

# Progress in electrospun polymeric nanofibrous membranes for water treatment: fabrication, modification and applications

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## **Abstract**

Research on membrane technologies has grown exponentially to treat wastewater, recycle polluted water and provide more freshwater. Electrospun nanofibrous membranes (ENMs) exhibit great potential to be applied in membrane processes due to their distinctive features such as high porosity of up to 90% and large specific surface area. Compared with other nanofiber fabrication techniques, electrospinning is capable of developing unique architectures of nanofibrous scaffolds by designing special assemblies, and it is facile in functionalizing nanofibers by incorporating multi-functional materials. This review summarizes the state-of-the-art progress on fabrication and modification of electrospun polymeric membranes with a particular emphasis on their advances, challenges and future improvement in water treatment applications. Firstly, we briefly describe the complex process governing electrospinning, illustrate the effects of intrinsic properties of polymer solutions, operational parameters and surrounding environment conditions on the formation of nanofibers and resultant nanofibrous membranes, and summarize various designs of electrospinning apparatus. This is followed by reviewing the methods to prepare multifunctional composite ENMs, which are assorted into three categories, including modification in nanofibers, loading target molecules onto nanofibers surface, and implementing selective layers on the ENM surface. Comprehensive discussion about past achievements and current challenges regarding utilization of composite ENMs in water treatment are then provided. Finally, conclusions and perspective are stated according to reviewed progress to date.

## **Keywords**

Electrospinning, nanofibrous membranes, water treatment, modification

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## Nomenclature

1,3-DBP	1,3-dibromo propane
1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AGMD	Air gap membrane distillation
AS-MBR	Active sludge MBR
BSA	Bovine serum albumin
CA	Cellulose acetate
CNTs	Carbon nanotubes
DCMD	Direct contact membrane distillation
DEAE	Diethylaminoethyl
<i>E. coli</i>	Escherichia coli
ECH	Epichlorohydrin
EMBR	Extractive membrane bioreactor
ENMs	Electrospun nanofibrous membranes
EO	Engineered osmosis
f-CNTs	Functionalized carbon nanotubes
FO	Forward osmosis
F-PBZ	Fluorinated polybenzoxazine
GA	Glutaraldehyde
GO	Graphene oxide
GS	Gas separation

ICP	Internal concentration polarization
IP	Interfacial polymerization
LbL	Layer-by-layer self-assembly
MBR	Membrane bioreactor
MD	Membrane distillation
MF	Microfiltration
MWCNTs	Multiwalled CNTs
MWCO	Molecular weight cut-off
NF	Nanofiltration
PA	Polyamide
PAN	Polyacrylonitrile
PCL	Polycaprolactone
PDMS	Polydimethylsiloxane
PDT	Poly(dodecylthiophene)
PE	Polyethylene
PEI	Polyetherimide
PEO	Poly(ethylene oxide)
PES	Polyethersulfone
PET	Polyethylene terephthalate
PLA	Poly(L-lactide)
PP	Polypropylene
PPy	Polypyrrole
PRO	Pressure retarded osmosis

PS	Polystyrene
PSU	Polysulfone
PTFE	Polytetrafluoroethylene
PU	Polyurethane
PVA	Polyvinyl alcohol
PVC	Polyvinyl chloride
PVDF	Polyvinylidene fluoride
PVP	Poly(vinylpyrrolidinone)
RH	Relative humidity
RO	Reverse osmosis
<i>S. aureus</i>	Staphylococcus aureus
SEM	Scanning electron microscope
SF	Silk fibroin
SGMD	Sweeping gas membrane distillation
SWCNTs	Single-walled CNTs
TBT	Tributyltin
TFC	Thin film composite
TF-MBR	Trickling MBR
TFNC	Thin film nanofiber composite
TMC	Trimesoyl chloride
TPC	Terephthaloyl chloride
UF	Ultrafiltration
UV	Ultraviolet

VMD Vacuum membrane distillation

WK Wool keratose

## **1. Introduction**

Water is essential for survival and well-being of humans, and therefore ensuring sufficient water resources is crucial. However, it has been reported that more than 80 countries around the world encounter severe water shortage and about 25% of the population do not have adequate access to fresh water with satisfactory quantity and quality [1]. Additionally, water scarcity is exacerbated by growing population and rapid economic development. Construction of massive infrastructure in the form of pipelines, aqueducts and dams dominated the water agenda in the 20th century, which offered tremendous benefits to billions of people [2]. But these approaches for water management, reservation and transportation are not enough to address the water crisis. More fresh water resources should be provided by treating wastewater and desalinating seawater to fulfil the growing water demands.

Water treatments are conducted to remove or reduce existing contaminants in water by physical processes such as sedimentation and filtration, chemical techniques such as disinfection and chemical oxidation, or biological methods such as anaerobic and aerobic digestions [3-5]. Among these processes, membrane technologies have attracted intensive interests of both academic and industries due to their merits of producing water with high quality and, in most cases, with lower energy [6]. Membrane technologies can be classified into different processes according to separation principles and membrane properties, such as microfiltration (MF), ultrafiltration (UF), nanofiltration (NF), reverse osmosis (RO), forward osmosis (FO), pressure retarded osmosis (PRO), gas separation (GS), pervaporation, membrane distillation (MD), membrane bioreactor (MBR), and separation by liquid membranes [6]. The distinctive benefits of membrane processes

compared with other water treatment processes are: (1) energy consumption is low; (2) membrane separation can be operated continuously under mild conditions; (3) membrane processes are feasible to be combined with other processes; (4) membrane properties can be optimized to fulfil diverse requirements; (5) small footprint.

In membrane separation processes, the membranes are critical. Their fabrication methods determine the intrinsic properties of resultant membranes. A number of different techniques including sintering, stretching, track-etching, and phase inversion are available to fabricate polymeric membranes [7]. The advantages and disadvantages of various membrane fabrication methods are listed in Table 1. Most commercial polymeric membranes are manufactured by phase inversion where a polymer is transformed in a controlled manner from a liquid to a solid phase. Over the last decade, electrospinning has become a prominent method to develop polymeric nanofibrous membranes. Apart from membranes obtained by other fabrication techniques, electrospun membranes are composed of overlapped nanofibers with diameters down to a few nanometers [8]. The formation of electrospun nanofibrous membranes (ENMs) is based on the uniaxial stretching and elongation of a viscoelastic jet derived from a polymer solution or melt under a high voltage field. The ENMs exhibit the unique characteristics such as high specific surface area, high porosity, and high orientation or alignment of nanofibers, which benefit strongly from the nanofiber-based architecture. Attributed to these key features, ENMs have been recognized as competitive candidates for a number of applications including energy storage, healthcare, biotechnology, as well as environmental applications [8-10]. Furthermore, the requirements of multifunctional membranes call for design and development of novel modified membranes. It is feasible

to embed functional materials into nanofibers, load target groups on the nanofiber surface and coat barrier layers on ENM surface [11].

This article presents a review of recent progress in fabrication and modification of electrospun polymeric nanofibrous membranes for water treatment. After introducing the basic setup and principles of electrospinning, the effects of polymeric dopes, operational parameters as well as surrounding environmental conditions on nanofibrous membranes are discussed in Section 2. Afterwards, the strategies to obtain multifunctional nanofibrous composite membranes by modification are assorted and illustrated. The subsequent section expounds the applications of these composite nanofibrous membranes in water treatment with an emphasis on past achievements and current challenges of electrospun membrane development for the specific applications. Finally, we provide a brief conclusion and perspective of ENMs in future research associated with water treatment. It is hoped that the systematic instruction presented here will acquaint the readers with the basic knowledge of membrane fabrication by electrospinning and development of composite ENMs for various water treatment applications, and will interest and inspire the readers to further explore more novel and effective ENMs for water treatment in a broad horizon.

**Table 1.** Advantages and disadvantages of different membrane fabrication methods

<b>Membrane fabrication methods</b>	<b>Advantages</b>	<b>Disadvantages</b>
<b>Electrospinning</b>	<p>High level of versatility allow controls over nanofiber diameter, microstructure and arrangement</p> <p>Vast material selection</p> <p>Easy to incorporate additives in nanofibers</p> <p>Membranes with high porosity above 90% and high surface-to-volume ratio</p> <p>One-step and straightforward process</p> <p>Practicability in generating nanostructures, including core-sheath, Janus, tri-layer nanofibers</p>	<p>Hard to obtain nanofibers with diameters below 100 nanometers</p> <p>Hard to obtain ENMs with maximum pore sizes smaller than 100 nanometers</p> <p>Slow yield speed</p>
<b>Sintering</b>	<p>Prepare symmetric membranes with mean pore size between 0.1 and 10 microns</p> <p>Suitable for chemically stable materials such as polytetrafluoroethylene (PTFE), Polyethylene (PE), Metals and Ceramics</p> <p>Solvents are not required</p>	<p>Requires particles with narrow size distribution</p> <p>Hard to achieve pores below 100 nanometers</p> <p>Low porosity: 10-20%</p> <p>Needs high operational temperature</p>
<b>Stretching</b>	<p>Prepare symmetric membranes with mean pore sizes between 0.1 and 3 microns</p> <p>Ladder like slits</p> <p>Porosity between 60% to 80%</p> <p>Can use chemically stable materials such as PTFE, PE, Polypropylene (PP) and Ceramics</p>	<p>Needs high operational temperature</p>
<b>Track-etching</b>	<p>Prepare symmetric membranes with mean pore sizes between 0.02 and 10 microns</p>	<p>Limited suitable polymers</p>

	Narrow pore size distribution Cylindrical pores	Low porosity 10% High cost
<b>Template Leaching</b>	Prepare symmetric membrane with pore size between 0.5 and 10 microns	Hard to achieve nano pores
	Extremely narrow pore size distribution High flux	High cost Difficult to scale up Complex procedures
<b>Phase inversion</b>	Can be used for a wide variety of polymers  Can fabricate flat-sheet and tubular membranes Simple to prepare and easy to scale up Fast yield speed Easy to optimize membrane thickness and pore size High porosity of around 80% Form small surface pores and large bulk pores naturally	The polymer must be soluble in a solvent or solvent mixtures

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## 2. The electrospinning process

Since the early 1990s, significant progress has been made in understanding complex electrospinning process and controlling nanofibers formation, which should be attributed to the surge of nanotechnology and the appearance of modern analysis methods [12, 13].

These achievements have in turn allowed an extension of electrospun membranes applications to a variety of fields including membrane fabrication. Compared with other approaches to generate nanofibers, such as gas jet techniques and melt fibrillation, electrospinning shows advantages with a lower cost and a higher production rate [14, 15]. In this section, the effects of parameters in electrospinning process, including the intrinsic properties of the polymeric dopes, operational parameters, as well as the surrounding temperature and humidity on the properties of resultant ENMs are elaborated.

### 2.1 Understanding electrospinning

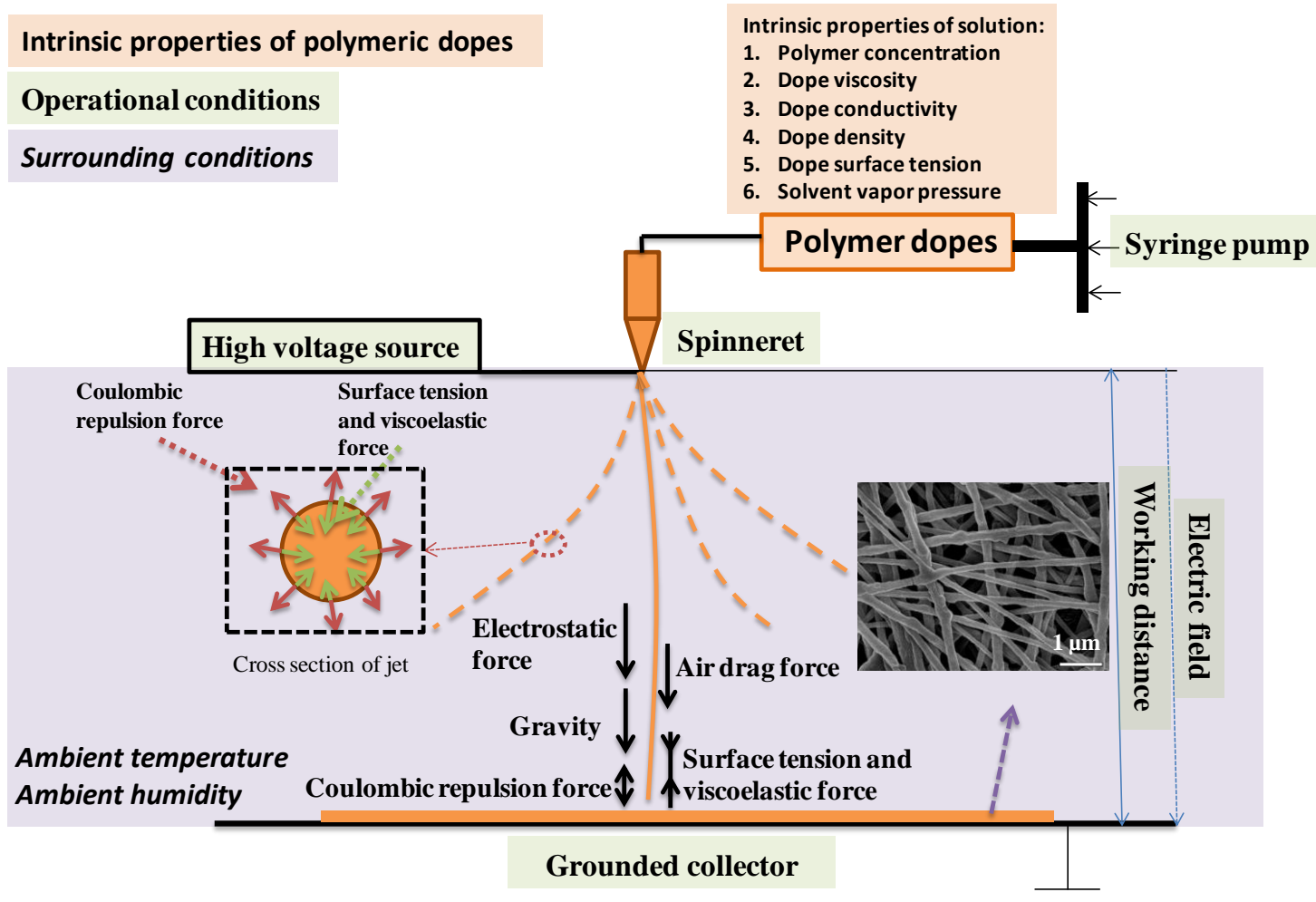
As shown in Fig. 1, a typical electrospinning setup has four essential parts: a high voltage supply, a dope driven system (a syringe pump), a spinneret and a grounded metal collector [10]. In the electrospinning process, polymeric nanofibers are prepared from a liquid jet which is created and elongated under an electrical field. The forces, including surface tension, Coulombic repulsion force, electrostatic force, viscoelastic force, gravity, and air drag force, are applied to the charged fluid jet as shown in Fig. 1. A gas stream applied in the outer channel of co-axial spinnerets can provide air drag force to the fluid jet, resulting in thinner nanofibers and a higher production rate [16]. In general, the nanofiber formation via electrospinning undergoes following three stages: (1) onset of jetting and rectilinear jet development; (2) bending deformation with looping and

spiralling trajectories, and nanofiber solidification with evaporation of solvents; (3) nanofibers collection [17].

First of all, in the electrospinning process, an electrical potential difference is applied between a polymer droplet at the tip of a spinneret and a grounded collector [18]. As shown in Fig. 2A, the shape of the droplet is gradually transformed into a conical shape named a Taylor Cone under an applied voltage, from which a jet emanates [19]. This cone shape can be maintained when a sufficient amount of solution is flowing in and replaces the droplet during electrospinning process. The critical voltage, beyond which nanofibers can be generated from a given dope solution, is determined by the dope surface tension, spinneret radius, and distance between spinneret tip and grounded collector [20].

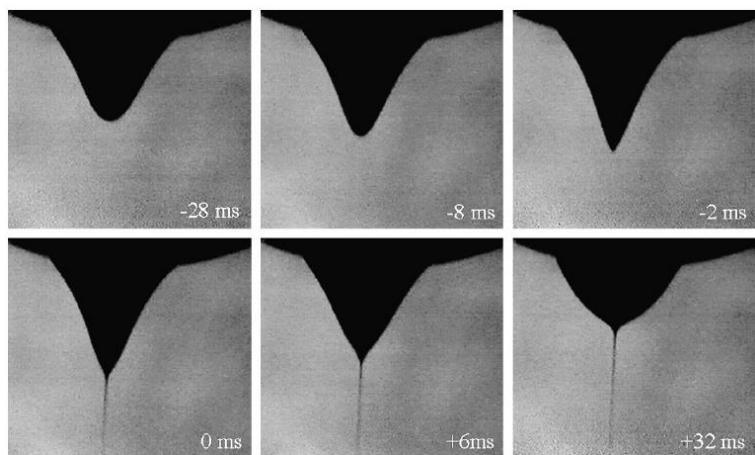
After the electrospinning is initiated, the jet of polymer solution follows a nearly straight line for a certain distance away from the orifice as shown in Fig. 2B [21, 22]. The distance has a critical value which is proportional to the applied electric field, conductivity, and dope flow rate but inversely proportional to liquid density and current passing through the jet. Beyond the straight segment, elongation of the jet can be observed as a result of electrical forces. This causes the onset of bending instability, characterized by successively bending coils rotating at increasing radius [21, 23, 24]. The electrically driven non-axisymmetric bending of jet at high frequencies is critical for reducing the jet diameter from micrometers to nanometers [25-28]. During the process of elongation and bending, the solvents in nanofibers evaporate simultaneously, resulting in solidification of nanofibers [24].

**Fig. 1.** Schematic illustration of the plausible nanofibers formation in electrospinning. The effects of intrinsic properties of polymeric dopes are marked in orange test box, operational conditions are marked in green text box and surrounding conditions in purple box.

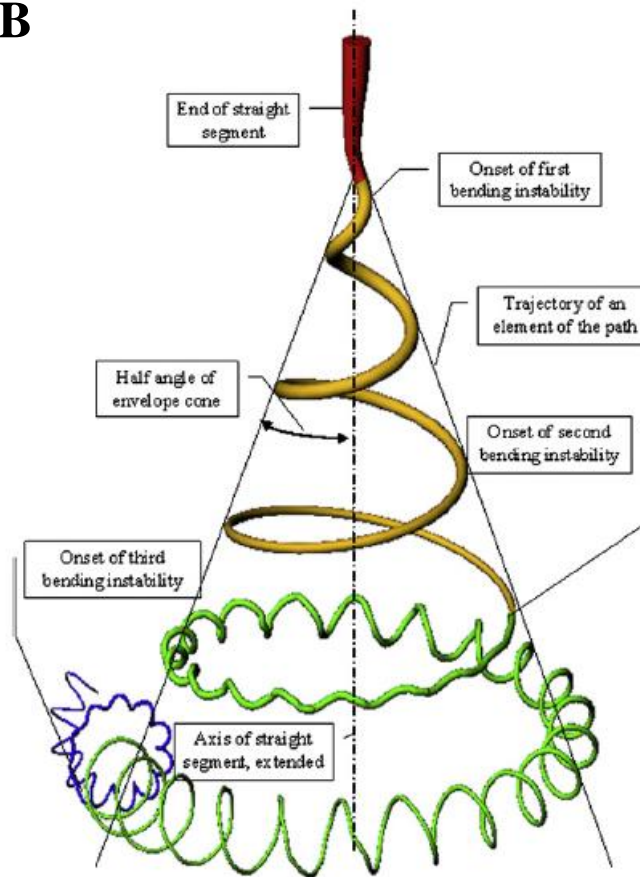


**Fig. 2.** (A) The evolution of a fluid droplet in the electrospinning process [18]. Copyright 2001, Reproduced with permission from Hanser Publishing; (B) A diagram showing the pathway of an electrospun jet [17]. Copyright 2006, Reproduced with permission from American Chemical Society.

**A**



**B**



After the bending deformation and solvent evaporation, the nanofibers are collected in grounded apparatus. The designs of spinnerets and collected apparatus are also important aspects affecting the morphologies and structures of obtained nanofibers [29]. The schematics of electrospinning systems with different spinnerets and grounded collectors, and as-developed nanofibers are summarized in Fig. 3 and discussed as follows:

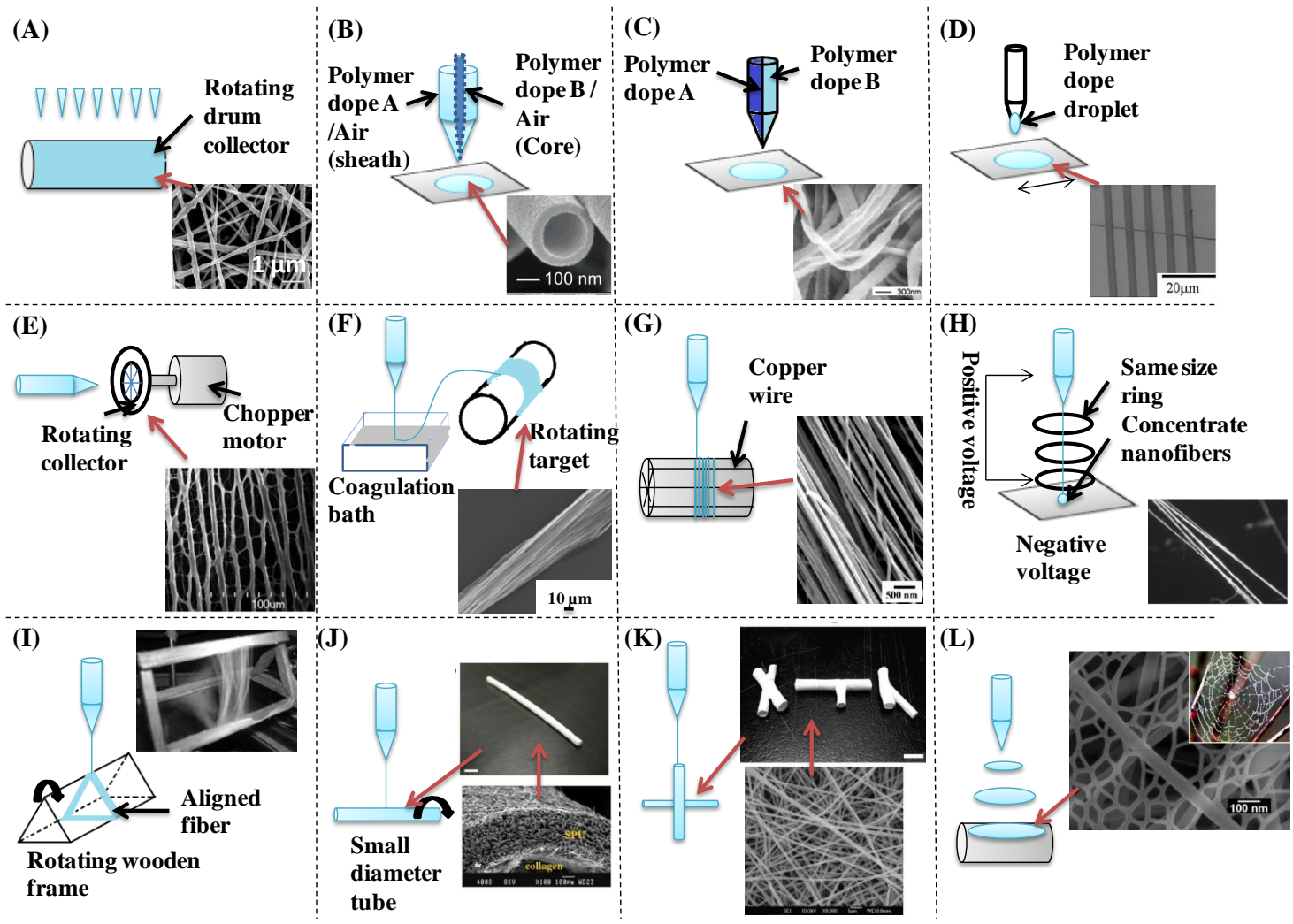
- (A) Nanofibrous membranes with designed thicknesses can be manufactured by a multi-spinneret electrospinning system [30]. Multiple spinnerets enhance productivity and exhibit the potential to fabricate bi-component and multi-component nanofibers;
- (B) Electrospinning setup with a coaxial spinneret results in novel nanofibers possessing core-sheath structures, which exhibited controlled drug release properties [31-33]. Besides, this spinneret is capable to generate hollow nanofibers (nanochannels) when polymer B is replaced by air [34]. If the outer tube is filled with gas saturated with corresponding solvent of polymer solution, it can produce nanofibers with smooth surfaces [35]. Additionally, the solvent evaporation rates can be optimized by changing air flow rate and temperature [36]. Furthermore, novel tri-axial electrospinning process has been developed to fabricate functional tri-layer nanofibers for drug delivery [37, 38];
- (C) Electrospinning setup with bicomponent-spinnerets has advantages in spinning two different polymers with a side-by-side arrangement to combine their distinctive properties [39]. The side-by-side spinneret facilitates the formation of high quality integrated Janus nanofibers, which can provide controllable biphasic drug release [40]. Besides, the width, interfacial area and volume of each component can be tuned by varying the angle between the two ports of the spinneret [41];

- (D) A spinneret tip with a droplet of polymer dope on its top can control the deposition position of nanofibers to manufacture nanofiber-based electronics and sensors [42];
- (E) One-dimensional nanofibers can be obtained by using an optical chopper motor [43];
- (F) Crystallization of nanofibers can be facilitated by removing residual solvent in a coagulation bath. These nanofibers can be collected for protective clothing and high performance fabrics [44];
- (G) The alignment of nanofibers can be achieved by using an appropriate rotating speed of the cylindrical collector [45];
- (H) Highly concentrated jets can be obtained by introducing copper rings along the pathway of the jets [46];
- (I) Rectangular frame collectors were developed to achieve effective nanofiber alignments [47]. **It was found that frame materials could affect nanofiber alignments;**
- (J) Tubular shaped nanofibrous membranes can be fabricated using a rotating and traversing mandrel-type collector [48];
- (K) Three-dimensional (3D) nanofibrous tubes can be achieved by controlling designs of collectors [49];
- (L) Spider-web-like nano-nets with ultrafine nanofiber diameters less than 20 nm can be generated by optimizing compositions of polymeric dopes [50].

In summary, a variety of nanofibrous productions has been developed by modifying electrospinning assemblies. **However, most reported nanofibrous membranes for water treatment were fabricated by multi-spinnerets electrospinning shown in Fig. 3A. A few works developed composite ENMs by coaxial electrospinning to adsorb contaminants in wastewater [51].** The nanofibrous productions from other electrospinning designs should

be exploited for water treatment by taking advantages of their unique strengths in future research.

**Fig. 3.** Schematics of electrospinning systems with various spinnerets and collectors, and the morphologies of as-developed nanofibers. The images have been inserted from references [30, 34, 39, 42-50].



### 2.3 Effects of different parameters on resultant nanofibrous membranes

A number of researchers in the electrospinning field have investigated the influence of different parameters on nanofibers, but the impacts of these parameters on resultant ENMs are seldom presented. As shown in Fig. 1, these parameters can be classified into three parts: (1) Intrinsic properties of the polymeric dopes; (2) Operational conditions; (3) Surrounding environmental conditions. These effects on resultant ENMs are summarized in Table 2 and discussed below.

**Table 2.** Effects of different parameters on electrospun nanofibers and resultant nanofibrous membranes

Parameters		Effects on nanofibrous membrane morphology	Reason	Influence Degree
<b>Intrinsic properties of polymeric dopes</b>	Polymer concentration increases	Nanofiber diameter increases; membrane pore size increases.	The jet elongation becomes more difficult and slowly.	☆☆☆
	Dope viscosity increases	Nanofiber diameter increases; membrane pore size increases.	The jet elongation becomes more difficult and slowly.	☆☆
	Solution conductivity increases	Suppress the formation of beads; nanofiber diameter decreases; membrane pore size decreases.	The charges carried by jets increase. Thus the repel force in jets increases and jets elongate fast.	☆☆☆
	Solution density increases	Nanofiber diameter increases; membrane pore size increases.	The jet elongation becomes more difficult and slowly.	☆☆
	Surface tension decreases	Nanofiber diameter decreases; membrane pore size decreases.	Small surface tension force makes jets elongate easily.	☆
	Solvent	Good solvents tend to give rise to beads; partial solubility systems tend to form stable nanofibers; poor solvents could not support effective spinning.	Dielectric constant of solvents shows a direct correlation with average electrospun nanofiber diameter.	☆☆
	Vapor pressure increases	Nanofiber diameter increases; nanofibers with high surface porosity are produced; membrane pore size increases.	Jets have less time to elongate before solidification. Phase separation can be induced by high vapor pressure.	☆☆
	Vapor diffusivity decreases	Nanofiber diameter decreases; membrane pore size decreases.	Jets have more time to elongate before solidification.	☆
<b>Operational conditions</b>	Applied voltage increases	Nanofiber diameter decreases after increasing applied voltage; if applied voltage is higher than a critical value, the nanofiber diameter could increase.	At first the jets carry more charges to elongate fast. But after an appropriate value, a higher voltage ejects more jets.	☆☆☆
	Working distance between spinnerets and	Nanofiber diameter decreases but beads tend to form.	The jet elongation time increase. It also makes the nanofibers unstable.	☆☆

collectors increases

Spinneret radius decreases Nanofiber diameter decreases; membrane pore size decreases. The initial diameter of jet decreases. ☆☆☆

Flow rate of polymeric dopes increases Nanofiber and beads diameters increase; membrane pore size increases A higher flow rate ejects more polymeric dopes in a jet and makes the initial jet diameter larger. ☆

**Surrounding conditions**

Ambient temperature decreases Nanofiber diameter decreases; membrane pore size decreases. The jet elongation time is prolonged. ☆

Ambient humidity decreases Nanofiber diameter decreases; membrane pore size decreases; more sticky nanofibers and beads appear The jet elongation time is prolonged. ☆☆☆

Working temperature increases (melt electrospinning) Nanofiber collection speed increases The viscosity of polymeric melts decreases, thus improving the flow behaviour of extruded polymer and accelerating nanofiber ejection ☆☆☆

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### *2.3.1 Effects of intrinsic properties of polymeric dopes*

Progress has been made in understanding the effects of polymeric dopes on nanofibers formation [8, 10, 52-54]. In this section, some crucial parameters including polymer concentration, conductivity, surface tension and solvent selection will be discussed briefly.

It is well-known that the morphologies and properties of nanofibers are primarily determined by the composition of electrospun polymeric dopes [47, 55-57]. For a given pair of polymer and solvent, there exists a threshold of polymer concentration for successful fabrication of nanofibers. Beads-on-string structures tend to be produced when polymer solutions with a lower concentration (i.e., a lower viscosity) are used. With increasing polymer concentration and viscosity, the beads on nanofibers gradually change from spherical to spindle-like shapes and eventually nanofibers with uniform diameters [58, 59]. The diameter of electrospun nanofibers increases with further increase of polymer concentration.

In addition, the electrical conductivities of polymeric dopes determine their rheological behaviours and significantly affect the spinnability [60, 61]. Solution conductivities are mainly determined by polymers and solvents in dopes, as well as the existence of ionisable salts [58]. For instance, the conductivity of a polymer solution can be dramatically enhanced by introducing ions in the solution. It has been illustrated that the jets containing ions with a smaller molecular diameter experience a more significant elongation force, attributed to higher mobility and charge density of the ions [30, 62-64]. Therefore, highly conductive solutions are preferred in electrospinning as they tend to

generate thinner nanofibers with dramatic bending and fast drying [30, 65]. However, excessive enhancement of conductivity can cause instability of the Taylor cone, which consequently generates micro-sized beads and dense-nets [66]. Thus, in order to obtain ENMs composed of overlapped ultrathin and uniform nanofibers, the conductivity of the polymer dopes should be optimized to an appropriate value.

It was revealed that surface tension of polymeric dopes is capable to influence the morphologies of electrospun nanofibers [63, 67-69]. Attributed to the reduced perturbation, a dope with a lower surface tension by adding more surfactants can produce uniform nano-nets. However, defects might be shaped on nanofiber surface if the surfactant concentration exceeds an optimum value due to the formation of colloidal aggregates resulted by the self-assembly of the excessive surfactants.

As nanofiber solidification is mainly controlled by solvent evaporation along the jet pathway from spinnerets to grounded collectors, the selection of solvents is among the critical factors governing nanofibers morphologies. To date, numerous kinds of solvents have been chosen to fabricate ENMs [50, 63]. A qualitative study on the impacts of solvents on ENMs revealed that polymer dopes prepared by partially soluble solutions tend to produce stable nanofibers [70]. Whereas, the polymeric dopes using solvents with high solubility are more likely to electro spray micro/nano-size beads.

### *2.3.2 Effects of operational conditions*

The structures and morphologies of nanofibrous membranes are highly governed by operational conditions in electrospinning. One of the key parameters is the magnitude of applied electric field, which decides the electrostatic force loaded on the polymeric

droplets on spinnerets as well as the amount of charges held in the jet [67]. The threshold voltage to generate jets is proportional to the dope concentration/viscosity [71]. The formation of thinner nanofibers is favoured under a higher applied voltage [66]. Meanwhile, a higher applied voltage can eject more dopes which give rise to nanofibers with larger diameters [71]. Thus, an optimum voltage is required to obtain thinner nanofibers after considering the contradictory effects.

As solidification of nanofibers relies on the solvent evaporation, a sufficient working distance between spinnerets and collectors is required to ensure formation of dry nanofibers before deposition on the collectors. Recently, it has been illustrated that beads on the nanofibers tend to form when the distance is out of an optimum range [72]. On the other hand, nanofiber diameter reduces with decreasing orifice size [73]. It was also revealed that the diameter of nanofibers increased with the increase of dope flow rate [8].

### *2.3.3 Effects of surrounding conditions*

Besides above-mentioned parameters, the effects of ambient temperature and humidity have been investigated. **A recent work reported that due to the reduction of dope surface tension and viscosity at a higher surrounding temperature, nanofibers with smoother surfaces and smaller diameters can be produced [74].** Meanwhile, the elevation of temperature can accelerate the evaporation of solvents, which solidify the nanofibers and terminate the electrical stretching of fluid jets prematurely. Thus, the contradictory influences of temperature on nanofiber diameter should be considered. Given the fact that numerous polymers are sensitive to temperature, more works should be conducted to study the effects of surrounding temperature on different polymers. Moreover, recent

studies demonstrate that relative humidity (RH) is a crucial parameter for nanofibrous membranes development. Compared with nanofibers fabricated at a higher RH, the nanofibers generated at a lower RH were thinner and possessed less sticky structure [50, 66, 67, 75].

Although most works focus on spinning of polymeric solutions, the melt electrospinning using polymer melts as dopes provides more approaches to fabricate nanofibers, which overcome the challenges governed by solvent toxicity [76]. Besides the intrinsic properties of polymers, the working temperature in melt electrospinning showed significant effects on resultant nanofibers [77]. Elevation of working temperature would reduce viscosity of polymer melts and enhance nanofiber production rate [78].

Based on above discussions, electrospinning is a versatile and superior technology to produce ordered and complex nanofibrous assemblies when compared with other nanofibers fabrication approaches. The polymer concentration, solution conductivity, applied voltage, spinneret radius, ambient humidity and working temperature in melt electrospinning show the most significant effects on resultant nanofibers. Five other parameters including dope viscosity, solution density, solvent type, vapor pressure, and working distance play moderate roles while other parameters have minor effects [79].

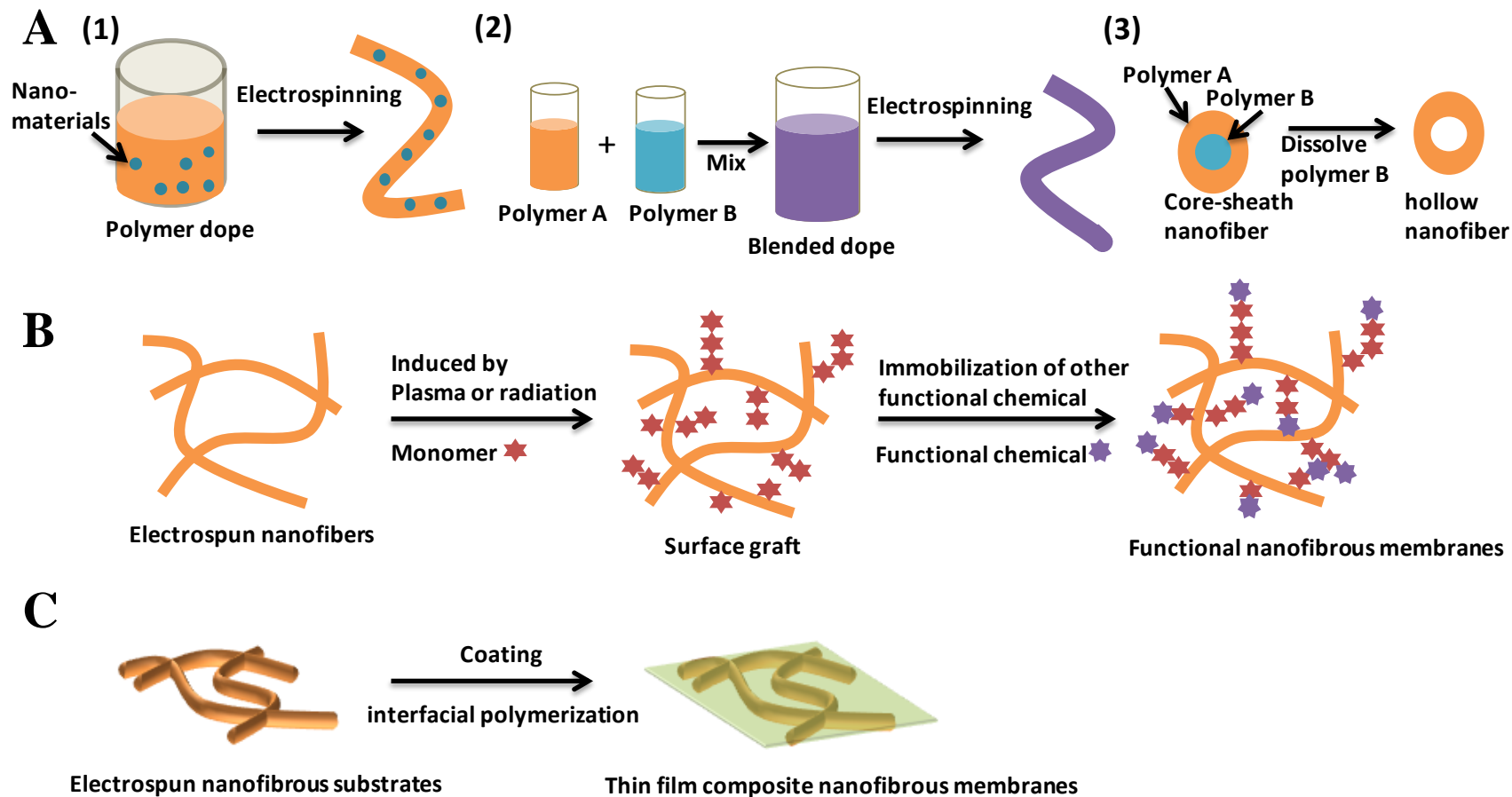
Despite of numerous studies which unravel the impacts of electrospinning parameters on nanofibers and nanofibrous membranes, further studies are still required to examine the possible cross-influences between different parameters. This can possibly extend the understanding of the electrospinning process from a qualitative to a predominantly quantitative level. In addition, the synergy effects of these parameters on pore size,

porosity, surface roughness, and topologies of ENMs are still uncertain, and demand further investigations.

### **3. Hierarchical organization of multifunctional composite nanofibrous membranes**

An effective multifunctional nanofibrous membrane goes beyond random dispersion of nanofibers. Hierarchical design of composite ENMs is required to improve properties of developed membranes and broaden their potential applications. Recently, a large number of studies have been devoted to engineering composite nanofibrous membranes. Functional nanofibrous membranes can be prepared by incorporating a variety of materials into/onto nanofibers and optimizing the nanofibrous architectures, either during one-step electrospinning or through post modifications. As shown in Fig. 4, these modification methods can be categorized into three groups, including (i) modification in nanofibers, (ii) functionalization on nanofibers outer surface, and (iii) development of thin film nanofibrous composite (TFNC) membranes. For instance, nanoparticles or a secondary polymer can be dissolved or dispersed in the primary polymer solutions to fabricate composite nanofibers, as shown in Fig. 4A. Assist with a coaxial-orifice spinneret, inner secondary materials can even be removed to produce hollow nanofibers. Additionally, target molecules with desired functional groups can be grafted on nanofiber surfaces as shown in Fig. 4B. Furthermore, Fig. 4C shows fabrication of TFNC membranes by coating or interfacial polymerization (IP) on nanofibrous substrates.

**Fig. 4.** Modification techniques of electrospun nanofibrous membranes. (A) (1) Immobilization of nano-materials in nanofibers, (2) electrospinning of blended polymers and (3) core-sheath/hollow nanofibers preparation; (B) Target molecules loading on the surface of nanofibers; (C) Surface coating and polymerization on nanofibrous substrates



### 3.1 Modification in polymeric nanofibers

#### *3.1.1 Immobilization of nanomaterials in polymeric nanofibers*

As mentioned above, electrospinning is one of the most effective approaches to produce polymeric nanofibers. However, polymeric nanofibers are not as strong as desired due to their small diameter and non-optimized molecular orientation in the nanofibers. Nanomaterials such as carbon-based nanomaterials, metal nanomaterials and inorganic nanoparticles can be incorporated into nanofibers to functionalize the nanofibers and extend their applications in nanomedicine, sensor, super capacitors and catalysts, separation and filtration.

Carbon nanotubes (CNTs), firstly used as fillers in polymer composites in 1994 by Ajayan *et al.*, have attracted great attention as reinforcement additives due to superior tensile modulus and strength [80]. However, effective dispersion and alignment of individual nanotube in polymer matrix are primary challenges to effectively confer their unique properties to resultant composites. Electrospinning is capable of immobilizing CNTs in nanofibers facily and strengthening resultant composite nanofibers significantly. The first poly(ethylene oxide) (PEO) nanofibers in which multiwalled CNTs (MWCNTs) were axially oriented have been successfully fabricated in 2003 [81]. Mechanical measurements confirmed that the Young's modulus of PEO membrane was improved by up to 3-fold with the aid of MWCNTs [82]. The same group developed single-walled CNTs (SWCNTs) embedded PEO nanofibrous scaffolds and found that nanotube alignment within the nanofibers strongly depended on well dispersion of CNTs in electrospun dopes [83]. The excellent mechanical strength and modulus should be

attributed to the strong bonding between CNTs and polymer matrix, which are formed between positively charged nanotubes and negatively charged functional groups of the polymer [84]. These robust composite nanofibrous mats possess great potential to be applied in high pressure membrane processes [85, 86]. Our group has developed a CNT-reinforced polyetherimide (PEI) nanofibrous substrate with a tiered structure [87]. The top fine PEI nanofibers incorporated with well-dispersed CNTs significantly enhanced mechanical stability of TFNC membrane, which can endure a trans-membrane pressure of up to 24 bars. Besides reinforced mechanical properties, a higher concentration of MWCNTs was found to effectively resist heat shrinkage of the MWCNTs/polyacrylonitrile (PAN) composite nanofibrous sheets [88]. The possible reason is that molecular segmental motions were restricted at the interface between CNTs and PAN by forming charge-transfer complexes at elevated temperatures. Moreover, CNTs were incorporated in polyvinylidene fluoride (PVDF) nanofibers as nano-fillers to achieve superhydrophobic properties [89]. Apart from one-dimensional (1D) CNTs, the two-dimensional (2D) graphene, which is an atomic layer of graphite, have emerged as attractive nano-fillers, attributed to its superior chemical and thermal stabilities, outstanding flexibility and solution processibility [90]. It was speculated that incorporation of graphene oxide (GO) into PVDF nanofibers by electrospinning a mixture of PVDF and GO can improve mechanical property, water flux and anti-fouling property of resultant hybrid ENMs [91]. Another study demonstrated that incorporation of graphene into PVDF nanofibers can obtain a robust and superhydrophobic nanocomposite membrane [92].

The composite nanofibers imbedded with metal nanoparticles can combine outstanding properties of metal nanoparticles such as antibacteria, with the unique characteristics of the polymer nanofibers, making them ideally for antibacterial applications [93]. Silver nanoparticles with strong antimicrobial activity were dispersed homogeneously in PAN, poly(vinylpyrrolidinone) (PVP) and chitosan/gelatin nanofibers by electrospinning [94-96]. In addition to silver, gold nanoparticles were incorporated into polyvinyl alcohol (PVA) nanofibers by electrospinning to improve the antibacterial properties of composite nanofibers [97].

Nowadays, multifunctional polymer/inorganic composite nanofibers have been fabricated to improve physical properties of hybrid nanofibers [59]. Morphologies and crystal polymorphism of composite nanofibers prepared by electrospinning mixtures of PVDF and nanoclays have been investigated [98]. The addition of nanoclays can decrease appearance of beads and make nanofibers more uniform due to increase of solution conductivity. It was found that nanoclays can induce more PVDF in beta and gamma phase and reduce the alpha phase conformers. In addition, the morphology and thermal properties of nanofibers were altered by adding silica nanoparticles [99]. Silica nanoparticles incorporated in nanofibers increased the polymer-nanoparticles interfacial interaction and reduced polymer segmental mobility, which resulted in a higher glass transition temperature. In another work, composite nanofibrous membranes made by nylon-6 and TiO<sub>2</sub> nanoparticles were developed. The presence of TiO<sub>2</sub> nanoparticles enhanced hydrophilicity, mechanical strength, and antimicrobial activity of the composite nanofibrous mats [100]. Besides, addition of TiO<sub>2</sub> could increase amorphous phase of polymer and improve the thermal stability of composite nanofibers [101]. The tunable

wettability from hydrophobic to superhydrophobic and from superoleophilic to superamphiphobic can be implemented by adding ammonia or 1H,1H,2H,2H-perfluorodecyltriethoxysilane into PVDF dopes [102]. Moreover, iron oxide ( $\text{Fe}_3\text{O}_4$ ) nanoparticles have been imbedded in polystyrene (PS) nanofibers to achieve magnetic nanofibrous mats [103].

### *3.1.2 Dual component polymeric nanofibers*

In conventional electrospinning, the electrospun polymers need to possess sufficient molecular weights and good solubility, which is not applicable for all polymers. But in dual component electrospinning system, only one of the components needs to be electrospinnable while the other can be chosen based on the functional requirements, broadening the material selections to a great extent. Besides, fabrication of dual component nanofibrous membranes can reduce membrane costs *via* use of cheap bulk materials. For example, wool protein, known as keratin and composed of various amino acids which have high affinity to ionic species such as metal ions, has been electrospun together with silk fibroin and polyamide (PA) 6 to improve electrospinnability [104-106]. Besides, a nanofibrous membrane made of polyethersulfone (PES) and PEI was fabricated by electrospinning [107]. PES was chosen as the matrix polymer due to its excellent electrospinnability while PEI was the functional polymer with a large amount of amino and imino groups.

### *3.1.3 Core-sheath or hollow nanofibers preparation*

One-dimensional nanostructures with core-sheath or hollow architectures prepared from a rich variety of materials are advanced in numerous applications such as catalysis, fluidics,

purification, separation, and energy conversion [108, 109]. Using conventional techniques, it is difficult to produce core-sheath or hollow nanofibers with long length as nanofibers tend to interconnect during the coating or etching processes. Advances in electrospinning have allowed the fabrication of long core-sheath or hollow nanofibers with diameters ranging from 20 nm to 1 $\mu$ m by simply replacing a single capillary spinneret with a coaxial spinneret [110].

Loscertales *et al.* demonstrated the capabilities of electrospinning to generate hollow silica-based nanofibers in a single step with the help of a coaxial spinneret [111]. The size and wall thickness of hollow nanotubes can be optimized by controlling a set of experimental parameters such as the dope flow rates in core/sheath sides and applied voltages [34]. The hollow silica nanofibers prepared by electrospinning 3-mercaptopropyl trimethoxysilane-PAN dope, followed by sol-gel polymerization and removal of PAN nanofibers, were found to be efficient in removing mercury from wastewater due to the enhanced surface area of the nanofibers [112]. Additionally, titania hollow nanofibers were fabricated by co-electrospinning a PVP solution containing titanium alkoxide and mineral oil, followed by selective removal of the liquid core and calcination. The inner and outer surface of the hollow nanofibers can be independently functionalized with molecular species or nanoparticles [113].

Porous carbon hollow nanofibers have attracted increasing attention due to their versatile applications in electronic devices, catalysis, gas and liquid separation, *etc* [114]. Novel Sn-carbon nanoparticles encapsulated in bamboo-like hollow carbon nanofibers were prepared by pyrolysis of coaxially electrospun nanofibers as a potential anode material for Li-ion batteries [115]. During electrospinning, the viscous liquid containing tributyltin

(TBT) and mineral oil solution was fed through the core capillary of the spinneret while a PAN solution was fed through the shell capillary. Then as-prepared nanofibers were immersed in *n*-octane to extract the mineral oil to obtain the hollow nanostructure. This specific structure enhanced the electro-chemical performance of Sn. Additionally, porous carbon nanofibers with hollow cores were achieved via electrospinning of two immiscible polymer solutions followed by thermal treatment in an inert atmosphere [116]. The carbon nanofibers exhibited controlled porosity, a low density, and excellent electrical and mechanical properties due to an interlinked nanofibrous structure.

Moreover, it was demonstrated that electrospinning was efficient to fabricate **core-sheath** nanofibers made of various pairs of polymers such as PEO-Poly(dodecylthiophene) (PDT) , poly(L-lactide)-Pd (PLA-Pd), and PEO-Polysulfone (PSU) [117]. Even though most composite core-sheath or hollow nanofibers mentioned above were prepared for catalysis, sensors and electronic devices, these membranes exhibit great potential to be applied in water treatment such as efficient adsorption of contamination in wastewater due to their extremely high surface-to-volume ratio and more active functional groups at the micro/nano-scale.

### 3.2 Target molecules loading on the surface of polymeric nanofibers

Chemical and physical properties are critical for advanced multifunctional composite membranes to filter and adsorb contaminants in wastewater. A great amount of surface modification techniques have been utilized to construct chemically active groups on nanofibers surface as described in this section.

#### 3.2.1 Plasma-induced graft copolymerization

Among various surface modification techniques, plasma-induced graft copolymerization is a facile and efficient way to introduce active groups onto nanofiber surfaces, transform polymeric nanofibrous membranes from symmetric to asymmetric structure and develop tighter pore membranes [118]. The plasma treatment can increase the number of polar groups, such as  $-\text{COOH}$ , on the nanofibers surface, which contribute to the enhancement of hydrophilicity [119]. These groups can be used for secondary chemical modifications on membranes, which have produced affinity, antibacterial and magnetic membranes [120-125]. For example, PVDF nanofibrous membranes were exposed to ethylene and argon plasma and further copolymerization to achieve smaller surface pores [126, 127]. Besides, superhydrophobic ENMs have also been developed by treating nanofibers with  $\text{CF}_4$  plasma [128, 129].

### *3.2.2 Layer-by-layer multilayer assembly*

The build-up of layer-by-layer self-assembly (LbL) multilayers is driven by the electrostatic attractions between the oppositely charged constituents, which distinguishes itself in its simplicity from other surface modification techniques [130]. Meanwhile, hydrogen bonding, hydrophobic interactions, and van der Waals forces may influence the stability, morphology, and thickness of the thin polymer films formed by LbL self-assembly [131]. The micro/nanostructure of the silver ragwort leaf was imitated by forming a beaded rough surface on cellulose acetate (CA) nanofibers using the LbL technique [132]. In addition, oppositely charged chitosan and alginate were deposited onto the CA nanofibers surface to improve the ENMs biocompatibility [133]. Dye and lipase were also assembled onto a cellulose nanofiber surface via LbL to immobilize enzymes [134]. Moreover, it was reported that the mechanical properties of

polyelectrolyte multilayer-coated nylon 6 nanofibers were remarkably enhanced [135]. Spray-assisted LbL deposition was developed to functionalize individual nanofiber to create selectively reactive membranes [136]. Although LbL assembly can endow nanofibers with multi-functions in a facile way by incorporating different materials in the multilayers such as polyelectrolytes, clay nano-materials and metal oxides, the stability of these layers in long term usage needs investigation, especially in harsh water treatment.

### *3.2.3 Grafting initiated by chemical means*

Modifications on nanofibers surfaces can be achieved via chemical reactions between monomers and functional groups of nanofibers [137]. Combining the target functional groups with the high specific surface area of nanofibers, novel generated composite nanofibers attract great interest in adsorption, separation and smart-responsive surface preparation. Polypyrrole was coated on PVDF ENMs by vapor polymerization to recover  $(\text{Au(III)Cl}_4)^-$  from continuous-flow aqueous solution [138]. Cellulose nanofibers were functionalized with diethylaminoethyl (DEAE) for bioseparations [139]. Thermo-responsive and solvent-resistant nanofibers have been produced by living radical polymerization [140]. PAN nanofibers were chemically modified with amidoxime groups for metal adsorption as the amidoxime groups possess high adsorption affinity to metal ions [141, 142]. Nitrile groups on PAN nanofiber surfaces were reduced into amino groups and reacted with polyhexamethylene guanidine hydrochloride to achieve antibacterial properties [143]. Polydopamine has been widely used to functionalize nanofiber surface with abundant catechol groups [144, 145]. Superhydrophobic PVDF ENMs have been successfully fabricated by dopamine surface activation, silver nanoparticles deposition and further hydrophobic modification [30]. PVA ENMs have

been modified to be superhydrophobic by chemical cross-linking with glutaraldehyde and modification via fluoroalkylsilane [146]. Moreover, graphene-based materials have been cross-linked on nanofiber surface to effectively inactivate both Gram-negative and Gram-positive bacteria [147]. Hierarchically structured membranes were developed by controlled assembly of GO on PAN nanofibers [148]. The acylation and nucleophilic reactions were carried out between the amine groups of modified PAN nanofibers and the carboxyl or epoxy groups of GO.

Chemical modifications have been used to functionalize nanofibers, which have produced smart responsive membranes, ion-exchange membranes, metal ion-absorbable membranes, anti-bacterial membranes and superhydrophilic/superhydrophobic membranes. However, it is still a key issue to simplify these modification methods so as to pave the way for commercialization.

### 3.3 Thin film nanofibrous composite membranes

ENMs exhibit a broad pore size range from hundreds nanometers to several micrometers, limiting their applications in water treatment. To extend their potential applications, a selective layer has been developed on electrospun nanofibrous substrates by coating and IP, resulting in TFNC membranes [87, 149]. Both nanofibrous substrate and selective layer can be tailored independently to achieve optimal properties for targeted applications. The selective layer primarily determines the membrane permselectivity while the nanofibrous support mainly serves to provide mechanical support for the membrane during fabrication, handling, and operation. Due to its highly porous and interconnected structure, the mass transfer resistance of the nanofiber mat is comparatively low.

Furthermore, it has been known that the effective hydraulic resistance of the selective layer can be influenced by underneath substrate porosity [150]. The highly porous ENMs would be highly potential to develop high performance TFNC membranes.

PVA has been coated and cross-linked on ENMs scaffolds as a selective layer due to its high water permeability, good chemical and thermal stability, easy processibility, and biocompatibility [149]. PVA with different degrees of hydrolysis and molecular weight have been used to optimize the overall mechanical strengths of resultant membranes. MWCNTs and cellulose nanofibers were incorporated into the PVA barrier layer to increase the permeation flux [151, 152]. Compared with conventional coating methods, a thin PVA skin layer with a thickness of several micrometers can be prepared by electrospinning the PVA on top of ENMs, followed by remelting the PVA nanofibrous layers by vapor treatment and chemical cross-linking [153]. The thickness of the PVA barrier layer can be easily controlled by the electrospinning time. In addition, a cellulose skin layer was casted on top of PAN ENMs to separate an emulsified oil-in-water mixture [154].

In addition, IP is a promising method to develop an ultrathin selective layer with a thickness around 300 nm on top of the nanofibrous mats. Typically, two reactive porphyrin monomers are dissolved separately in immiscible liquids. A highly cross-linked ultrathin polymer film with a network structure can be created at the interface between these two immiscible solutions after rapid chemical reaction. This method has been broadly used to fabricate TFNC membranes for NF, oil/water separation and engineered osmosis (EO) processes including FO and PRO [87, 155-157]

Various parameters associated with IP process, including reactant composition, reaction time, substrate pore size, and processing procedure such as post-treatments, decide the performance of resultant TFNC membranes. The piperazine concentration plays an important role in determining the flux and rejection as well as mechanical integrity of the selective layer [158]. To optimize the permeation flux and salt rejection, different ions were incorporated in the selective layer. It was found that small ions reduced permeation flux and increased salt rejection simultaneously while larger ion enhanced permeation flux but sacrifice salt rejection [159].

Furthermore, the structures of nanofibrous scaffolds, including the nanofibers diameter, substrate pore size and intrinsic polymer properties such as the hydrophilicity, showed significant influences on formation of selective layers [158]. The effects of nanofibers diameter on the separation efficiency of TFNC membranes developed by IP have been investigated [160]. The results indicated that with decrease of nanofiber size, the membrane pore size decreased, resulting in an enhancement in salt rejection at the expense of water permeability [160]. Moreover, the nanofibrous mats fabricated by blended polymers of PAN and CA were found as effective supports for TFNC membranes due to their intrinsically wetted and open pore structures with superior interconnectivity [161].

Recently, new approaches to develop novel GO-coated TFNC membranes have been reported. A highly ordered GO selective layer with 2D nanochannels has been developed on ENMs surfaces by vacuum suction method [162]. The obtained GO layer exhibited ideal pathways for water molecules between the well-stacked GO nanosheets and rejected Congo red and  $\text{Na}_2\text{SO}_4$ .

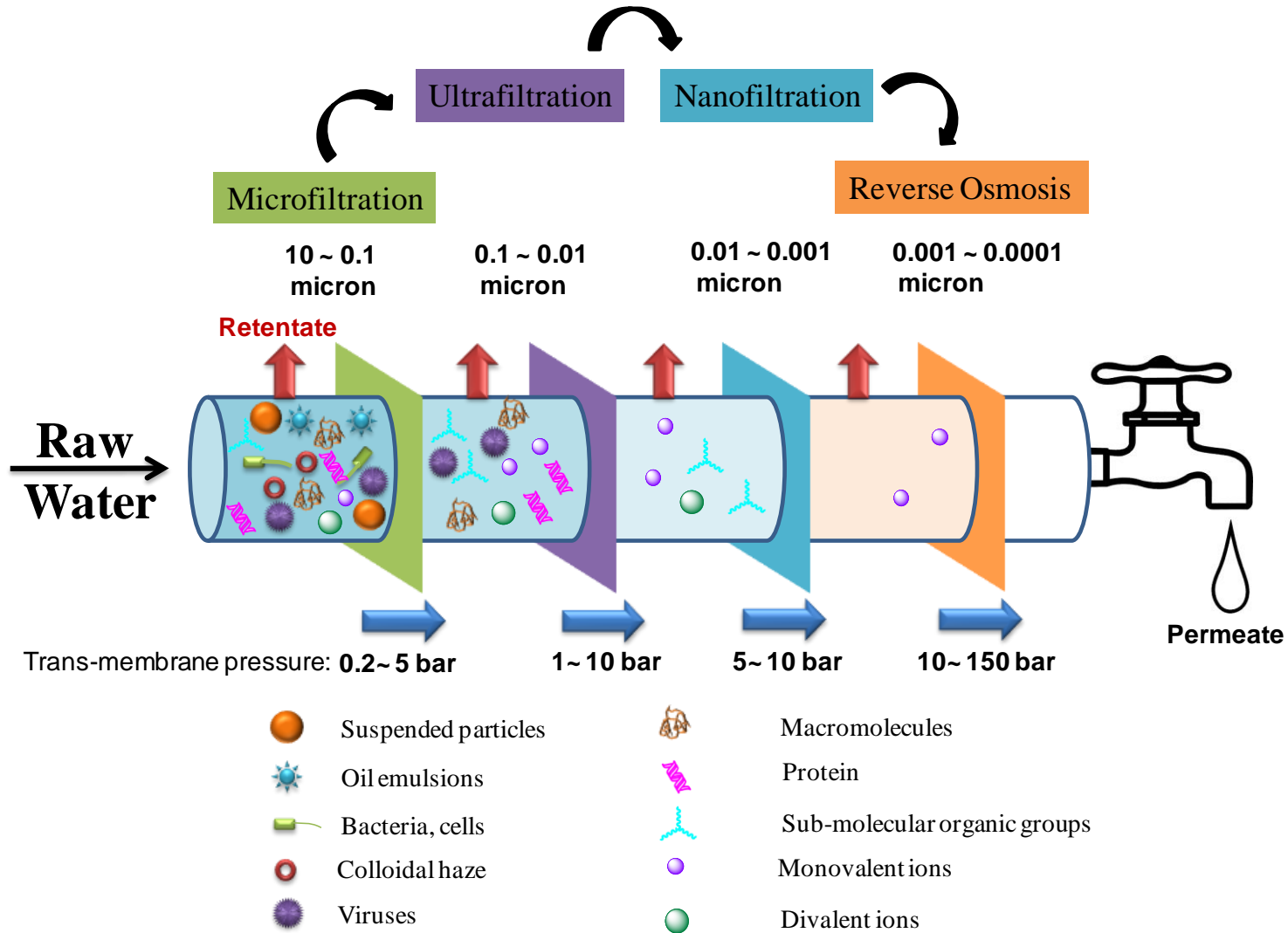
Construction of TFNC membranes certainly improve water permeation and preserve satisfactory rejections attributed to highly porous substrates and ultrathin selective skins. However, due to the large pore size of nanofibrous substrates, the formation of a thin film barrier on the surfaces without defects and penetration into the matrix *via* a convenient and continuous technique is the main challenge. In addition, the stability of these composite membranes under harsh chemical environments and elevated mechanical pressures demands further investigation and optimization.

#### **4. Applications of nanofibrous composite membranes in water treatment**

##### **4.1 Pressure-driven membrane processes**

In pressure-driven membrane processes including MF, UF, NF and RO, a pressure imposed on the feed side of the membrane serves as a driving force to separate water into two streams: permeate and retentate as shown in Fig. 5. Usually, the permeate is purified water while the retentate is a concentrated solution which needs to be disposed or treated before discharge. The specific permeability and selectivity of membranes govern their roles in filtration processes from MF to RO. A recent review of the status and future of membrane processes in the water industry is available [6]. Depending on the type of technique, suspended particles, oil emulsions, bacteria, cells, colloidal haze, viruses, macromolecules, proteins, sub-molecular organic groups, divalent ions and even monovalent ions can be retained from raw water, as shown in Fig. 5. The applied pressure differs from each technique. This section reviews the research status of ENMs used in the pressure-driven membrane processes.

**Fig. 5.** Schematics of membrane water treatment system.



#### 4.1.1 Microfiltration (MF)

Microfiltration (MF) is a pressure-driven and sieving-based filtration for water pre-treatment (Fig. 6A). The lower and upper ranges of typical MF filter size are about 0.1  $\mu\text{m}$  and 1.0  $\mu\text{m}$ . The membranes with larger, supra-micron pores (between 1.0  $\mu\text{m}$  and 10.0  $\mu\text{m}$ ) are more usual in cartridge MF used for pre-filtration to remove particles above 1.0  $\mu\text{m}$  prior to typical MF/UF processes. Compared with membranes fabricated by other methods, nanofibrous membranes prepared via electrospinning are good candidates for both typical MF and cartridge MF as their porosities are higher and the pore size can be qualitatively optimized from sub-micron levels to a few micrometers [163].

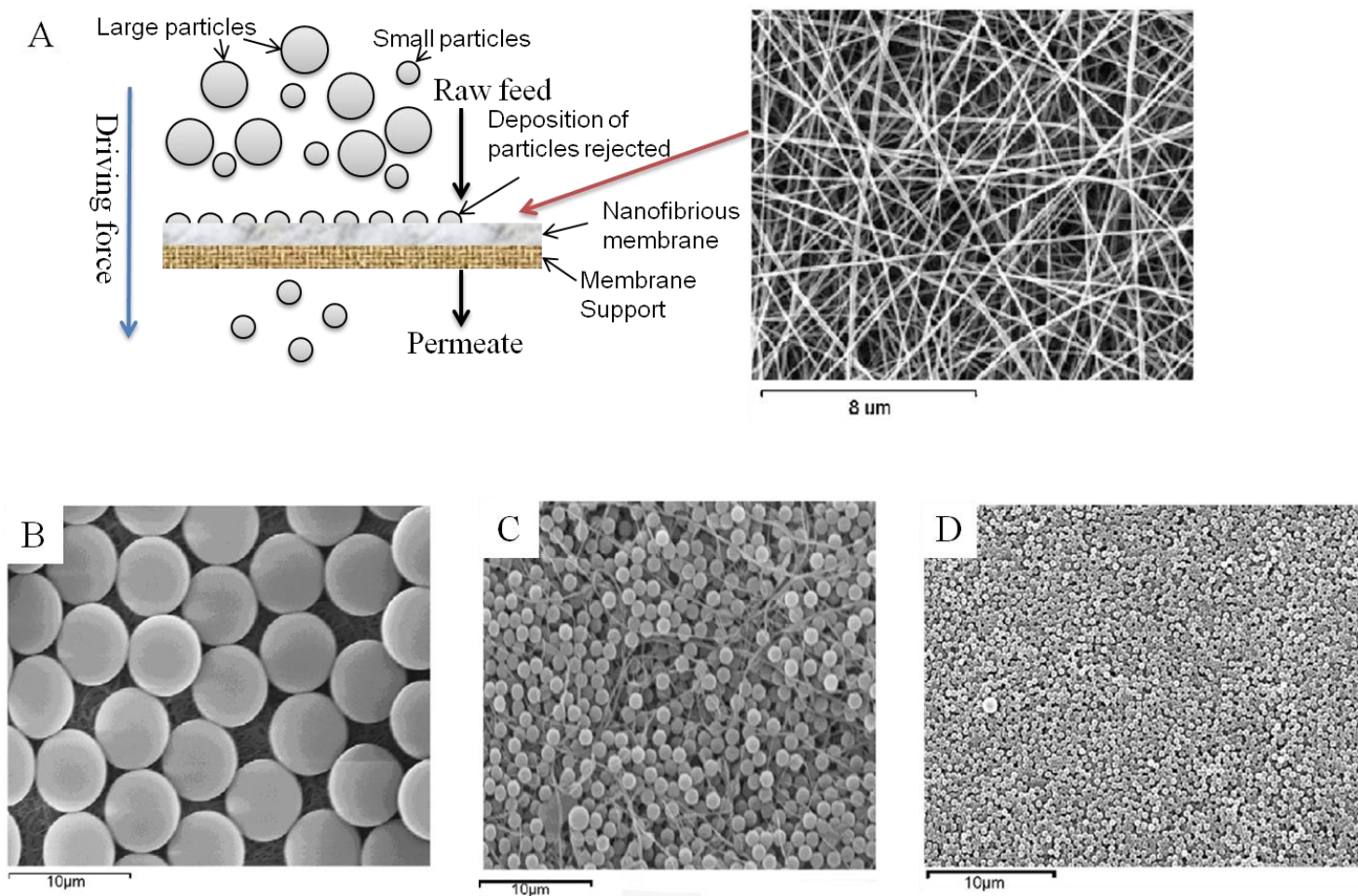
Gopal *et.al* first demonstrated that electrospun nanofibrous mats can be used for liquid separation and particle removal [164]. Characterization of PVDF nanofibrous membranes revealed that they had similar properties to conventional MF membranes and rejected over 90% of the 1, 5, and 10  $\mu\text{m}$  polystyrene particles from solutions. To further understand the effects of electrospun nanofibrous structure on membrane performances, a series of nanofibrous membranes have been fabricated by PAN, PSU, PES, and nylon-6 [165-169]. The performance of these ENMs with different nanofiber diameters and membrane thicknesses, were investigated. The results illustrated that the structure of ENMs significantly affects filtration properties. In addition, chemical modification is effective to further optimize ENMs properties. For instance, a short term oxidation treatment was carried out to modify PES nanofibrous membranes to be more hydrophilic ( $\sim 28^\circ$ ) and possess instant water wettability [170]. The pure water flux of modified PES ENMs was enhanced. With high effective porosity, interconnected pores, optimized small

pore size and high wettability, the nanofibrous membranes performed significantly better in terms of flux over conventional MF membranes.

Meanwhile, the nanofibrous membranes were able to achieve a high rejection level in the micro-particle retention test as shown in Fig. 6B-6D [168]. However, due to the characteristic structures of electrospun membranes, the membrane fouling issues could arise. In a study involving filtration of feed solution containing small particles (diameter  $< 2 \mu\text{m}$ ), an irreversible cake-like fouling layer was observed on the membrane surface, as shown in Fig. 6C [168]. When the particle size in feed solution was further reduced to below  $1 \mu\text{m}$ , the particles were deposited onto and into the nanofibrous membrane, causing the membrane to behave as a depth filter as shown in Fig. 6D, which caused the flux to decline drastically as a consequence of pore blocking [168]. Thus, in order to apply ENMs in MF, severe membrane fouling needs to be addressed.

Additionally, the nanofibrous membranes can undergo mechanical failure as nanofibers may be detached and washed away by the water flow under high flux and operational pressures. As such, mechanical strengthening of individual nanofibers and physical integration of nanofibers are critical before large-scale applications of ENMs in water industry. Several approaches, including but not limited to, heat treatment, solvent induced inter-nanofiber bonding, and use of crosslinking agents, have been used to knit the individual nanofiber into mats [171, 172]. Another strategy is the reinforcement of individual nanofiber, which improves its compact resistance under pressure. For example, compared with neat PES nanofibrous membranes, incorporation of zirconia nanoparticles into the PES nanofibers resulted in better filtration efficiency mainly due to the enhanced mechanical robustness [173].

**Fig. 6.** (A) A schematic of microfiltration system with electrospun nanofibrous membranes; (B) SEM images of membrane top surface after filtering 6.0  $\mu\text{m}$  PS micro-particles, (C) 1.0  $\mu\text{m}$  PS micro-particles and (D) 0.5  $\mu\text{m}$  PS micro-particles [168]. Copyright 2008, (B-D) has been reproduced and inserted with permission from Elsevier.



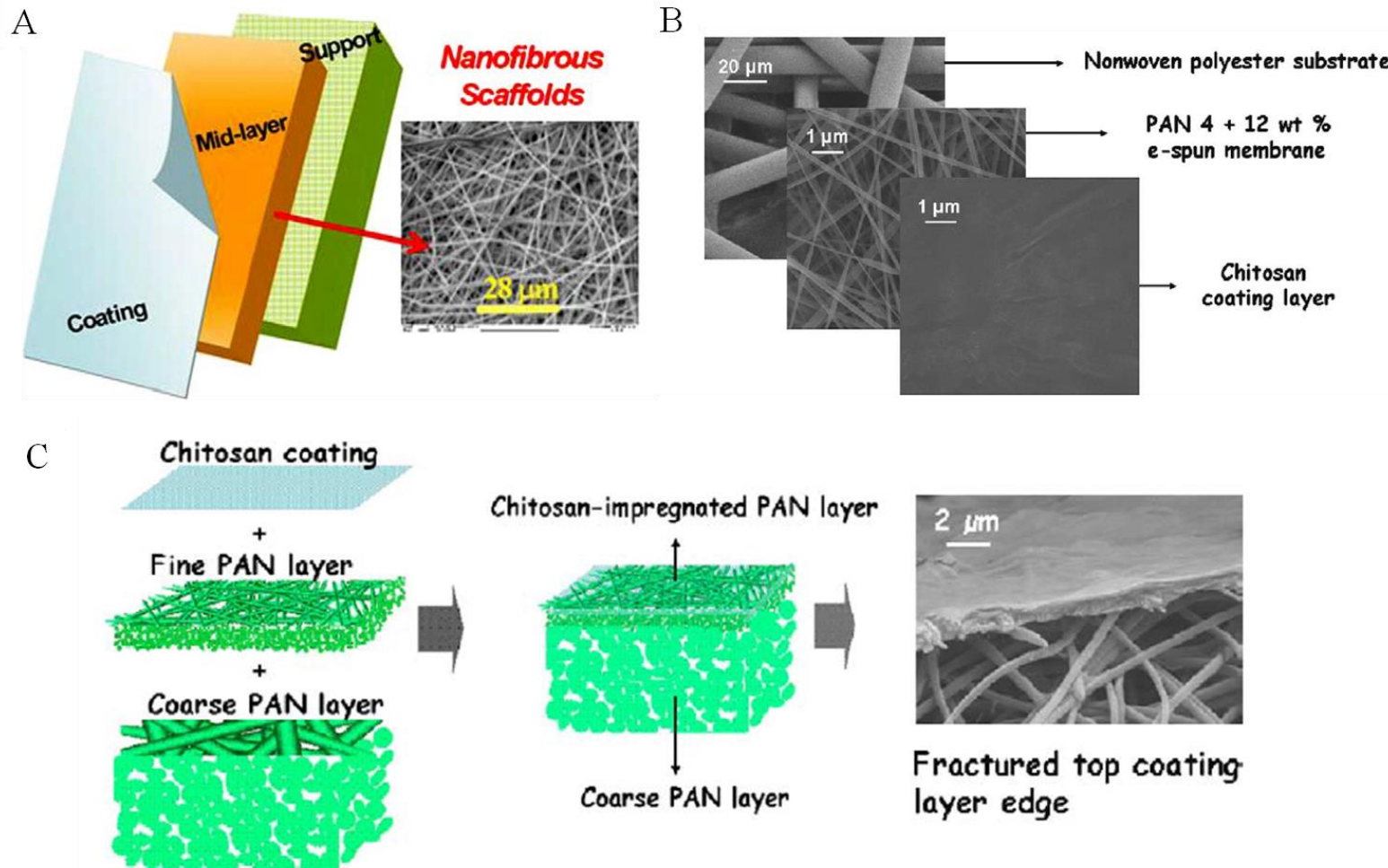
#### 4.1.2 Ultrafiltration (UF)

Ultrafiltration (UF) is a membrane filtration process with pores in the range of 0.01 to 0.1  $\mu\text{m}$  (10 to 100 nm) in which a liquid is forced through the membrane by hydrostatic pressure. In UF, water and low molecular weight solutes pass through the membrane while large species are retained. UF is an important component in water and wastewater treatment for removing bacteria, colloids and viruses. Its applications include potable water treatment, pre-treatment prior to RO desalination, reclamation and MBRs.

Currently, conventional polymeric UF membranes are fabricated by the phase inversion, and tend to suffer from low to modest flux and high fouling rates. The major limitation of current UF membranes is the wide pore size distribution that appears to be inherent in the phase inversion process. The large pores in the distribution exacerbate fouling and allow incomplete retention. A major target for ideal UF membranes is isoporosity of surface pores along with high porosity [6]. This requires a thin selective layer that is not formed by phase inversion, but produced by self-assembly or other means for controlled architecture films. Meanwhile, a highly porous and hydrophilic substrate such as nanofibrous scaffolds is required. An example to prepare such nanofibrous composite UF membranes is illustrated in Fig. 7A [174]. Fig. 7B shows the surface morphologies of each layer in the composite nanofibrous membrane, which includes a coating layer, an electrospun asymmetric scaffold, and a non-woven substrate [174]. Fig. 7C shows the schematic diagrams and the scanning electron microscope (SEM) images of the nanofibrous composite membrane with a tiered structure [174]. The nanofibrous composite UF membranes overperformed the conventional flux-limited UF membranes

by achieving a higher flux ( $>130 \text{ L m}^{-1} \text{ h}^{-1}$ ) while maintaining high rejection ( $> 99.9\%$ ) for filtration of oily waste water [174].

**Fig. 7.** (A) A three-tier approach to fabricate high flux and low-fouling ultrafiltration (UF) membranes, (B and C) SEM images of each layer in the three-tier composite nanofibrous membrane for UF [174]. Copyright 2006, Reproduced with permission from Elsevier.



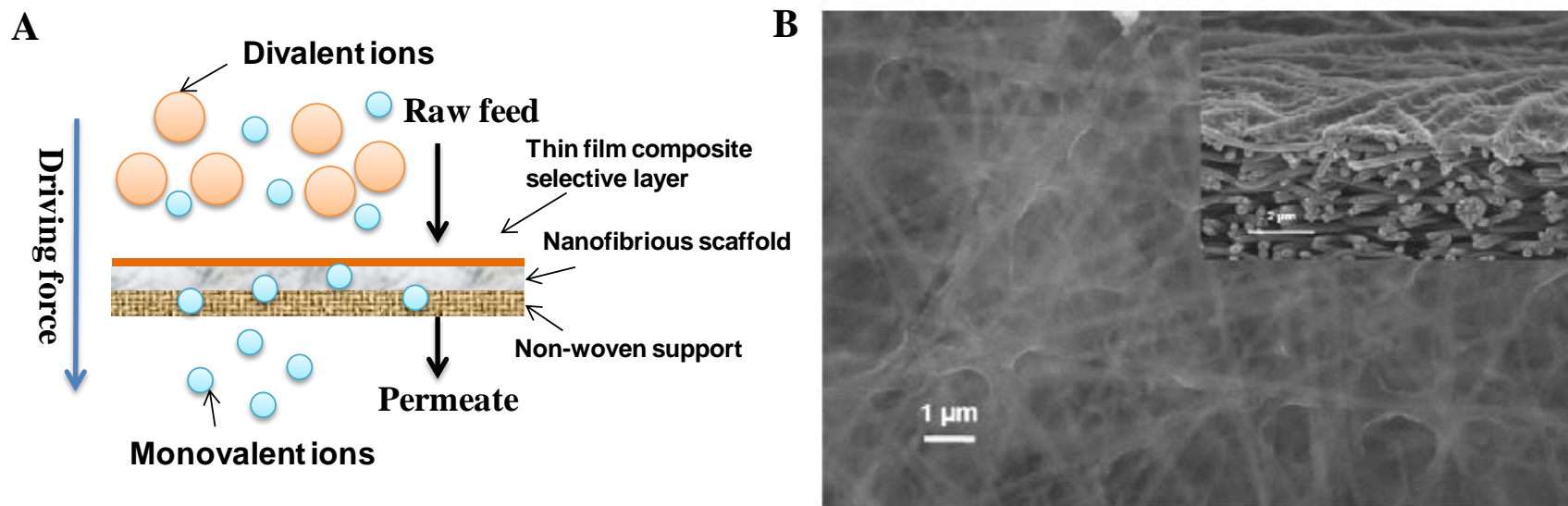
To develop more novel nanofibrous composite membranes for UF, different coating materials such as PVA and chitosan have been used to create barrier layers on the ENMs surface. For instance, composite nanofibrous membranes composed of a PVA nanofibrous support and a PVA hydrogel coating selective layer have been fabricated [149]. It was found that the composite nanofibrous membrane exhibited a high rejection efficiency ( $> 99.5\%$ ) while maintaining a high flux ( $> 130 \text{ L m}^{-2} \text{ h}^{-1}$ ) when separating an oil/water emulsion. Chitosan is an attractive coating material due to its hydrophilicity and high water permeability. An UF membrane composed of a hydrophobic PVDF nanofibrous scaffold and a chitosan ultrathin selective layer was developed [175]. With further surface modification by glutaraldehyde (GA) and terephthaloyl chloride (TPC), this composite membrane exhibited excellent performance in water-protein filtration, which offered a flux of  $70.5 \text{ L m}^{-2} \text{ h}^{-1}$  and a bovine serum albumin (BSA) rejection of  $98.8\%$  at  $0.2 \text{ MPa}$ . In addition, the membrane demonstrated good antifouling properties over the operation period of 24 h. In summary, both hydrophobic and hydrophilic polymers have been electrosun as the porous substrates for UF membrane fabrication, while the hydrophilic substrates are likely to be better for most applications attributed to antifouling properties. Further developments are required to optimize the network architecture and thickness of the top coating layers to enhance water permeability, hydrophilicity and antifouling properties.

#### 4.1.3 Nanofiltration (NF)

Nanofiltration (NF) takes the lower end of UF and the upper end of RO. Typical separation size of NF ranges from 100 to 1000 Daltons in terms of molecular weight cut-off (MWCO) [176]. NF is widely used in water treatment as it is capable to soften and disinfect water, and remove color, taste, odour, some trace organic contaminants and divalent ions. The separation in NF involves both the sieving (steric hindrance) effect and Donnan (electrostatic) effect, and is driven by a high trans-membrane pressure [177]. As shown in Fig. 8A, the difference between NF and RO is that RO is able to reject monovalent salts such as sodium chloride while NF is mainly effective in retaining divalent ions and multivalent salts such as sodium sulphate.

Most current NF membranes are thin film composite (TFC) membranes with an ultrathin skin layer produced *via* IP on top of a porous substrate. As illustrated in section 3.3, the surface porosity of the substrate is critical for development of high performance TFC membranes as it determines the effective flow path through the skin layer. Nanofibrous scaffolds, which have a high surface and internal porosity, should be attractive for TFC membranes development. This is particularly so for NF, owing to the modest pressures and compressive forces applied. An example of the potential benefit of using a nanofibrous substrate is the filtration performance of a PA-covered PAN TFNC membrane compared with a lab-made TFC membrane fabricated on a commercial UF support and commercial NF membranes: the novel TFNC membrane exhibited over 2.4 times higher permeate flux while maintaining the same rejection (98%) [158]. Typical surface and cross-section morphologies of a TFNC membrane are shown in Fig. 8B [158].

**Fig. 8.** (A) Schematic of nanofiltration (NF) with a thin film nanofibrous composite (TFNC) membrane; (B) Typical surface and cross-section (inserted images) morphologies of a TFNC membrane, Copyright 2009, (B) has been reproduced and inserted with permission from Elsevier [158].



The effects of structural properties of nanofibrous supports on NF performance have been studied. It was revealed that the TFNC membrane flux increased by increasing the nanofiber diameters, as the surface pore size and porosity of the substrate increased [160]. However, there was an upper limit for nanofiber diameter and membrane surface pore size, beyond which nanofibrous membrane cannot support the barrier layer. It was also observed that although increasing the nanofiber size enhanced permeation flux, it simultaneously reduced the rejection. On the other hand, due to a decrease in hydraulic resistance of nanofibrous support, the permeation flux can be improved by reducing the nanofibrous membrane thickness. Additionally, the influence of heat press post-treatment on nanofibrous membrane properties and subsequently the separation of salt after IP has been investigated [178]. The TFNC membranes with heat-pressed substrates were able to withstand a trans-membrane pressure of up to 13 bars and possessed a higher flux than a commercial NF membrane while maintaining a rejection of over 88% for 2000 ppm  $\text{MgSO}_4$ .

In addition to the structural properties of substrates, the IP protocol also showed great influences on membrane performance. Kaur *et al.* carried out two IP approaches, named A and B, on the surface of PVDF nanofibrous membranes [179]. The two approaches led to different surface topologies and subsequently different permselectivities. In Approach A, nanofibrous substrates were soaked in an aqueous phase followed by an organic phase while the sequence was reversed in Approach B. Compared with Approach A, the TFNC prepared by Approach B had a more uniform PA layer, and possessed a rejection of 80.7% and a flux of  $0.51 \text{ L m}^{-2} \text{ h}^{-1}$  for 2000 ppm  $\text{MgSO}_4$  at a pressure of 5 bar.

Besides IP, cross-linked hyperbranched polymer networks have been developed as the barrier skins for NF. For example, PEI-laden nanofibrous PVDF scaffolds were reacted with trimesoyl chloride (TMC), 1,3-dibromo propane (1.3-DBP), and epichlorohydrin (ECH) respectively, to produce a cross-linked PEI selective layer with positive charges on membranes surface [180]. It was found that the TFNC with cross-linked PEI/TMC networks had a high water flux of  $30 \text{ L m}^{-2} \text{ h}^{-1}$  and a rejection of 88% for  $\text{MgCl}_2$  and 65% for NaCl at a trans-membrane pressure of 7 bars.

In summary, electrospinning is a feasible technique to fabricate promising substrates with high surface porosity and interconnected pore structures for pressure-driven membrane processes. As electrospinning is not able to produce dense membranes with nanometer-sized pores in one step, most previous works have been focused on designing and developing TFNC membranes to explore their applications. However, the lack of studies on examining the stability of the selective layers under high pressure, anti-fouling properties of as-developed TFNC membranes in real water treatment, and upscaling preparation of TFNC membranes for mass production limited their practical applications.

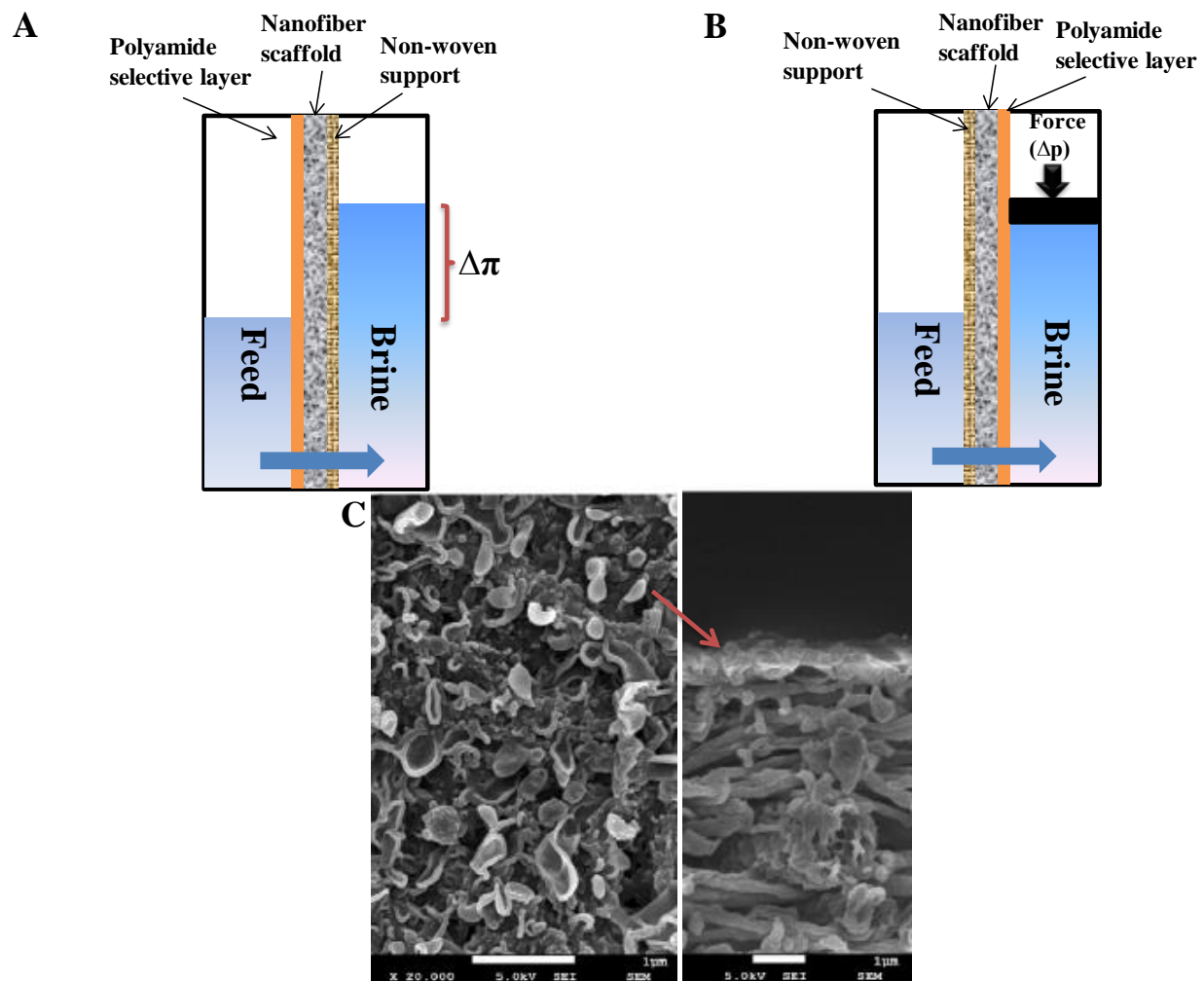
#### 4.2 Osmotically driven membrane processes

Osmotically driven membrane processes, also known as engineered osmosis (EO), including FO and PRO, exploit the natural phenomenon of osmosis as the primary driving force for membrane processes [181]. Conventionally, osmosis is the net movement of water through a selectively permeable membrane, which allows the passage of water and rejects solute molecules or ions, driven by a difference in osmotic pressure across the membrane. These processes can be applied for water extraction and

recovery, and also enable the harvesting of salinity gradients for electricity generation [182, 183].

As shown in Fig. 9A, FO uses the osmotic pressure difference ( $\Delta\pi$ ) across the membrane as the driving force for the transport of water through the membrane, which results in concentration of the feed stream and dilution of the highly concentrated draw stream [184]. In the PRO process (Fig. 9B), a closely related process, hydraulic pressure is applied to the draw solution optimally at about half the osmotic pressure difference, so that water flows from low to high pressure. The extracted and pressurised water can pass through a turbine to generate power, or through a pressure exchanger to transfer pressure energy to seawater RO. In effect, PRO provides an alternative to produce renewable energy free of CO<sub>2</sub> emissions [184]. However, despite being proven to be feasible, there are important obstacles hindering its further commercialization, including the availability of suitable membranes. In order to enhance the membrane performance in EO applications, it is essential to prepare membranes with a specially designed support with high porosity and low tortuosity, which is capable of mitigating the severe internal concentration polarization (ICP). Recently, nanofibrous membranes with higher porosity have attracted increasing interests as a promising scaffold-like porous support to fabricate EO membranes. The typical top view and cross section of a TFNC membrane used in EO are shown in Fig. 9C [185].

**Fig. 9.** Solvent flows in (A) forward osmosis (FO) and (B) pressure retarded osmosis (PRO) processes; (C) Typical top view and cross section of a TFNC membrane for engineering osmosis (EO) [185].



McCutcheon *et al.* was the first group to develop a novel high flux FO membrane comprising an electrospun nanofibrous support and a PA skin layer [157]. This TFNC membrane achieved two to five times higher flux with up to hundred times lower salt flux than a commercial membrane due to its superior porosity and interconnected pore structure which reduced ICP significantly. They further fabricated more hydrophilic nanofibers by electrospinning mixtures of PAN and CA to combine the hydrophilicity, spinnability, and flexibility of PAN with the toughness and lower hydrolyzability of CA [161]. The resulting composite membrane exhibited a two to three times enhanced water flux and 90% rejection in salt passage when compared with commercial membrane due to its higher hydrophilicity. In another study, nylon 6,6 ENMs were used as substrates to prepare FO membranes [186]. The resultant membrane exhibited better performance because of its hydrophilic, porous and non-tortuous support. It was also found that compared with conventional FO membranes, the TFNC FO membrane worked equally well in both FO and PRO mode, as the diffusive resistance in the FO mode was greatly reduced [187]. Our group explored the feasibility of using PVDF ENMs as the substrates to make high-performance FO membranes [185]. It was shown that a denser PA layer with low permeation flux was attained on a substrate with a smaller pore size while a looser PA layer with higher permeation flux was formed on the substrate with larger pore size. In addition, we incorporated functionalized carbon nanotubes (f-CNTs) in PEI nanofibers [188]. The well-distributed f-CNTs in nanofibers enhanced substrate porosity (30%) and mechanical strength (53%) simultaneously, resulted in higher FO performance. Our recent work reported that embedding of silica nanoparticles in PEI nanofibers could alleviate substrate compaction and subsequent minimize porosity reduction during heat-

press post-treatment, which eventually mitigated undesired ICP and enhanced osmotic water flux [150]. In addition, crosslinked PVA nanofibers and PVA/Polyethylene terephthalate (PET) interpenetrating networks with remarkable hydrophilicity have been fabricated as supports for FO membranes to mitigate ICP [189, 190].

In order to operate TFNC membranes in PRO process, the mechanical strength of the membranes requires significant improvement. A TFNC membrane composed of electrospun PET nanofibers, a phase separation formed microporous PSU layer, and a PA selective layer was fabricated to overcome the limitations. It was found that the PET nanofibers in the support layer enhanced membrane resistance to high shear stress and high hydraulic pressure [191]. A TFNC membrane composed of an IP layer on PVA-coated PAN nanofibrous support has been successfully prepared for high pressure PRO process [192]. The nanofibers were effectively strengthened by incorporated nano-silica while inter-connective bonding force between nanofibers was enhanced by heat press post-treatment and cross-linking *via* PVA. It was shown that the ENMs tiered with layers of nanofibers with different diameter could successfully withstand a pressure up to 11.5 bar and generate a power density of  $8.0 \text{ W m}^{-2}$  [193]. Besides, our group has successfully fabricated a TFNC PRO membrane consisting of a tiered PEI nanofibrous support reinforced by f-CNTs and a PA barrier layer [87]. The ultrafine nanofibers reinforced with f-CNTs effectively supported the PA top layer, allowing the obtained TFNC membrane to withstand a trans-membrane pressure of up to 24 bar in the PRO process. Our optimized membrane can produce a peak power density as high as  $17.3 \text{ W m}^{-2}$  at 16.9 bar, which demonstrated the great potential of the nanofiber-supported PRO membranes.

Despite reported endeavours on the development of effective TFNC membranes for EO processes, many critical challenges remain unsolved, such as the loss of porous structure and membrane integrity due to membrane compaction under high pressures, the reducing selectivity of PA layers under elevated pressures, fouling of TFNC membranes in EO processes, and membrane durability in long-term PRO operation, which demand further investigation.

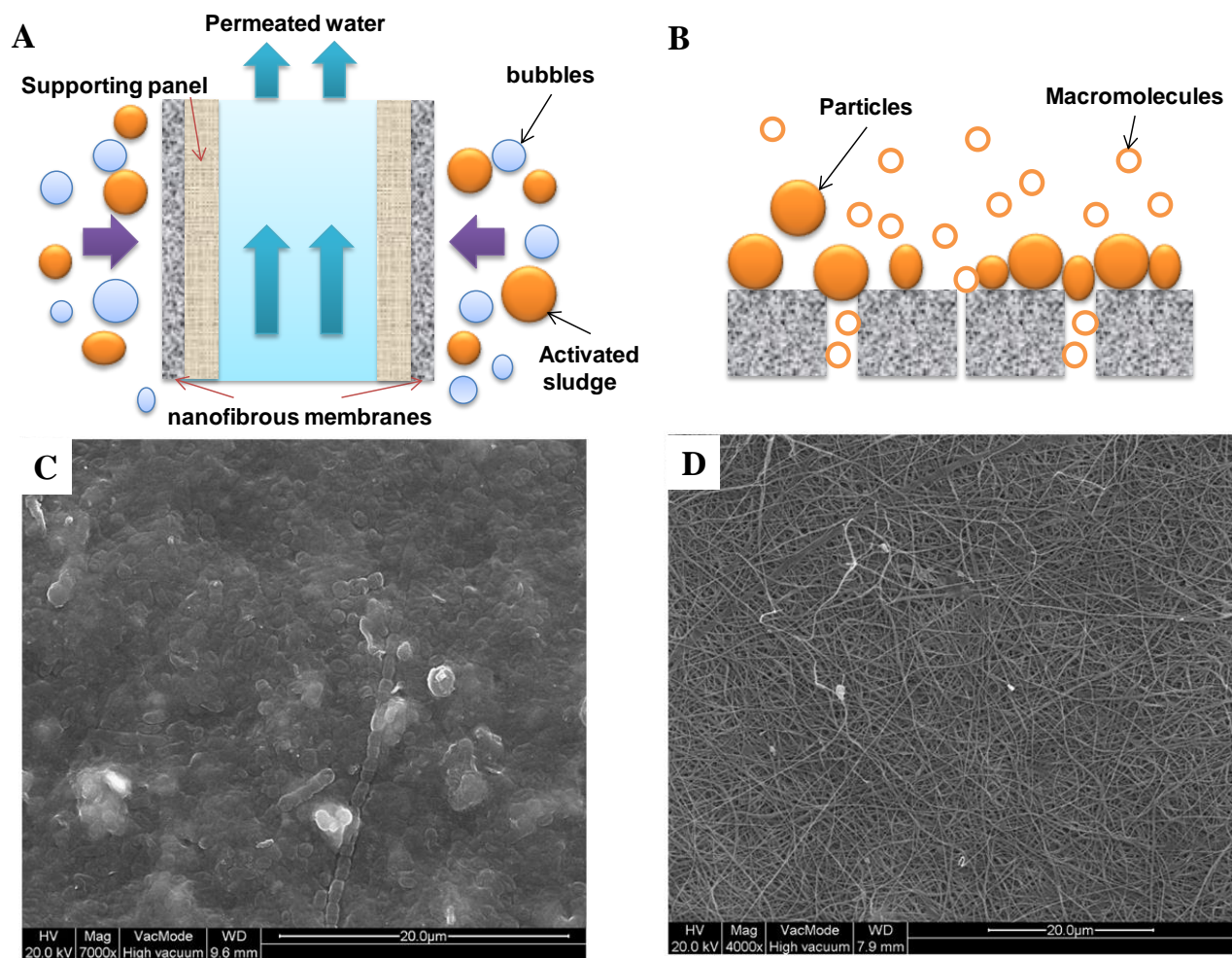
#### 4.3 Membrane bioreactor (MBR)

As shown in Fig. 10A, membrane bioreactor (MBR) technology combines a suspended growth bioreactor with membranes, which directly separates solid and liquid with a biological degradation process by activated sludge. MBRs are widely used to treat municipal and industrial wastewaters and produce water effluents with high quality [194]. Due to the membrane technologies, the MBRs show a great number of advantages compared with conventional wastewater treatment processes, including a smaller footprint, high effluent quality, good disinfection capability and less sludge production [195]. The MF or UF membranes are usually utilized in MBRs to separate the biomass from permeate. Nanofibrous membranes, with typical pore size falling into the range of MF, have also been applied in MBR configurations.

However, it was observed that the membrane performance tends to decrease with filtration time in MBRs [195]. This was caused by deposition of soluble and particulate foulants onto and into the membranes due to the interaction between the foulants and membranes surface as shown in Fig. 10B. For example, a study with a PA nanofibrous membrane in a submerged MBR concluded that the PA nanofibrous membrane was not

competitive with existing commercial membranes due to the irreversible fouling [196]. It was evident that some strategies, such as changing process configurations and modifying the membrane surface, had to be employed to mitigate fouling. Further study evaluated the performance of PA nanofibrous membranes in three different MBR configurations, including an activated sludge MBR (AS-MBR), AS-MBR with flux performance enhancer (a polymer additive), and a trickling filter MBR (TF-MBR) [197]. The study showed that the nanofibrous membranes possessed best performance in the TF-MBR process as particles that tended to cause irreversible fouling were removed by the trickling filter. The permeation flux was stable for 85 days and it was proven that the morphology and strength of the nanofibrous membranes were not damaged by chemical cleaning with 0.5% NaOCl and 0.2% HCl, as shown in Fig. 10 C and D [197]. However the TF-MBR may lose some of the special features of the AS-MBR, such as small footprint and operational flexibility.

**Fig. 10.** (A) Schematic of a membrane bioreactor; (B) Illustration of membrane fouling in membrane bioreactor process; SEM images of (C) the nanofibrous membrane with a fouling layer on the surface after MBR operation and (D) the same nanofibrous membrane surface after cleaning [197]. Copyright 2010, (C and D) have been reproduced and inserted with permission from Elsevier.



To examine the effects of membrane materials on fouling, comparative performance of nanofibrous membranes made of PA, PSF, commercial PVDF, and PE, was studied [198]. It was found that the nanofibrous membranes fabricated from more hydrophilic polymer possessed better performance. In addition, heat press treatment was efficient to prevent layered fouling on the nanofibrous membranes. The nanofiber diameter and area-weight of nanofiber-sheets did not show significant effects on membrane performance.

Recently, our group has developed novel composite nanofibrous membranes consisting of PVDF nanofibrous substrates with a tiered structure and a dense polydimethylsiloxane (PDMS) selective layer for extractive membrane bioreactor (EMBR) system [199]. The EMBR combines an extractive membrane process and a biodegradation process to extract and biodegrade recalcitrant organic contaminants in industrial wastewater simultaneously. It was demonstrated that the tiered PVDF nanofibrous scaffold with ultrafine nanofibers on top could support a uniform PDMS selective layer, resulted in a defect-free composite nanofibrous membrane. Optimization of PDMS cross-linking method could mitigate PDMS intrusion into substrates, which reduced the overall mass transfer resistance of the composite membranes.

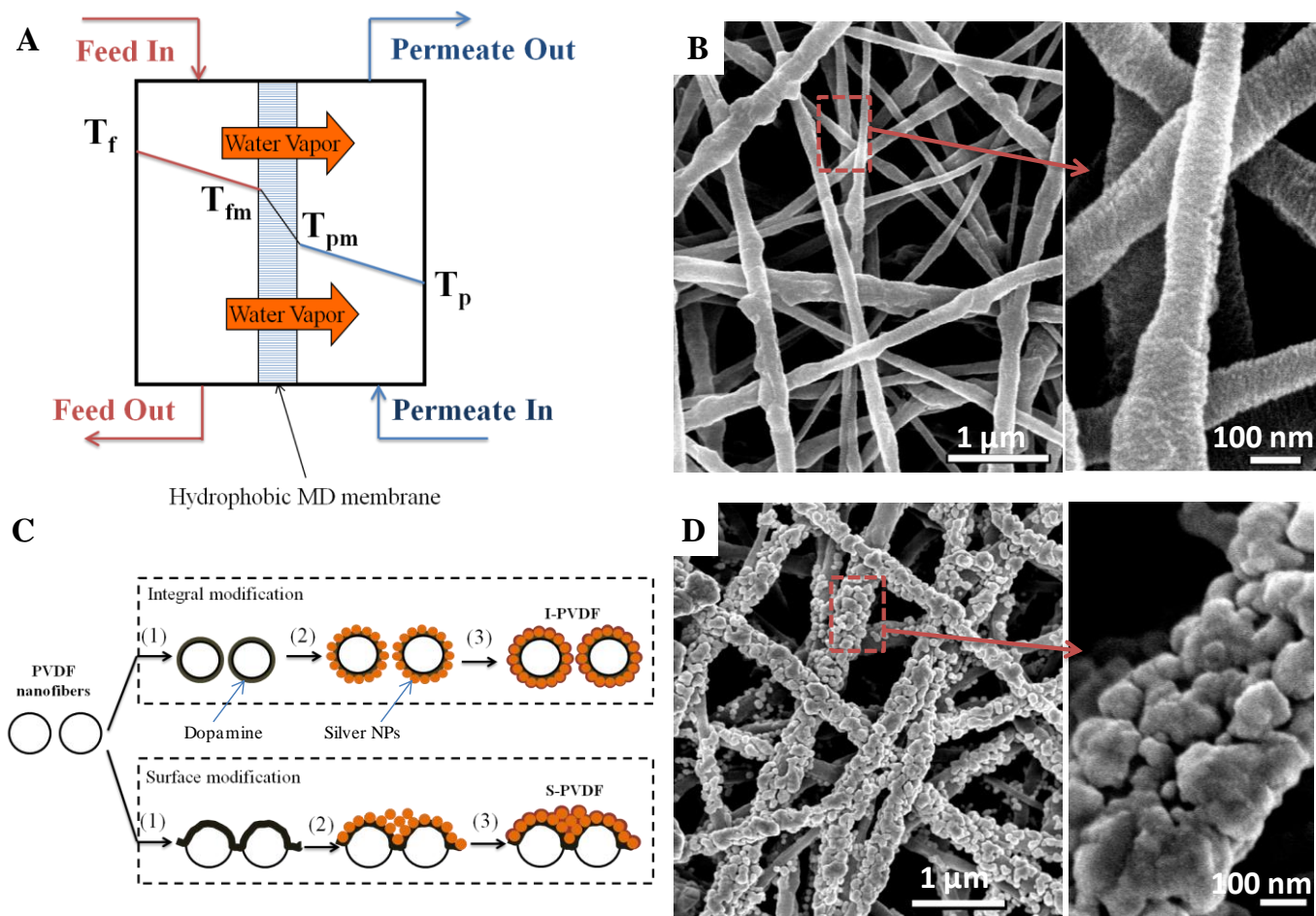
In contrast to other water treatment processes, few works have been conducted to study the feasibility of nanofibrous membranes in MBR systems. One possible reason is the high fouling tendency of nanofibrous membranes due to high surface roughness. Thus, there remain a number of research gaps to be addressed before applying ENMs in MBR systems, in particular developing anti-fouling nanofibrous composite membranes with competitive and stable performance in long-term operation.

#### 4.4 Membrane distillation (MD)

Membrane distillation (MD) is a thermally driven process, in which water vapor is transported through microporous hydrophobic membranes. MD has four configurations, which are direct contact membrane distillation (DCMD), air gap membrane distillation (AGMD), sweeping gas membrane distillation (SGMD) and vacuum membrane distillation (VMD) [200]. Among these different MD configurations, the DCMD is the most studied [201]. As shown in Fig. 11A, in a typical DCMD process, volatile molecules evaporate at the liquid/vapor interface at the high temperature feed side, then cross through the hydrophobic and porous membrane, and finally condense at the cold permeation side. Compared with conventional desalination processes, MD processes can be carried out at a lower operating temperature (than thermal desalination) and hydrostatic pressure (than RO), and provide theoretically 100% rejection of non-volatiles. These features make MD more attractive than other desalination processes [202]. However, most membranes used in MD are designed and fabricated for other processes such as microfiltration. Thus, one of the key issues that need to be tackled for MD applications is the availability of specially designed MD membranes.

The essential requirement of a MD membrane is that at least one layer of the membrane should be hydrophobic so that only vapor and non-condensable gases are present within membrane pores [203]. In addition, the membrane should possess high porosity to enhance vapor permeation and guarantee high water production. The unique features of electrospun membranes, including high porosity, overlapping nanofibrous structures and interconnected open pores, make them attractive for MD applications.

**Fig. 11.** (A) Schematic of direct contact membrane distillation (DCMD); (B) Surface morphology of a PVDF nanofibrous membrane fabricated for DCMD; (C) Schematic diagram of preparing superhydrophobic PVDF nanofibrous membranes by silver nanoparticles and 1-dodecanethiol hydrophobic modification and (D) surface morphology of a superhydrophobic PVDF nanofibrous membrane after modification [30].



PVDF nanofibrous membranes were first fabricated by Feng *et al.* for AGMD to produce drinking water from saline water [204]. The membrane flux was comparable to those obtained by commercial microfiltration membranes ( $5\sim 28 \text{ kg m}^{-1} \text{ h}^{-1}$ ) at feed temperatures ranging from 323 to 358 K. Our group optimized PVDF nanofibrous membranes for DCMD by controlling polymer dope concentration and electrospun parameters, and conducting a heat-pressed post treatment [171]. The surface morphology of the as-prepared PVDF nanofibrous membranes is shown in Fig. 11B [30]. It was demonstrated that the heat-press post-treatment was critical to improve the nanofibrous membrane integrity, enhance permeation flux and prevent membrane wetting. Besides, clay nanocomposite and fluorosilane-coated  $\text{TiO}_2$  have been embedded in PVDF nanofibers to enhance membrane hydrophobicity for MD [205, 206]. Moreover, dual-layer nanofibrous membranes composed of a hydrophobic PVDF surface layer and a hydrophilic support layer electrospun by PVA, nylon-6 or PAN have been reported [207]. The hydrophilic layer could enhance the AGMD performance due to the wettability of the support layer.

In order to further stabilize MD performance, we have designed and developed superhydrophobic nanofibrous composite membranes [30, 208, 209]. Two types of superhydrophobic modification, integrally-modification and surface-modification have been carried out as shown in Fig. 11C [30]. It was shown that modifications altered the topology of membrane surface and made the membranes superhydrophobic due to the hierarchical structures as shown in Fig. 11D. The integrally-modified PVDF membrane achieved a high and stable MD water flux of  $31.6 \text{ L m}^{-2} \text{ h}^{-1}$  using a 3.5 wt% NaCl aqueous solution as feed when feed and permeate temperatures were fixed at 333 K and

293 K, respectively. However, the long-term stability of the superhydrophobic layers in the MD process needs to be further improved. In a subsequent study, a facile strategy to fabricate robust superhydrophobic membranes consisting of a superhydrophobic silica-PVDF selective layer formed on PVDF nanofibrous support was developed in our group [208]. It was demonstrated that the superhydrophobic surface layer exhibited excellent durability in both continuous DCMD operation and when subject to ultrasonic treatment. In further work, we fabricated a 3D superhydrophobic membrane by electrospinning superhydrophobic layers on a nonwoven support [209]. The resultant membrane exhibited greater mechanical strength due to the excellent combination between the superhydrophobic layers and the non-woven substrate. It showed better long-term stability due to the thicker 3D superhydrophobic structure.

To address the wetting and fouling issues in MD, there has been growing number of studies on developing electrospun membranes with superhydrophobic surface in recent years [146, 210]. Superhydrophobic and self-cleaning PSF-PDMS nanofibrous membranes with competitive DCMD performance have been prepared by electrospinning PSU nanofibers followed by PDMS modification and post-treatment [211]. Similarly, the superhydrophobic PDMS/PVDF hybrid membranes were also developed and showed antifouling properties in treating dyeing wastewater by MD [212]. CNTs as nanofillers were incorporated in nanofibers by one-step colloidal electrospinning to impart additional mechanical and hydrophobic properties to resultant nanofibrous MD membranes [89]. The presence of CNTs in/on nanofibers produced beads-on-string morphology and increased membrane roughness, leading to a superhydrophobic surface. Besides, silica, TiO<sub>2</sub>, Al<sub>2</sub>O<sub>3</sub> nanoparticles and graphene have also been embedded in electrospun

nanofibers to develop hierarchically superhydrophobic or superamphiphobic membranes for MD [89, 213-217].

It can be seen that significant efforts have been made to develop novel hydrophobic, superhydrophobic or even superamphiphobic membranes by electrospinning for MD. Although membrane hydrophobicity is of crucial importance to prevent wetting in MD, the large surface pore size of electrospun membranes also gives rise to high wetting tendency. In addition to increasing hydrophobicity, more effects should be made on developing electrospun membranes with smaller pore sizes and narrower pore size distribution. The long-term performance of these membranes requires examination prior to practical applications. Furthermore, scaling and fouling on membranes surface caused by salt crystals, surfactants and oils in the feed solutions should be addressed. This requires further optimization of membrane properties including the surface chemistry, topology and charge.

#### 4.5 Water-oil separation

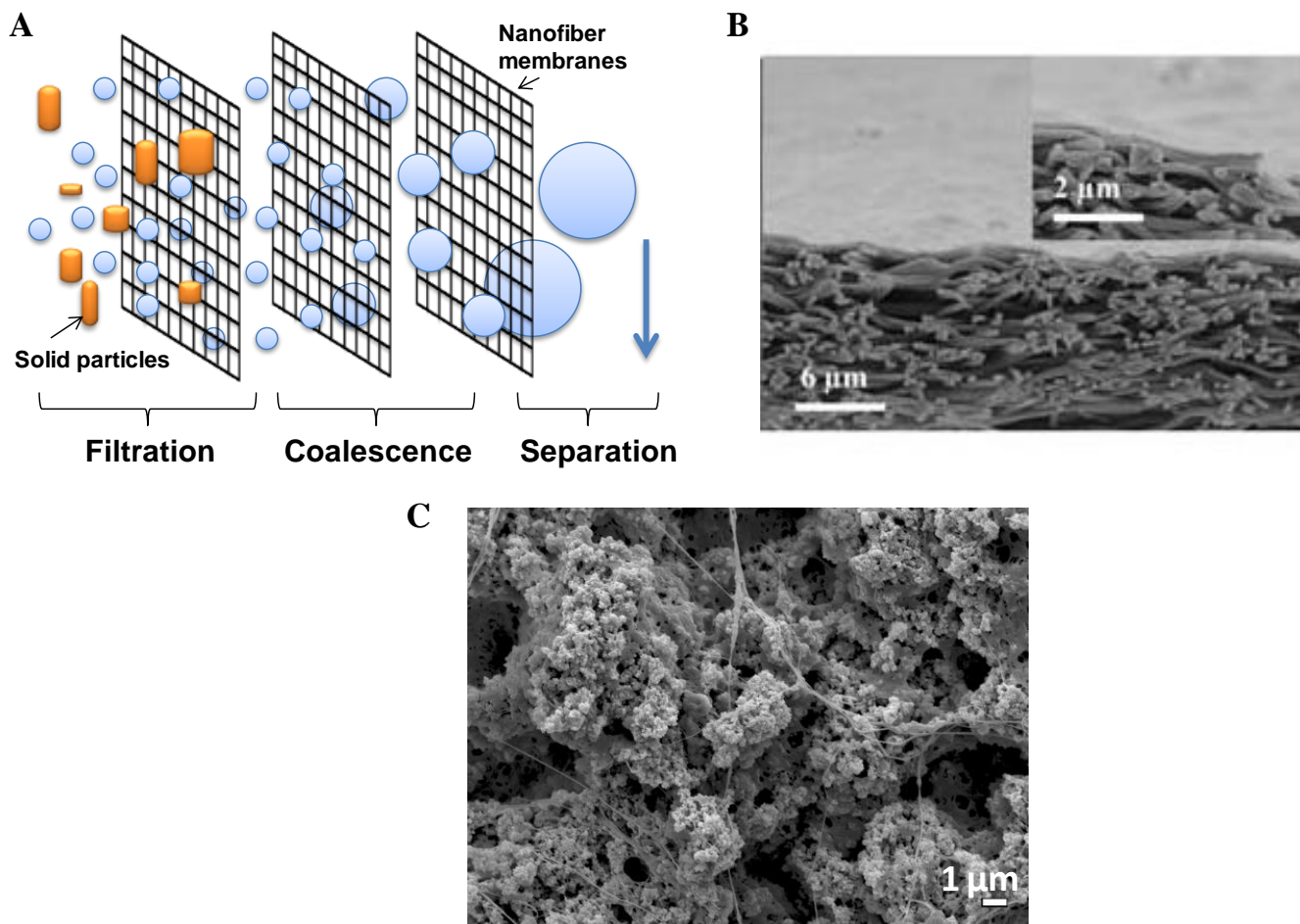
Due to adverse impacts of worldwide oil spills, separation and recycle of oil/water streams *via* energy- and cost-effective, environmentally friendly techniques have drawn increasing attention. Coalescence filtration is effective to separate oil/water emulsions by demulsification. As shown in Fig. 12A, there are three main steps for the coalescence filter to separate emulsions. Firstly, solid particles are removed from the fluid stream by the filter medium. Secondly, the fibrous bed captures droplets and the collected droplets coalesce within the fibrous network. Small oil/water droplets are merged into large ones as they pass through several layers of nanofiber filter in the coalesce system. Finally, the

gravity separation splits the stream into an oil layer and a water layer. The large water droplets settle when treating water-in-oil emulsions and large oil droplets rise to the surface when treating oil-in-water emulsions. Coalescence performance depends on flow rate, bed depth, nanofiber surface properties and droplet size.

The performance of glass fibers covered with polymer nanofibers in oil/water separation has been reported [218-220]. It was shown that the addition of even a small amount of nanofibers enhanced the capture efficiency of the filter media. However, it also increased the pressure drop [218]. It was also observed that the diameter and wettability of the nanofibers controlled the performance of coalesce filter media. A decrease in nanofiber size improved the overall separation efficiency; materials with better wettability promoted water-in-oil coalescence. In their study, the filter performance was optimized by electrospinning nylon 6 nanofiber with a diameter of 250 nm onto the glass filter surface, which significantly promoted the efficiency with minimal increase in pressure drop [219]. Additionally, PA nanofibers with a diameter of 150 nm deposited on micro-sized glass fibers increased the separation efficiency from 71 % to 84 % [220].

Besides coalescence, electrospun membranes have been fabricated for separating water/oil emulsions [221, 222]. These ENMs have been demonstrated to successfully separate kerosene/water, gasoline/water and hexane/water immiscible mixtures, and dodecane-in-water emulsions into their constituents. Addition of silica nanoparticles and GO in PSF electrospun nanofibers has strongly enhanced separation efficiency [221]. The membrane flux decreased in proportion to the increase of oil concentrations in oil-in-water emulsions [222]. Compared with a commercial membrane with similar pore size, the ENMs possessed several times higher flux and comparable rejection.

**Fig. 12.** (A) Schematic of coalescence filtration; (B) Cross-sectional view of cellulose-based TFNC membrane and (C) the surface morphology of a superwetting membrane fabricated for water/oil separations [223]. Copyright 2010, (B) has been reproduced and inserted with permission from Elsevier.



The pressure-driven membrane processes such as UF and NF are attractive alternatives for oil/water separation, considered their high discharge quality and easy implementation. In these processes, the oil droplets are removed from oil-in-water emulsions. However, commercial NF and UF membranes usually suffer from low fluxes due to limited permeability. A series of TFNC membranes were developed for oil/water separations by coating a thin hydrophilic nonporous layer on nanofibrous substrates [149, 152, 153, 155, 156, 223-225]. For example, TFNC membranes composed of a PAN electrospun scaffold coupled with a selective layer of crosslinked PVA have been fabricated for separation of oil/water mixtures [225]. With an optimized structure consisted of a mid-layer PAN scaffold with a porosity of 85 % and a PVA top layer with a thickness of 0.5  $\mu\text{m}$ , the TFNC membrane exhibited a permeation flux 12 times higher than that of the conventional PAN UF membrane and excellent rejection of 99.5 % for separation of oil/water mixture over 190 h. Additionally, a TFNC membrane consisted of a cellulose selective layer, a nanofibrous mid-layer, and an non-woven substrate has been developed to separate an emulsified oil and water mixture [223]. The permeation flux of the as-prepared cellulose-based TFNC membrane was significantly higher than a commercial UF membrane with the similar rejection. A typical cross-sectional image of this kind of TFNC membrane is given in Fig. 12B [223]. On the other hand, serious fouling by oils on membrane surface can significantly decrease membrane permeability for oil-water separation. The presence of a hydrophilic layer on TFNC membranes can mitigate the fouling. For instance, an ultraviolet (UV)-cured PVA coated TFNC membrane not only possessed high flux and rejection, but also had good fouling resistance due to its high hydrophilicity [224].

Increasing attempts have been made to develop biomimetic superwetting membranes for oil/water separation. These membranes with special wettability can be achieved via synergy between surface chemistry and topology. After functionalized by the fluorinated polybenzoxazine (F-PBZ), the composite CA nanofibrous membranes were endowed with a superhydrophobicity with a water contact angle of  $161^\circ$  and a superoleophilicity with an oil contact angle of  $3^\circ$  [226]. This as-prepared membrane possessed fast and efficient separation for oil-water mixtures, suggesting its potential as a promising separation membrane for industrial oil-polluted water treatment. Our recent work developed a novel membrane with switchable super-wettability for oil/water separation [227]. This membrane was in-air superamphiphilic, underwater superoleophobic and under-oil superhydrophobic, attributed to its hierarchically nano/micro-beaded surface morphology as shown in Fig. 12C. It could treat a number of oil/water mixtures, from immiscible mixtures to stable emulsions (including oil-in-water and water-in-oil emulsions with and without surfactants) without external driving forces or under an ultralow hydraulic pressure of 0.1 bar. The membrane also displayed an excellent robustness, remarkable antifouling and easy-cleaning properties, which demonstrated its potential for practical applications.

Smart membranes with responsive wettability have been prepared as promising candidates for oil/water separation. The  $\text{CO}_2$ -responsive polymers containing amine groups have been electrospun to prepare smart nanostructured membranes, whose oil/water wettability can be controlled by an alternating  $\text{CO}_2/\text{N}_2$  stimulation [228]. Thermo-responsive smart membranes have also been constructed with rejections of 98% in the gravity-driven oil/water separation process [229]. In addition, isotropically bonded

elastic aerogels with a hierarchical cellular structure were synthesized by combing electrospun nanofibers and the freeze-shaping technique [230]. The resultant nanofiber aerogels exhibited ultralow density, rapid recovery and superhydrophobic-superoleophilic wettability. These aerogels can separate surfactant-stabilized water-in-oil emulsions using gravity with high flux and high separation efficiency.

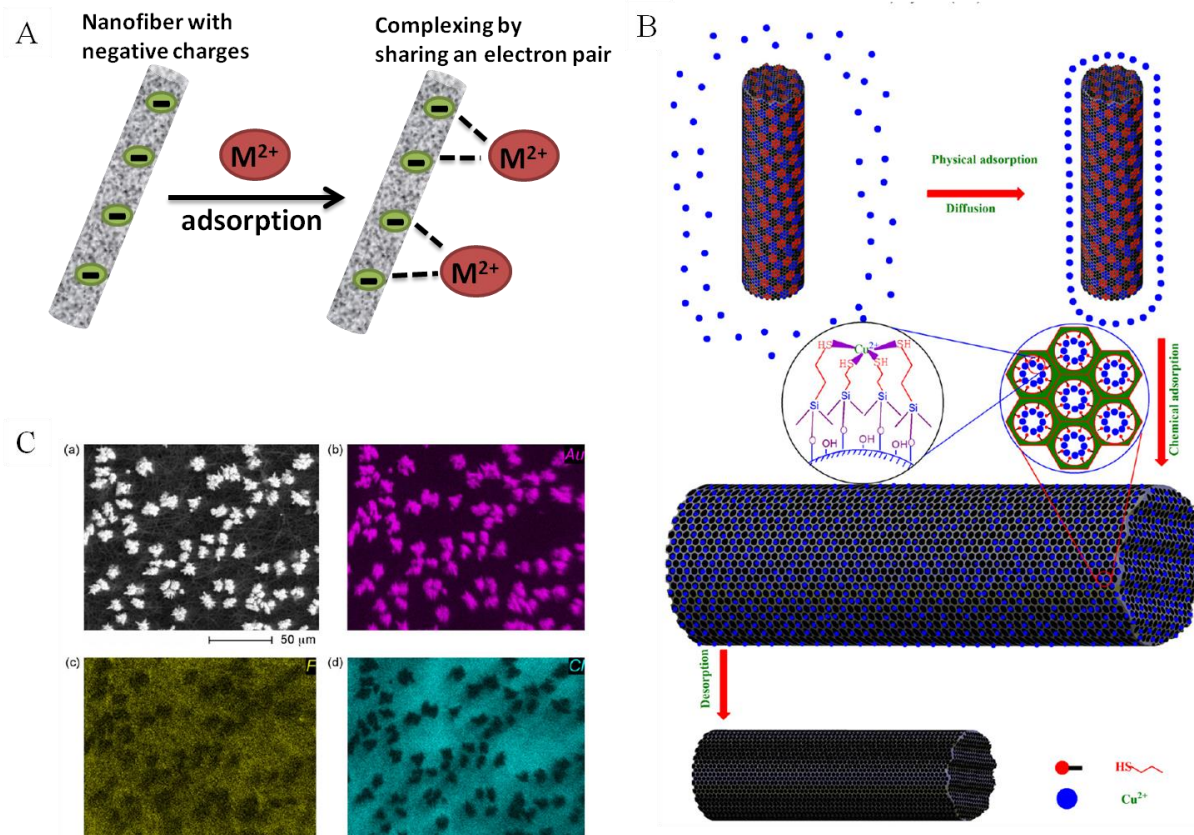
In this section, it has been illustrated that a great number of works has been carried out to develop superior oil/water separation membranes by electrospinning. However, several critical issues, including the quick decline of membrane permeability due to surfactant adsorption and pore plugging by oil droplets, and degradation of the polymeric membrane during usage remained unsolved. Future studies should be focused on designing novel membrane architecture to mitigate membrane fouling and developing new materials to address stability issues.

#### 4.6 Heavy metal ion adsorption

As heavy metal ions in water tend to accumulate, cannot be biodegraded and cause negative impacts to both ecosystem and human being, removal of them is of considerable importance [104]. As shown in Fig. 13A, exclusion of heavy metal ions can be achieved by adsorption based on ionic interactions between positively charged metal ions and negatively charged matrix containing functional groups, or coordinating bonds between metal ions and functional matrix by chelation [141]. As the amounts of ions adsorbed is limited by the surface area available for ionic interactions, the matrix with a large surface area and a great amount of functional groups is essential for adsorbing heavy metal ions

with high efficiency, making ENMs an attractive candidate. A large amount of research on the fabrication of metal-ion removal membranes by electrospinning has been reported.

**Fig. 13.** (A) Schematic of heavy metal ion adsorption; (B) The mechanism of adsorption of  $\text{Cu}^{2+}$  on PVA/SiO<sub>2</sub> composite nanofibers; (C) (a) FESEM images of the PPy-coated PVDF nanofibers membrane after Au recovering, (b-d) EDX maps of the same area, the abundant pink, grass green and navy blue indicated the locations of Au (Ma), F and Cl elements, respectively [138, 231]. Copyright 2010, (B) has been reproduced and inserted with permission from Elsevier. Copyright 2007, (C) has been reproduced and inserted with permission from Elsevier.



Wool keratin (WK), which is composed of hydrophilic amino acid groups, has gained increasing interest as metal ions adsorbents due to its high affinity to metal cations. The adsorption capacity of  $\text{Cu}^{2+}$  ions on randomly oriented nanosized filament mats, prepared by electrospinning WK/PA 6 blends has been evaluated [106]. Similarly, a WK/silk fibroin (SF)-blended nanofibrous membrane has also been fabricated by electrospinning as a heavy metal ion adsorbent [104, 105]. In the adsorption tests, the WK-blended nanofibrous mat exhibited a high  $\text{Cu}^{2+}$  adsorption capacity due to the large specific surface area. Furthermore, the adsorption capacity of the as-prepared membrane can be maintained after several recycling process. Another promising polymer for heavy metal adsorption is chitosan, which owns numerous polar and ionizable groups for adsorbing toxic metal ions by chelation. The adsorbability of chitosan ENMs in an aqueous solution was examined, which suggested that the chitosan ENMs can effectively remove toxic metal ions without losing their biocompatibility, hydrophilicity, bioactivity, non-antigenicity and non-toxicity [232].

The adsorption affinity of polymeric nanofibers can be improved by grafting functional groups. For instance, PAN nanofibers have been modified with amidoxime groups to adsorb metal ions [141]. Most adsorbed metal-ions can be desorbed in a 1 mol/L  $\text{HNO}_3$  solution within 1 h, demonstrating the potential for recycling metals from wastewater by functional nanofibers. Additionally, diethylenetriamine has been used to modify PAN nanofibers to adsorb copper ions [142, 233]. The results indicated that the adsorption efficiency of modified nanofibers was three times higher than microfibers and the saturate adsorption capacity was five times more than other reported materials.

The sulfur atom in the mercapto group is also utilized for metal ion removal as it can form chelates with heavy metal ions. Thiol-functionalized mesoporous PVA/SiO<sub>2</sub> composite nanofibers were fabricated as shown in Fig. 13B [231]. The as-prepared membranes, with a larger surface to volume ratio and a great number of mercapto groups, possessed outstanding Cu<sup>2+</sup> adsorption capacities that could also be maintained after six adsorption-desorption cycles [231, 234]. Furthermore, mesostructured PVP/SiO<sub>2</sub> composite nanofibers functionalized with mercapto groups showed high selectivity and capacious adsorption of Hg<sup>2+</sup>, as well as good recycling properties of adsorption and desorption [235]. Hollow nanofiber membranes with mercapto groups were also developed for heavy metal ions adsorption [112]. The functional silica nanofibers were fabricated by sol-gel polymerization of 3-mercaptopropyl trimethoxysilane on electrospun PAN nanofibers, followed by dissolving PAN from the prepared nanofibers in solvents [112]. The removal of PAN templates resulted in a higher specific surface area, making it more efficient in removing mercury from aqueous waste streams.

Incorporation of reactive nanoparticles into nanofibers is another effective method to prepare functionalized nanofibers for metal adsorption. Polycaprolactone (PCL) and nylon-6 nanofibrous membranes were impregnated with nano-boehmite particles, which are widely used for sorption of pollutants, to prevent the particles from releasing into the environment [236].

In addition to adsorption, nanofiber mats have also been used to electrolessly recover Au from aqueous (Au(III)Cl<sub>4</sub>)<sup>-1</sup> solutions based on a continuous-flow membrane separation process [138]. When a (Au(III)Cl<sub>4</sub>)<sup>-1</sup> solution passed through the polypyrrole (PPy)-coated PVDF nanofibrous membrane, the Au(III) ions were converted into elemental Au

and the recovered gold was deposited onto the nanofibrous membrane surface in the form of Au particles as illustrated in Fig. 13C [138].

This section demonstrates that nanofibrous membranes have great potential in metal ion adsorption, mainly due to their exceptionally high surface-to-volume ratio. Future developments of highly functional ENMs for metal ion removal from wastewater should focus on more reliable, scalable and eco-friendly modification methods and enhancement of removal efficiency and recycle life.

#### 4.7 Bactericidal effects

Among the worldwide waterborne outbreaks from 1991 to 2008, 842,000 deaths annually were caused by parasitic protozoan outbreaks, which remain to be the second leading cause of death in children under 5 years old [237]. Increasing public health and environmental concerns drive efforts to disinfect water effectively. A mass of functional nanofibers have been fabricated by impregnating selected agents to achieve antibacterial properties for medical devices [238]. CA, PAN and polyvinyl chloride (PVC) nanofibrous membranes with silver nanoparticles showed antimicrobial activity [238]. Electrospun polyurethane (PU) nanofibrous membranes were modified by pyridine groups [122]. The functional PU nanofibrous membrane possessed antibacterial activities against both Gram-positive *Staphylococcus aureus* (*S. aureus*) and Gram-negative *Escherichia coli* (*E. coli*) [122]. Moreover, a modified coaxial electrospinning with  $\text{AgNO}_3$  solution as sheath fluid was conducted to produce nanofibers with functional ingredients [239]. The obtained nanofibers exhibited effective antimicrobial activities attributed to the uniform distribution of silver nanoparticles on nanofibers surfaces.

Nonetheless, more studies are required to examine the performance of these antibacterial nanofibrous membranes in practical wastewater treatments.

## 5. Summary and outlook

Over the recent decades, electrospinning has established itself as a globally recognized facile method to fabricate nanofibers. The unique characteristics of nanofibers, including high specific surface area, high porosity of up to 90%, one dimensional arrangement, facile incorporation of functional nano-materials and diverse architectures, make them highly attractive for both academic studies and industrial applications. Impressive progress has been achieved in fundamental understanding and modelling of the complex electrospinning process as well as novel apparatus development, even at the industrial scale. One area which has received countless benefits from this progress, and will continue to profit in future, is the fabrication of novel electrospun membranes for water treatment. In this article, previous studies on fabrication, modification, and applications of electrospun composite membranes have been classified, reviewed and discussed. The potential applications of nanofibrous composite membranes in water treatment have been demonstrated. In spite of these endeavours, further investigations should be conducted on optimization of nanofibrous membranes with ultrafine nanofibers and superior porosity, development of robust and ultrathin selective layers on nanofibrous substrates, creation of complicate and multi-functional nanostructures and mass manufacture of these advanced nanofibrous membranes.

Most unmodified ENMs possess a maximum surface pore size larger than 1  $\mu\text{m}$  and nanofibers diameter ranging from 100 nm to 1000 nm. Optimizations of membrane

surface pores from micro-size to submicron size, or even nano-size, as well as reduction of nanofiber diameter from above 100 nm to several nanometers, are indispensable. By using ultrafine nanofibrous membranes, the filtration efficiency of smaller particles can be enhanced without significantly sacrificing the water permeation flux, attributed to the high porosity of the nanofibrous substrates. Meanwhile, ultrafine nanofibers can effectively support grafted or polymerized skin layers and mitigate their intrusion into substrates even under elevated pressure, facilitating the applications of TFNC membranes in high pressure processes. Controlling over dope conductivity, surface tension and viscosity can be conducted to obtain the ultrafine nanofibers. But mass production of nanofibers with diameters smaller than 100 nm is still challenging at the current stage.

In addition to supporting surface coating layers and alleviating their intrusion, optimized membrane substrates also provide benefits of enhancing adhesion between selective layers and substrates. More studies regarding the effects of substrate material, surface roughness, surface porosity and charge, and their synergistic effects on the bonding between the selective layers and nanofibrous substrates are expected. In addition, one of the major challenges in membrane processes is the reduction of flux to far below the theoretical capacity due to membrane fouling. The prospect of developing antifouling membranes by electrospinning and further modification is exciting. More coating approaches should be attempted to prevent the growth of fouling layers on membranes surface.

Electrospinning has been exploited to produce well-defined functional nanostructures, such as hollow nanotubes and nanofibers with well-controlled orientation and size. Nevertheless, controllable and reliable production of these unique nanofibers is still

challenging. The design and construction of electrospinning equipment for stable and continuous mass production are essential and merit more studies.

Apart from the above-mentioned water treatment processes, new applications should be explored for ENMs. The advances in nanomaterials and their convergence with ENMs can offer opportunities in developing nanotechnology-enabled multifunctional membranes, which are capable of performing multiple tasks such as water disinfection, decontamination and separation in one step. The electrospun nanofiber-based multifunctional membranes would be developed as a novel solution for efficient point-of-use water treatment.

The last few years have witnessed significant progress in research activities regarding electrospun membrane fabrication for water treatment and also elucidated crucial challenges as documented in this review. It is anticipated that further efforts can address these issues and motivate rapid developments of new electrospun membranes for water treatment.

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## Figure Captions and Tables

**Fig. 1.** Schematic illustration of the plausible nanofibers formation in electrospinning. The effects of intrinsic properties of polymeric dopes are marked in orange test box, operational conditions are marked in green text box and surrounding conditions in purple box.

**Fig. 2.** (A) The evolution of a fluid droplet in the electrospinning process [18]. Copyright 2001, Reproduced with permission from Hanser Publishing; (B) A diagram showing the pathway of an electrospun jet [17]. Copyright 2006, Reproduced with permission from American Chemical Society.

**Fig. 3.** Schematics of electrospinning systems with various spinnerets and collectors, and the morphologies of as-developed nanofibers. The images have been inserted from references [30, 34, 39, 42-50].

**Fig. 4.** Modification techniques of electrospun nanofibrous membranes. (A) (1) Immobilization of nano-materials in nanofibers, (2) electrospinning of blended polymers and (3) core-sheath/hollow nanofibers preparation; (B) Target molecules loading on the surface of nanofibers; (C) Surface coating and polymerization on nanofibrous substrates.

**Fig. 6.** (A) A schematic of microfiltration system with electrospun nanofibrous membranes; (B) SEM images of membrane top surface after filtering 6.0  $\mu\text{m}$  PS micro-particles, (C) 1.0  $\mu\text{m}$  PS micro-particles and (D) 0.5  $\mu\text{m}$  PS micro-particles [168]. Copyright 2008, (B-D) has been reproduced and inserted with permission from Elsevier.

**Fig. 7.** (A) A three-tier approach to fabricate high flux and low-fouling ultrafiltration (UF) membranes, (B and C) SEM images of each layer in the three-tier composite nanofibrous membrane for UF [174]. Copyright 2006, Reproduced with permission from Elsevier.

**Fig. 8.** (A) Schematic of nanofiltration (NF) with a thin film nanofibrous composite (TFNC) membrane; (B) Typical surface and cross-section (inserted images) morphologies of a TFNC membrane, Copyright 2009, (B) has been reproduced and inserted with permission from Elsevier [158].

**Fig. 9.** Solvent flows in (A) forward osmosis (FO) and (B) pressure retarded osmosis (PRO) processes; (C) Typical top view and cross section of a TFNC membrane for engineering osmosis (EO) [185].

**Fig. 10.** (A) Schematic of a membrane bioreactor; (B) Illustration of membrane fouling in membrane bioreactor process; SEM images of (C) the nanofibrous membrane with a fouling layer on the surface after MBR operation and (D) the same nanofibrous

membrane surface after cleaning [197]. Copyright 2010, (C and D) have been reproduced and inserted with permission from Elsevier.

**Fig. 11.** (A) Schematic of direct contact membrane distillation (DCMD); (B) Surface morphology of a PVDF nanofibrous membrane fabricated for DCMD; (C) Schematic diagram of preparing superhydrophobic PVDF nanofibrous membranes by silver nanoparticles and 1-dodecanethiol hydrophobic modification and (D) surface morphology of a superhydrophobic PVDF nanofibrous membrane after modification [30].

**Fig. 12.** (A) Schematic of coalescence filtration; (B) Cross-sectional view of cellulose-based TFNC membrane and (C) the surface morphology of a superwetting membrane fabricated for water/oil separations [223]. Copyright 2010, (B) has been reproduced and inserted with permission from Elsevier.

**Fig. 13.** (A) Schematic of heavy metal ion adsorption; (B) The mechanism of adsorption of  $\text{Cu}^{2+}$  on PVA/ $\text{SiO}_2$  composite nanofibers; (C) (a) FESEM images of the PPy-coated PVDF nanofibers membrane after Au recovering, (b-d) EDX maps of the same area, the abundant pink, grass green and navy blue indicated the locations of Au (Ma), F and Cl elements, respectively [138, 231]. Copyright 2010, (B) has been reproduced and inserted with permission from Elsevier. Copyright 2007, (C) has been reproduced and inserted with permission from Elsevier.

**Table 1.** Advantages and disadvantages of different membrane fabrication methods

**Table 2.** Effects of different parameters on electrospun nanofibers and resultant nanofibrous membranes