, single-layer graphene membranes with tunable nanopores were fabricated via

TABLE 8 The separation performance and specifications of several chemical vapor deposition (CVD)-modified membranes developed for hydrogen production and purification.

Substrate	Modifying material(s)	Gas mixture	Modification technique	H ₂ permeability upon modification (mol m ⁻² s ⁻¹ Pa ⁻¹)		Selectivity upon modification		Ref.
				Before	After	Before	After	
Alumina	Silica	H ₂ /N ₂	CD-CVD	≈6E-6	5.6 E-7	3.4	13.4	145
Alumina	Silica	H ₂ /SF ₆	CD-CVD	≈6E-6	5.6 E-7	5.9	907	145
Alumina	Silica	H ₂ /SF ₆	CVD	-	2.04 E-6	-	39,300	144
Alumina	Silica	H ₂ /SF ₆	CD-CVD	-	2 E-7	-	1000	257
Alumina	Silica	H ₂ /SF ₆	CD-CVD	-	4.1 E-7	-	-	146
Alumina	Silica	H ₂ /N ₂	CVD	1E-5	1.5 E-7	3	>100	156
Alumina-Ni	SiC	H ₂ /CO ₂	CD-CVD	8E-7	1.2 E-7	4.47	2600	147
Alumina	Silica	H ₂ /N ₂	CD-CVD	-	1.6 E-7	-	4230	148
Alumina	Silica	H ₂ /CH ₄	AP-CVD	≈6E-6	8.3 E-7	2	140	78
Alumina	Silica	H ₂ /C ₂ H ₆	AP-CVD	≈6E-6	8.3 E-7	2	180	78
Alumina	Silica	H ₂ /N ₂	CVD	≈9E-6	1.7 E-7	-	990	79
Alumina	ZIF-8	H ₂ /N ₂	CVD	-	7.6 E-8	-	3.04	160
Alumina	ZIF-8	H ₂ /CO ₂	CVD	-	7.6 E-8	-	5.24	160
Alumina	ZIF-8	H ₂ /CH ₄	CVD	-	7.6 E-8	-	3.3	160
Alumina	Silica-zirconia	H ₂ /CH ₄	CVD	2.1E-5	2.3 E-7	2.5	1600	76
Alumina	Silica-zirconia	H ₂ /CO	CVD	2.1E-5	2.3 E-7	3.7	750	76
Alumina	Silica-zirconia	H ₂ /CO ₂	CVD	2.1E-5	2.3 E-7	3.2	570	76
Zeolite 5A	Polyindene	H ₂ /N ₂	PECVD	5.02E-6	3.83 E-8	3.1	4	204
Zeolite 5A	Polyindene	H ₂ /CO ₂	PECVD	5.02E-6	3.83 E-8	3.8	8.2	204
Alumina	Silica	H ₂ /N ₂	CD-CVD	3E-6	2.8 E-7	≈3	2333	149
Alumina	Silica	H ₂ /N ₂	CVD	2.7E-5	4.9 E-7	3.5	500	163
Alumina	Silica	H ₂ /C ₂ H ₆	CVD	8.5E-6	4 E-7	≈3.5	240	164
Alumina	Silica	H ₂ /CO ₂	CVD	≈8E-6	5.4 E-7	-	95	141
Alumina	Silica	H ₂ /N ₂	CVD	≈8E-6	5.4 E-7	3.5	170	141
Alumina	Silica	H ₂ /CO	CVD	≈8E-6	5.4 E-7	-	170	141
Alumina	Silica	H ₂ /CH ₄	CVD	≈8E-6	5.4 E-7	-	480	141
Alumina	Silica	H ₂ /N ₂	CVD	1.1E-5	2.1 E-7	2.97	581	165
Alumina	Silica	H ₂ /SF ₆	CVD	1.1E-5	2.1 E-7	5.48	3220	165
Alumina	Silica	H ₂ /N ₂	CVD	-	1.53 E-7	-	574	151
Alumina	Silica	H ₂ /SF ₆	CVD	-	1.53 E-7	-	3241	151
Alumina	Silica-zirconia	H ₂ /CO ₂	CVD	7E-6	3.8 E-7	-	1100	77
Alumina	Silica-zirconia	H ₂ /N ₂	CVD	7E-6	3.8 E-7	3.4	1400	77
Alumina	Silica-zirconia	H ₂ /CH ₄	CVD	7E-6	3.8 E-7	-	3700	77
Alumina	Silica	H ₂ /SF ₆	CD-CVD	≈2.5E-6	1.07E-6	≈6	12,000	152
Alumina	Silica	H ₂ /SF ₆	CD-CVD	≈2.5E-6	1.1E-6	≈6	10,000	252
Alumina	Silica	H ₂ /SF ₆	CD-CVD	-	1.2E-6	-	9600	323

Abbreviations: AP-CVD, atmospheric pressure chemical vapor deposition; CD-CVD, counter-diffusion chemical vapor deposition; PECVD, plasma-enhanced chemical vapor deposition; ZIF, zeolitic imidazolate frameworks.

CVD for high performance separation of hydrogen.³²¹ It was demonstrated that application of annealing could smoothen the surface of Cu substrate evidenced by the reduction in surface roughness. Accordingly, the modified low-cost Cu foils transformed into Cu(111) served effectively for the fabrication of efficient single layer graphene membranes with H₂ permeance in the order of 1000 GPU and attractive selectivity of 13 and 26 for H₂/CH₄ and H₂/C₃H₈, respectively. Recently, a novel procedure was introduced and implemented successfully for systematic control of the density of intrinsic graphene pores in the course of CVD process.³²² The advantage was that it enabled retaining the desirable pore sizes for molecular sieving of H₂ from its mixtures with other gases. This procedure combined with the optimization of growth temperature, precursor concentration, and noncovalent decoration of the graphene surface enabled direct synthesis of single-layer graphene membranes with H₂ permeance exceeding 4000 GPU and H₂/CH₄ selectivity beyond 2000. A summary of notable advances in the development of CVD membranes for hydrogen production and purification is provided in Table 8.

Two principal factors that are often taken into account for materials selection for hydrogen selective membranes are thermal and hydrothermal stability. The importance of these factors stems from the fact that in membrane reactors, membranes are exposed to high temperatures and in the presence of water vapor which have detrimental impacts on the stability and performance of the membranes.¹⁵⁶ Thus, certain measures are always recommended to provide a greater protection and stability for the membranes. Surface modification by CVD methods is among the useful approaches.

Figure 15 shows the changes in permeability and selectivity of a few modified membranes as a function of exposure time to the moisture. It can be noticed that after about 100 h, the permeability of different silica-coated membranes decreased by 50%–75% and similarly selectivity decreased by 45%–70% mainly due to the densification of the silicon-based structures. The vulnerability of performance caused by the insufficient membrane stability is regarded as one of the limitations of silicon-based modifications for hydrogen separation applications. To handle this problem, different techniques were used such as incorporation of new functional groups and inorganic oxides like zirconia.^{76,79} There are still more rooms and requirements for further improvements in this field.

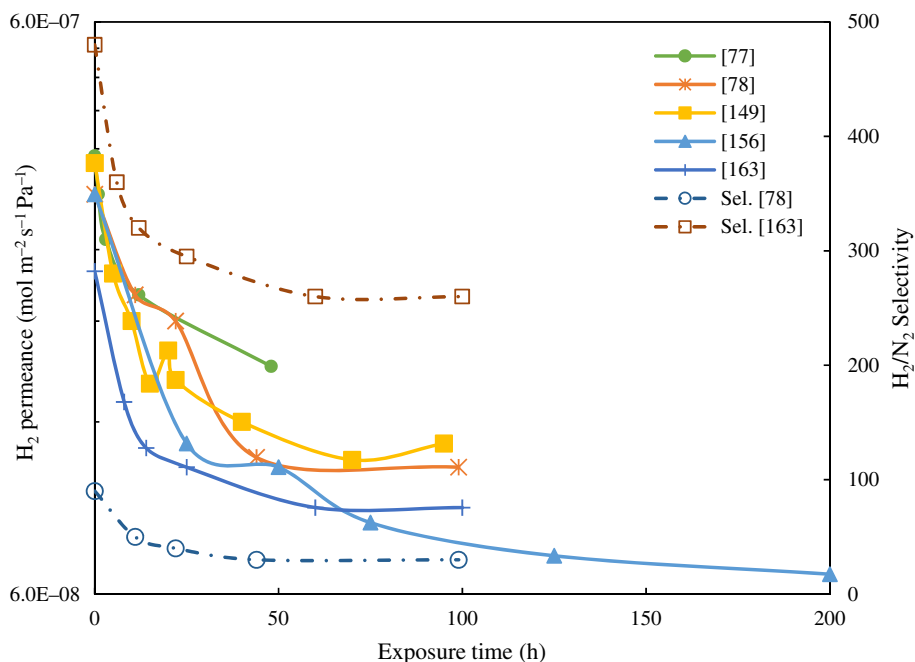
7.2.3 | Fuel cells

Proton exchange membrane fuel cells or polymer electrolyte membrane fuel cells (PEMFC) are established as

practical means for transformation of chemical energy of fuel into electrical energy.³²⁴ Polymer electrolyte membranes (PEMs) constitute the heart of PEMFCs. In the PEMFCs, hydrogen, often used as a fuel, is split into protons and electrons at the anode side. To avoid short circuit and cross mixing between cathode and anode, a cation-exchange membrane is required to let the protons to transfer from anode towards cathode. In reserve, electrons move to cathode through an external route. At cathode, oxygen flow is applied to react with protons and electrons and consequently water is produced.^{303,325} A proton permeable membrane should be used through which electrons, hydrogen, oxygen, and water are not allowed to penetrate. To serve this purpose, and increasing the mechanical stability, the membranes are required to meet certain requirements through altering their properties.

One of these modification techniques is CVD, which has proven to impart beneficial effects on the membrane characteristics and performance.³²⁶ In this regard, CVD techniques have also been used to modify the surface of cathodes and anodes, while in some other studies the focus has been on the improvement of the membrane characteristics. Recently, Leoga et al. used RF-PECVD process to deposit phosphonic acid-based membranes on silicon wafer and Nafion[®] 212 substrate with the aid of dimethyl allylphosphonate as the precursor in order to create a dense, homogeneous, and strongly adherent coating.³²⁶ The resultant membrane exhibited a hydrophilic surface with an improved water sorption and lower water diffusion capabilities. In another study, uniform and highly crosslinked anion exchange membranes were prepared for alkaline fuel cells based on 4-vinylpyridine by plasma polymerization.³²⁷ The advantage of the modified membrane compared to the commercial membrane was a lower effective resistance due to the possibility of forming a thinner film with the aid of plasma polymerization. Proton exchange membranes were also produced by hierarchical combination of a nonconductive membrane based on PTFE and a proton conductive coating.^{328–330} The proton conductive coating was deposited by iCVD and consisted of copolymers of perfluorodecyl acrylate (PFDA) and methacrylic acid (MAA). It was demonstrated that the copolymers crystallized into a bilayer structure formed by the perfluorinated pendant chains of PFDA perpendicular to the substrate surface whereas the MAA molecules formed COOH-enriched regions among the bilayers, parallel to the substrate surface to function as ionic channels for proton conduction when the acid groups become deprotonated. In another study, free-standing ion conductive membranes were obtained by iCVD polymerization of an ionic liquid.³³¹ Results revealed that the conductivity of the

FIGURE 15 The changes in hydrogen permeance and selectivity as a function of exposure time to the moisture.^{77,78,149,156,163} [Color figure can be viewed at wileyonlinelibrary.com]



fabricated film was comparable to the ionic liquid at the liquid state. In addition, the conductivity of the membranes was stable which indicates that using iCVD had no negative impact on the mobility of anions in the ionic liquid during the deposition process. A useful review published just recently covering some aspects of modification of alkaline exchange membranes by various methods including CVD-based techniques.³³²

7.2.4 | Hydrocarbon separation

Separation and recovery of hydrocarbons from diverse sources is particularly important especially from energy and environmental points of view. Membrane processes have created valuable opportunities for applications in this field.^{333–335} Despite a wide range of polymers and techniques of membrane preparation, only a few studies have focused on the CVD coated membranes. All these studies are on ceramic membranes modified with the aid of silica. A summary of the characteristics and performance features are provided in Table 9.

Among the recent activities, attempt was made on the preparation of silica membranes by CVD modification of various methyl-substituted silanes.⁷⁹ The results revealed that depending on the selection of the type of methyl functional groups, the permeance and selectivity of the membranes could be tuned for the recovery of CH₄ and C₂H₈. The permeation properties of silica membranes derived with the aid of CD-CVD were investigated with special focus on hydrocarbon separations including the mixtures of CH₄, C₂H₆, C₃H₆, C₃H₈, C₆H₆, and C₆H₁₂.³³⁶

Another interesting study was post treatment of silica NF membranes with nanopore structures by conducting CVD intended for the separation of hydrocarbons namely CH₄ and C₃H₈ from mixtures with other gases.³³⁷ Also, fabrication of silica-coated alumina membranes performed using counter-diffusion CVD enabled high temperature separation of propylene from its mixture with propane.³³⁸ It was demonstrated that the separation performance could be tuned by adjusting the deposition time and temperature to obtain the best combination of permeability and selectivity.

Research has also been devoted to the tailoring of single-atomic thick nanoporous graphene membranes for effective molecular transport and particularly CO₂/CH₄ separations.^{339,340} This includes experimental fabrications as well as mathematical modeling and simulation of transport of CO₂ and CH₄ through the pores of graphene membranes with elaborations on the mechanisms of molecular adsorption to the pore mouth and then passage through the pores.³⁴¹ The results exhibited a trade-off between the permeance and selectivity for the CO₂/CH₄ gas mixture, represented by an upper bound in a Robeson graph.

Based on the promising results obtained from the analysis of silica membranes, there is a vast opportunity for extension of this method to other materials that may offer even better performance for hydrocarbon separations. In addition, considering the presence of distinct features between the ingredients in olefin/paraffin separation, embedding of certain functionalities to enable facilitated transport of olefins through the deposited layer may provide exceptional performance values compared to the conventional membranes.

TABLE 9 Performance of a few chemical vapor deposition (CVD)-modified membranes for separation and recovery of hydrocarbons.

Substrate	Modifying material	Gas mixture	Technique	Permeance of the fast-permeating component	Gas pair selectivity	Ref.
Alumina	Silica	CH ₄ /C ₂ H ₆	CVD	3.21E-9 ^a	43.02	154
Alumina	Silica	CH ₄ /C ₃ H ₈	CVD	3.21E-9 ^a	110.53	154
Alumina	Silica	CH ₄ /i-C ₄ H ₁₀	CVD	3.21E-9 ^a	304.11	154
Alumina	Silica	C ₃ H ₆ /C ₃ H ₈	CD-CVD	1E-8 ^a	414	338
-	Silica	CH ₄ /C ₂ H ₆	CD-CVD	-	37	336
-	Silica	C ₃ H ₆ /C ₃ H ₈	CD-CVD	-	414	336
-	Silica	C ₆ H ₆ /C ₆ H ₁₂	CD-CVD	5.6E-3 ^b	53	336

Abbreviations: CD-CVD, counter-diffusion chemical vapor deposition; CVD, chemical vapor deposition.

^amol m⁻² s⁻¹ Pa⁻¹.

^bkg m⁻² h⁻¹.

7.2.5 | Carbon capture and separation

Nowadays, the ever-increasing demand for the consumption of fossil fuels has contributed to the large production of CO₂ as the main cause of global warming and climate change. To mitigate these problems, there is a need to limit the amount of CO₂ emission to the atmosphere by either preventing its excessive production or by removing it from the effluent streams.^{277,342,343} Various technologies have been used for CO₂ separation and capture from the rich or low content streams such as membrane separation processes, absorption and adsorption.³⁴⁴ Among these techniques, membrane processes are highly favorable thanks to their tremendous benefits including low operational cost, high effective surface area, high efficiency and their green and energy saving merits.^{345,346}

Beside the presence of inorganic membranes, gas separation membranes made of polymeric materials have attracted particular attention for CO₂ elimination. Commercial gas separation membranes are mostly produced using cellulose acetate, PSf and aromatic polyimides.^{347,348} Although these membranes have demonstrated desirable characteristics, application of modification techniques such as CVD has been helpful in improving the membrane characteristics and separation performance. According to Table 10, which displays the specifications of some of the CVD-modified membranes used for carbon capture, modified membranes in general can be found having a higher selectivity though the trends in permeance were highly materials specific. It also should be noted that like hydrogen permeation membranes, CO₂ separation membranes may also be exposed to elevated temperatures and humidity. One of the studies in this field was carried out by Messaoud et al.²⁵³ in which hybrid organic-inorganic silica membrane coating were fabricated with different precursors. They investigated hydrothermal stability of coated membrane by analyzing at 120°C and exposure time of 60 hours. It was found that the

permeability declined by about 65% whilst the selectivity, despite fluctuations, did not drop more than 20%.

7.2.6 | Helium separation

Helium as a noble gas with inert and nontoxic behavior is used extensively for medical, scientific, and industrial applications. Extraction of helium from natural gas which contains CH₄, N₂, CO₂, and other hydrocarbons is the most dominant method of helium recovery.³⁵⁰ Among the various mature technologies for helium recovery such as cryogenic and adsorption, membrane separation has emerged as an efficient and cost-effective method.^{351,352} To achieve high purity helium, often a dense selective layer is essential. CVD techniques can be used to create a dense layer onto the surface of various substrates for this application. However, nanoporous graphene membranes have also been favorably used for helium separation.³⁵³ In majority of the research investigations, silica has been deposited on substrates like alumina to provide He selective features. The study lead by Labropoulos et al.³⁵⁴ demonstrated achieving selectivities in the order of 3, 4, and 5 for He/N₂, He/CO₂ and He/SF₆, respectively. Table 11 shows the specifications of some of the CVD-modified membranes developed for He separation and purification.

7.3 | Biomedical and life science

Membranes and thin films have gained attention and popularity for a variety of biomedical and life science applications such as artificial organs, drug delivery, tissue engineering, and so forth. Owing to the need for the membrane to be in close contact with a natural organ or the living cells, such films must meet some of essential requirements such as biocompatibility, biodegradability,

TABLE 10 Separation performance of a number of chemical vapor deposition (CVD)-modified membranes developed for carbon capture and separation.

Substrate	Modifying material	Gas mixture	Technique	CO ₂ permeance upon modification		Selectivity upon modification		Ref.
				Before	After	Before	After	
PDMS	SiOCH	CO ₂ /N ₂	PECVD	–	≈20 ^a	–	8	186
PDMS	SiN _w O _x C _y H _z	CO ₂ /N ₂	PECVD	9300	≈760 ^a	9	15	195
PDMS	SiN _w O _x C _y H _z	CO ₂ /CH ₄	PECVD	9300	≈760 ^a	3	8	195
SPPO	Propylene	CO ₂ /N ₂	CVD	–	5E–10 ^b	–	32	158
SPPO	Propylene	CO ₂ /CH ₄	CVD	–	5E–10 ^b	–	437	158
Carbon	Propene	CO ₂ /CH ₄	CVD	1.51E–4	7.748 ^a	6	249	349
Alumina	Silica	CO ₂ /CH ₄	AP-PECVD	–	1.9E–7 ^b	–	166	210
Alumina	Silica	CO ₂ /N ₂	AP-PECVD	–	1.9E–7 ^b	–	46	210
PTMSP	P(DVB-co-ZnTPC)	CO ₂ /CH ₄	iPE-CVD	≈1200	≈10 ^a	2	150	183
PTMSP	P(DVB-co-ZnTPC)	CO ₂ /N ₂	iPE-CVD	≈1200	≈10 ^a	5.3	60	183
Alumina	Organo-silica	CO ₂ /CH ₄	CVD	≈10 ^{–5}	1.8E–7 ^b	low	84	253
Alumina	Silica	CO ₂ /CH ₄	CVD	≈10 ^{–5}	2.3E–7 ^b	low	40	251

Abbreviations: AP-PECVD, atmospheric pressure plasma-enhanced chemical vapor deposition; DVB, divinylbenzene; iPE-CVD, initiated plasma-enhanced chemical vapor deposition; PDMS, polydimethylsiloxane; PECVD, plasma-enhanced chemical vapor deposition; PTMSP, poly(1-trimethylsilyl-1-propyne); SPPO, sulfonated poly(2,6-dimethyl-1,4-phenylene oxide); ZnTPC: zinc (II) meso-tetraphenylchlorin.

^aGPU.

^bmol m^{–2} s^{–1} Pa^{–1}.

TABLE 11 The characteristics and performance of a number of chemical vapor deposition (CVD)-modified membranes developed for helium separation and purification.

Substrate	Coating material	Gas mixture	Technique	He permeability/permeance after modification	Modified selectivity	Ref.
PDMS	SiOCH	He/N ₂	PECVD	≈300 ^a	37	186
PDMS	SiOCH	He/CO ₂	PECVD	≈300 ^a	11	186
Alumina-ZSM-5	Carbon	He/SF ₆	CVD	30 ^b	4	159
Silica	Nanographite	He/Ne	PECVD	1.4E–16 ^c	48	206
Alumina	SiO ₂ -Ni	He/H ₂	CD-CVD	1E–7 ^c	2.5	355
Alumina	Silica	He/N ₂	Cyclic CVD	5.22E–7 ^c	164.2	337
Alumina	Silica	He/N ₂	PECVD	5.2E–7 ^c	4200	356
Alumina	Si-Zr-C-N	He/N ₂	PECVD	4.5E–8 ^c	58	357
Alumina	a-SiC _x N _y :H	He/N ₂	PECVD	1.64E–7 ^c	20	258

Abbreviations: CD-CVD, counter-diffusion chemical vapor deposition; PDMS, polydimethylsiloxane; PECVD, plasma-enhanced chemical vapor deposition.

^aGPU.

^bm³ m^{–2} h^{–1} bar^{–1}.

^cmol m^{–2} h^{–1} Pa^{–1}.

sterilizability, depending on the prevailing regulations. CVD techniques have found great applications in this field for surface functionalization in to render the desirable characteristics. In the following sections, some of the applications of CVD techniques within the domain of biomedical and life science are discussed.

7.3.1 | Artificial organs

Artificial organs are human-made devices used to replace the entire or a part of a natural organ in case its proper function is impaired due to some diseases or injuries. In most artificial organs such as membrane oxygenators,

artificial kidney, artificial liver and artificial pancreas, the vital role is played by the thin film membranes. As these membranes are often in contact with blood or certain cells, they have to well designed and fabricated in order to offer the required properties and also last for the entire period of operation.^{358,359} Among the recent studies, PECVD was employed for the modification of flat-sheet Matrimid membrane oxygenators.³⁶⁰ The main goals were to increase the biocompatibility and reduce protein adsorption by functionalizing the surface with fluorine groups using carbon tetrafluoride (CF₄) in the gas phase. Upon modification, protein adsorption to the membrane surface decreased by 81% and oxygen permeability increased by 33%. Furthermore, Sreenivasan et al.³⁶¹ used iCVD method for deposition of p(MA-co-DEGDVE) coating onto the surface of PTFE porous substrates. Their main aim was to create a denser coating to prevent plasma leakage while the total performance of their microfluidic artificial lung remains acceptable. Their results showed that the modified membranes were 33% more permeable than silicone membranes. By an 8 μm coating, the liquid permeation reduced by more than 99.9%. In another attempt, Perrenoud et al.³⁶² introduced different coatings of heparin/isopropanol and heparin/HMDSO on a glass film by RF-PECVD to alter the biocompatibility of surface. They demonstrated that modification could successfully improve the surface biocompatibility more than what was achieved by SF₆ plasma treatment.

7.3.2 | Blood purification

One of the applications of membrane processes is in the field of blood purification. The separation of immunoglobulin (IgG) from blood is performed with the aid of affinity membranes. The major application of affinity membranes in blood plasma treatment and cell fractionation. While the former deals with the separation of blood plasma from cells, the latter deals with the separation of cells like mesenchymal progenitor cells, endothelial cells, and mononuclear cells from tissues and blood. These membranes should possess some of the key characteristics such as biocompatibility and high performance which can be achieved by CVD techniques as one of the approaches.

In 2021, Song et al.¹⁵⁵ employed a novel coated composite membrane in order to remove bilirubin from blood. As this toxin cannot be separated via hemodialysis membranes, they used an anticoagulant affinity membrane made of nylon composite. In their study, poly(pyrrole-3-carboxylic acid) was coated on the nylon using CVD to enhance biocompatibility and adsorption

capacity and then heparin and poly(L-arginine) were immobilized onto the surface. The modified membrane could remove the bilirubin by 86%. Also, PECVD was employed for the coating of hydrogenated tetrahedral amorphous carbon and amorphous hydrogenated carbon onto the surface of titanium-based substrates intended for petal valves in pulsatile ventricular devices.³⁶³ All the coatings demonstrated high haemocompatibility when assessed using human blood especially in the presence of arterial shear stress.

7.3.3 | Drug delivery

Drugs are often delivered to the organs, tissues, and cells through conventional techniques such as tablets, solutions, and pills. However, these techniques of drug administration are not often selective. Also, it is not possible to regulate the amount and the rate of drug release to the target cells. To address these problems, new systems have been emerged to deliver the drugs just to the specific targets and at a controlled rate. The novel drug delivery systems are also capable of reducing side effects, increasing pharmacological activity and enhancing the aqueous solubility and chemical stability of active agents.³⁶⁴

Membranes containing osmotic and diffusion-controlled membrane systems play important roles in drug delivery. For instance, transdermal membranes are placed on the skin and let the drug be released at a controlled rate with the aid of membranes.³⁶⁵ CVD modifications have been found useful for the manipulation of membrane-based drug delivery systems. In a study, Shi et al.¹⁷⁶ aimed to develop a new pH-responsive drug delivery system involving iCVD modification for rifampicin encapsulation. They first fabricated polylactide (PLA) membranes and then coated the surface by biodegradable polymethacrylic anhydride (PMAH) via iCVD. The main objective of the coating was to store drugs and release them after the degradation of the PMAH coating to PMAA at a specific pH range. It is considered as the first study in which a biodegradable coating is applied using a CVD method. In another research, You et al.³⁶⁶ used iCVD to coat a polyester fabric with poly(3,3,4,4,5,5,6,6,7,7,8,8,9,9,10,10,10-heptadecafluorodecylmethacrylate) (PHFDMA). They created a Janus membrane with a hydrophobic side produced by iCVD and a hydrophilic side prepared through the base catalyzed hydrolysis of ester bond in the PHFDMA polymer backbone. The purpose of their work was to produce a patch with a controlled drug release in just one direction. The final permeability of the Janus membrane patch experienced a significant increase compared to the bare patch. This study showed the capability of CVD techniques for the

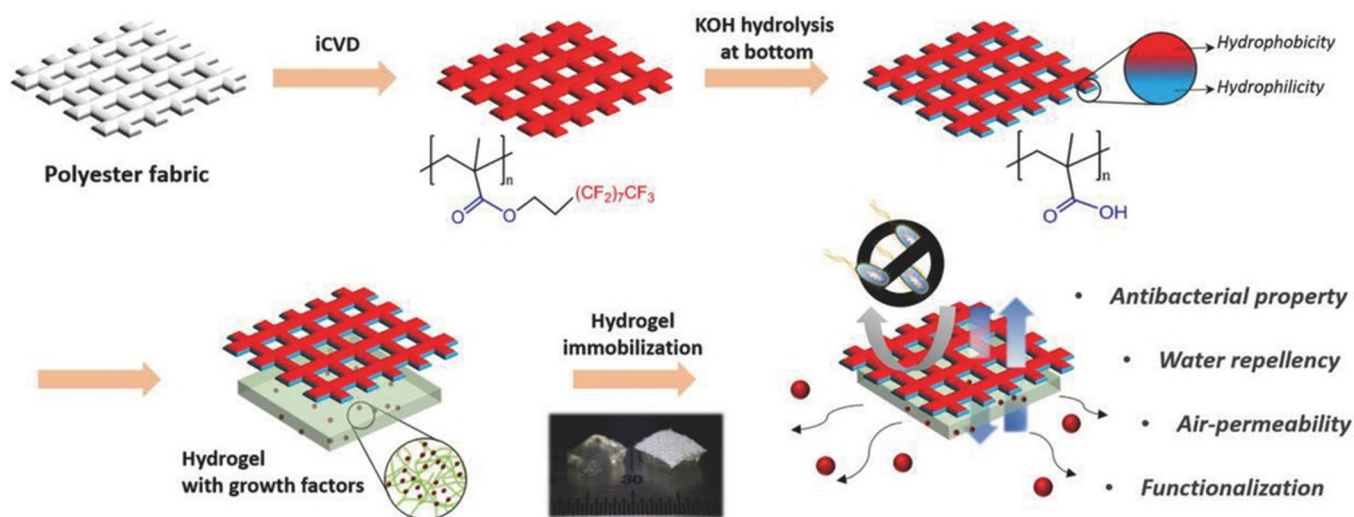


FIGURE 16 Typical steps involved in the development of Janus membranes by iCVD.¹⁷⁸ [Color figure can be viewed at wileyonlinelibrary.com]

modification of patch membranes involving mono-directional drug delivery.

Other examples of drug-delivery membranes were include deposition of a hydrogel by iCVD on textiles to develop a model dressing for wound protection and healing.³⁶⁷ The patch of textile-drug-hydrogel indeed preserves the wound from the surrounding atmosphere, maintains the moisture and delivers the drug. For this purpose, several drugs have been encapsulated including antibiotics,³⁶⁸ anti-inflammatory,³⁶⁹ antifungal,³⁷⁰ and the possibility of regulating their delivery only in case of high temperatures was studied by using a temperature-responsive hydrogel.³⁷¹

7.3.4 | Tissue engineering

Tissue engineering is an attractive branch of biomedical science, which aims to improve tissue function by replacing, repairing or regenerating damaged tissues using the state of the art procedures.³⁷² Membranes have found the opportunities to play roles in tissue engineering. One of these applications is in the regeneration of tissues such as skins, nerves, and bones. For example, in repairing bone defects by guided bone regeneration (GBR), barrier membranes are used to prevent formation of soft tissues through fibrosis and at the same time, to reserve the space for the growth of new bones at the defect sites.³⁷³ This procedure is currently being applied in dental treatments and tooth implantations.

Among the relevant studies, Terriza et al. used PECVD to coat a thin layer of SiO₂ and TiO₂ onto the surface of poly(lactide-co-glycolide) (PLGA) thin films

for GBR.^{374,375} The plasma polymerization was performed at 60 and 400 W and HDMSO and TTIP were utilized as the precursors for SiO₂ and TiO₂ coating, respectively. The results revealed that the modified membranes offered novel biomaterial features due to exhibiting a high bioactivity and human osteoblasts cells response. In another effort, Karfeld-Sulzer et al.¹⁶⁶ used N-methylpyrrolidone (NMP) to improve the bone regeneration of a barrier membrane by loading different amounts of NMP on PLGA with the aid of CVD. The modified membranes were resorbable and at the same time bioactive due to the incorporation of NMP and this could promote the bone regeneration process. Very recently, iCVD was employed for the functionalization of composite patches based on PLA by poly(2-hydroxyethyl methacrylate-co-ethylene glycol dimethacrylate) (p(HEMA-co-EGDMA)) as a copolymer to enhance the wettability and biocompatibility.³⁷⁶ The characteristics of the coated film improved by promoting the hydrophilicity without deterioration of morphological and structural properties with ideal cell adhesion for human osteoblasts. It has also been demonstrated that iCVD enabled solvent-free deposition of osteogenic polyelectrolyte materials on the polystyrene cell plates imparts different surface charges.³⁷⁷ This offered useful effects on osteoconduction and osteoinduction and facilitated inducing of nucleation and crystallization of apatites during mineralization.

Another interesting application of CVD-modified membranes is in the skin regeneration and wound dressing. In some cases, the injury that is inflicted to the skin can be severe and membranes and thin films are used to cover the wound to avoid bacterial infection by acting as

TABLE 12 An overview on the specifications and characteristics of gas barrier chemical vapor deposition (CVD)-modified membranes and thin films used for packaging applications.

Gas	Substrate	Coating material(s)	Technique(s)	Permeation upon modification		Unit	Ref.
				Before	After		
H ₂ O	PET	a-SiN _x :H	PECVD	–	0.007	a	98
H ₂ O	Textile-based OLED	AT nanolaminate (p(V ₃ D ₃))	ALD/iCVD	–	9.94E–6	a	381
H ₂ O	PET	SiN _x	R2R-PECVD	–	0.0307	a	32
H ₂ O	PET	SiO _x	R2R-PECVD	–	0.0649	a	32
He	TPU	Graphene	CVD	48	36	b	379
H ₂ O	PLA	SiO _x	PECVD	287.1	205.2	a	190
O ₂	PLA	SiO _x	PECVD	451.3	205.2	c	190
O ₂	PET	Silica	PECVD	68.85	2.45	d	192
H ₂ O	PET	Silica	PECVD	30.74	2.47	d	192
H ₂ O	ITO-glass	SiO ₂ /SiO _x C _y	PECVD	15.3	0.011	a	191
H ₂ O	PET	a-SiN _x :H/n-SiO _x N _y /h-SiO _x	PECVD	5.44	0.086	a	193
O ₂	PLA	SiO _x	PECVD	510	125.7	c	194
H ₂ O	PLA	SiO _x	PECVD	104.8	48.4	a	194
H ₂ O	PEN	SiN _x	PECVD	0.013	0.003	a	196
O ₂	PET	SiO _x N _y	PECVD	12	0.09	c	197
H ₂ O	PET	SiO _x N _y	PECVD	4.7	0.2	a	197
H ₂ O	PEN	Poly(HMDSO)	PECVD	18.4	5.09	a	198
O ₂	PET	Silica	CCVD	110	0.36	d	142
H ₂ O	PET	Silica	CCVD	16	4.4	a	142
H ₂ O	PET	SiO _x N _y	PECVD	3.61	0.06	a	199
O ₂	PE	SiO _x	PECVD	700	70	e	203
O ₂	PET	SiO _x N _y	RF-PECVD	21.8	0.08	d	215
H ₂ O	PET	SiN _x	RF-PECVD	0.7	0.018	a	216
H ₂ O	PET	SiO _x N _y	ICP-CVD	–	0.001	a	167
O ₂	PCL	SiO _x	RF-PECVD	2395	1870	c	170
CO ₂	PCL	SiO _x	RF-PECVD	23,043	12,600	c	170
H ₂ O	PCL	SiO _x	RF-PECVD	100	97	a	170
H ₂ O	Parylene C	Alumina	CVD	–	8E–4	a	162
O ₂	PLLA	Silica	PECVD	263	156	c	168
H ₂ O	PLLA	Silica	PECVD	319	149	c	168
N ₂	PLLA	Silica	PECVD	46	19	c	168
CO ₂	PLLA	Silica	PECVD	760	527.5	c	168
O ₂	PET	Graphene	Cold-war CVD	≈60	≈4	d	153
O ₂	PET	SiO _x	PECVD	75.3	42.9	c	184
O ₂	PET	Silica	PEALD	80	0.3	c	382
O ₂	PET	Al ₂ O ₃	PEALD	70	1.1	c	382
H ₂ O	PEN	SiN	C-CVD	–	1.31E–6	a	143
H ₂ O	PET	SiN _x	R2R-PECVD	1.4	0.0167	a	214
O ₂	PET	Silica	PECVD	75.3	0.89	d	209
O ₂	PET	DLC	RF-PECVD	15.39	3.32	c	100
CO ₂	PET	DLC	RF-PECVD	4.6	1.23	c	100

TABLE 12 (Continued)

Gas	Substrate	Coating material(s)	Technique(s)	Permeation upon modification		Unit	Ref.
				Before	After		
H ₂ O	PET	DLC	RF-PECVD	–	45.4	a	100
H ₂ O	PEN	Silica	R2R-PECVD	–	6.9E–4	a	211
H ₂ O	–	SiN _x	PECVD	–	0.046	a	212
O ₂	PET	Silica	AP-PECVD	–	8.2	e	213
H ₂ O	PEN	SiO _x /polyHVDSO	PECVD/iCVD	1	0.01	a	383

Abbreviations: AP-PECVD, atmospheric pressure plasma-enhanced chemical vapor deposition; CCVD, combustion chemical vapor deposition; HMDSO, hexamethyldisiloxane; ICP-CVD, inductively coupled plasma chemical vapor deposition; iCVD, initiated chemical vapor deposition; OLED, organic light-emitting diode; PCL, polycaprolactone; PE, polyethylene; PE-ALD, plasma-enhanced atomic layer deposition; PECVD, plasma-enhanced chemical vapor deposition; PEN, polyethylene naphthalate; PET, polyethylene terephthalate; PLA, polylactic acid; PLLA, poly(L-lactide); R2R-PECVD, roll-to-roll plasma-enhanced chemical vapor deposition; RF-PECVD, radio frequency plasma enhanced chemical vapor deposition; TPU, thermoplastic polyurethane.

^ag day⁻¹ m⁻².

^bmbar L mm s⁻¹ m⁻² atm⁻¹.

^ccm³ day⁻¹ m⁻².

^dcm³ day⁻¹ m⁻² bar⁻¹.

^ecm³ day⁻¹ m⁻² atm⁻¹.

a barrier against moisture and yet permeable to oxygen. In this field, An et al. developed Janus membrane with hydrophobic and hydrophilic parts using iCVD.¹⁷⁸ A polyester membrane was functionalized by PHFDMA as a hydrophobic polymer and then KOH hydrolysis was conducted at the bottom of the modified membrane to produce the hydrophilic side. The steps are shown in Figure 16. The role of the PHFDMA coating was to create a barrier against water permeation and to prevent bacterial adhesion. On the other hand, gelatin (GelMA) was immobilized on the hydrophilic surface to improve the biocompatibility as well as wound healing speed and quality. The final microporous membrane showed an incredible decrease in bacterial growth along with a good water resistance.

Another emerged concepts in the field is exploitation of iCVD for the growth of polymeric films on the substrates with complex curvature and microstructure for mimicking the natural surfaces.³⁷⁸ The advantage of the “self-wrinkling” is that it eliminates the need for the separate growth and other steps involved in previous methods. Furthermore, it can be applied onto solid and liquid substrates by forming desirable textures or patterns. Also, the properties of the resultant coating can be tuned by manipulation of the parameters. It is anticipated that this field will catch more attention especially for some interesting applications like robotics and soft skins.

7.4 | Packaging

CVD techniques have also found applications in creation of a gas barrier layers over a polymeric film. These

impermeable films have diverse demands specifically in food packaging, electronics, and aerospace. Such barrier films are either intended to prevent the leakage of certain gas from the chamber or to avoid penetration of unwanted elements into the site for the sake of protection. One of the solutions to achieve such properties is through the application of thin coatings of inorganic materials onto the surface of flexible polymeric ones via CVD modifications. Chaitoglou et al.³⁷⁹ successfully deposited a stack of graphene onto the thermoplastic polyurethane (TPU) film through layer-by-layer assembly by CVD to improve the helium barrier properties in flexible films. The resultant composite films could desirably reduce He permeability by about 10% compared to the neat TPU. Further reduction in He permeability up to ~25% was possible but required stacking five layers of graphene deposition. In another attempt, Wilski et al.¹⁹² employed low pressure PECVD to coat silica on a PET film. Their best membrane showed 96% and 92% decrease in oxygen and water vapor transmission rates, respectively, compared to the neat PET. However, depending on the process conditions and procedure, defects could occur in the coating with possible impacts on the mass transport and diffusion.²⁰⁹ Table 12 provides an overview of different CVD techniques for altering the barrier properties of selected membranes and thin films with respect to certain gases to reveal part of the ongoing trends in the field. It can be realized that the popularity of PET, PLA and PEN is high for being used as the substrate. In addition, the prominent objectives of such coatings have been to prevent the penetration of water vapor followed by prevention of oxygen. Also, single layer free-standing graphene membranes with atomic thickness were fabricated

via pressure controlled CVD involving high temperature O_2 etching for creating nanopores within the structure.³⁸⁰ They were explored in terms of pressure and temperature stability for industrial gas separations and as barrier membranes. It was revealed that the membranes remained intact over weeks of testing at pressure differentials of >0.5 bar and repeated temperature cycling from 25 to 200°C. Data revealed that the graphene membranes function as effective barriers to the permeation of several gases H_2 , He, CH_4 , CO_2 , Kr, and SF_6 , with extremely low or close to zero flux.

8 | SUMMARY AND OUTLOOK

The rapid pace of growth in advanced materials for the technological applications with reliance on thin films and membranes continues to attract more attention. This is coincided with the design and synthesis of new materials with exciting features, which is in progress in parallel to the modification of existing materials. The both approaches have so far created wonderful opportunities and breakthroughs. One of the promising approaches for the exploitation of the advantageous features of such advanced materials is through deposition of a fine and yet functional layer onto the surface of other materials. Owing to the significance of thin films and membranes in various industries, such modifications impart novel characteristics to meet the requirements.

Among the multiple choice of physical and chemical approaches for deposition, CVD techniques have progressed considerably and exhibited promising results with unique characteristics. Accordingly, they are expected to play dominant roles, especially for the emerging applications as evidenced by the number of research and patent documents released over the past years as well by noting the existing trends. As new materials with special functionalities emerge which has resulted in several derivative techniques of CVD, the associated challenges also require serious attention. For instance, despite the successful features of CVD techniques, still controlled deposition onto the surface of thin films require careful procedures, as essentially the nature and behaviors for the dense or porous substrate structures determine the final quality of the deposition. This translates to the fact that often, to ensure a high quality deposition, attempts should be done on the synthesis of substrates featuring new characteristics. Another line of intensive investigations is on the morphology and architecture of the surface porosity and pore connectivity to ensure uniform deposition in order to avoid intrusions of species into the bulk phase. In addition, the selection of ingredients such as precursor and modifying agent must be well formulated to avoid formation of defects in the course of

process. Equally important is attention to the interactions between the substrate and reactants especially considering the process kinetics and the steps involved aside to the operational conditions.

In terms of technique, iCVD is growing rapidly due to the involvement of radical initiators that can be activated at low temperatures for the subsequent reactions while preserving the precursor. It was demonstrated that iCVD has been successfully applied in the case of PA, PP, PVDF, PAN which are typical membrane materials for the separation applications. Another promising opportunity would be to compare the performance of such materials after CVD for the existing applications in order to evaluate added values. This also motivates researchers to extend CVD to other conventionally used materials for the membrane separation and film barrier applications.

From the materials perspective, ceramic and polymeric substrates still will dominate as the prominent materials of choice. However, silicone-based materials are expected to provide greater opportunities by serving as the modifying and precursor materials. Besides, mixed ceramic precursors are gaining increased attention due to the provision of utilizing the synergistic features of few materials together.

Even though the effect of some of the process parameters are well established by the number of past works, the predictability of dominance of such trends on the new materials especially in terms of quality and other critical features should be treated with care. Such circumstances may require optimization of process duration, pressure, temperature, atmosphere, the type, and flow rate of the gas as well as input power as the most important variables that play great roles in the process. Nevertheless, considering the valuable library of data available from the past trials in literature, researchers may find useful initial setting followed with possible pathways for implementing further tuning and adjustments in order to achieve the expected outcomes.

Finally, always the key determining factors is the performance in the application as well as cost. The large potentials of CVD for the variety of applications demonstrated in this review highlight the fact that CVD-modified thin films and membranes still hold great promises for the new applications to emerge. This especially applies to the use of CVD modifications for biomedical and life science applications. All these indicate that this field deserves more investments in time, efforts, and resources for making further breakthroughs to reduce the costs and also to tackle the remaining challenges in the way for implementations especially for scale ups.

AUTHOR CONTRIBUTIONS

Amir Hossein Mostafavi: Data curation (lead); formal analysis (lead); investigation (equal); visualization (lead);

writing – original draft (lead); writing – review and editing (supporting). **Ajay Kumar Mishra:** Methodology (supporting); supervision (supporting); writing – review and editing (supporting). **Fausto Gallucci:** Methodology (supporting); supervision (supporting); writing – review and editing (supporting). **Jong Hak Kim:** Methodology (supporting); supervision (supporting); writing – review and editing (supporting). **Mathias Ulbricht:** Conceptualization (supporting); methodology (supporting); supervision (supporting); writing – review and editing (supporting). **Anna Maria Coclite:** Conceptualization (lead); methodology (lead); supervision (equal); writing – review and editing (supporting). **Seyed Saeid Hosseini:** Methodology (lead); project administration (lead); supervision (lead); writing – review and editing (lead).

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DATA AVAILABILITY STATEMENT

Data sharing is not applicable to this article as no new data were created or analyzed in this study.

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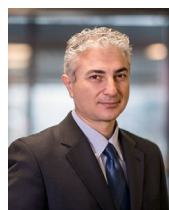
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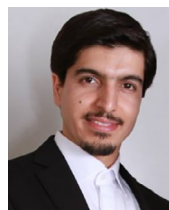


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