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The potential of Kevlar aramid nanofiber composite membranes

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Kevlar aramid nanofibers (KANFs), a nanoscale version of poly(paraphenylene terephthalamide), are a fascinating class of one-dimensional organic nanomaterials with a combination of electrical conductivity, flexibility, mechanical robustness, physical stability and resistance to solvents. The interest in Kevlar aramid nanofibers with high mechanical strength is mainly due to the effectiveness of the interactions between nanofibers and matrices. They have been widely used as high-performance composites. In sharp contrast to other nanomaterials, due to their intrinsically ordered and asymmetric alternating nanostructure of molecular chains and abundant intermolecular hydrogen bonds, KANFs have received much attention in diverse fields including membrane separation technology. In recent years, research studies appeared ranging from synthesis strategies to separation application of KANF-based membranes. This review analyses and summarizes the synthesis and applications of KANF-based membranes in different processes, such as nanofiltration membranes, mixed matrix membranes, ion exchange membranes and proton exchange membrane fuel cells. Particular attention is paid to the tunable structure, chemical/physical stability, hydrophobicity/hydrophilicity and chemical reaction required in order to develop suitable KANF-based composite materials for membrane fabrication. In addition, approaches to fabricate KANF-based membranes, such as blending, grafting, amide reaction, network interpenetrating, interfacial polymerization and gel-confined conversion, are highlighted. Based on this, the application of KANF-based membranes in water treatment (including oil/water separation, water purification and desalination, emulsion separation, and dye wastewater separation), organic solvent treatment, ion separation, separation of battery and proton exchange membrane fuel cells is discussed. Finally, the advantages and disadvantages of KANF-based membranes are summarized; on this basis, the challenges and future opportunities in this field are defined. This tutorial review provides an overview of the promising potential applications of Kevlar aramid nanofibers in membrane science.

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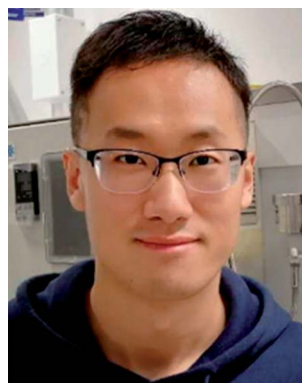
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separation.

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1. Introduction

Health, energy and the environment are crucial themes with global significance. The increasing demand for energy leads to pressing environmental problems, such as air pollution, and water pollution and scarcity, which pose a great challenge to life quality and environmental degradation.¹ The implementation of separation technology in the context of pollution control and treatment, resource recovery and extraction, proton exchange and sustainable development has played a significant role in industry and daily life.^{2–4} Although there has been extensive research in many traditional separation technologies such as evaporation, precipitation, crystallization, salting out, solvent extraction and ion-exchange, the accompanying high economic costs, environmental pressures and low separation efficiency of

these processes limit the development of methodologies and techniques.^{5–7} Membranes for use in separation processes have been rapidly developed in recent years due to their specific separation performance, eco-friendly potential due to a lack of secondary pollutant production and high energy efficiency.^{8–11}

Membranes with finely porous and nonporous structures have been fabricated from organic and inorganic materials.^{12,13} The organic membranes are the most popular separation materials due to their chemical stability, controllable hydrophobicity or hydrophilicity, chemical reaction, and excellent mechanical strength, achieved using various charged groups.¹⁴ With different driving forces, these organic membranes can be classified into pressure-driven membranes (microfiltration, ultrafiltration, nanofiltration and reverse osmosis), electro-driven membranes (electrodialysis and fuel cells), concentration-driven membranes (dialysis, pervaporation and forward) and temperature-driven membranes (distillation).¹⁵ Traditional polymer membrane materials may be chemically degraded or incur other damage in challenging environments, such as high temperatures and exposure to organic solvent treatments. Therefore, polymers with ordered structures and controllable chemical activity are important for the synthesis of advanced separation membranes.

Kevlar aramid nanofibers (KANFs), are a class of one-dimensional organic nanomaterials, comprising the nanoscale version of poly(paraphenylene terephthalamide) (PPTA), which is one of the strongest polymeric materials, better known by its trade name Kevlar.¹⁶ In comparison with conventional polymers, PPTA has a highly ordered, asymmetric chemical structure of alternating benzene rings and aramid bonds of long molecular chain PPTA polymers; the connections between PPTA polymers are strengthened by hydrogen bonding, π - π stacking bonds and van der Waals forces.¹⁷ Therefore, KANFs have superior mechanical properties, an excellent resistance to most



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electrodialysis, distillation, extraction, adsorption, separation techniques, technical aspects of the production of process water and drinking water.



Congjie Gao is an Academician of the Chinese Academy of Engineering and Dean of the School of Oceanic Science and Engineering at the Zhejiang University of Technology. He is a pioneer in membrane technology development for seawater desalination, wastewater treatment, and water reuse in China. Over the past 40 years, Congjie Gao has been working on all aspects of

membrane separations involving reverse osmosis, ultrafiltration, nanofiltration, electrodialysis and pervaporation. He was a Visiting Professor in the department of Chemical Engineering, University of Waterloo (early 1980s). His accomplishments are recognized by the top prize of the National Science & Technology Progress Award of China (1992), the Science and Technology Progress Prize (1998) from the Hong Kong-based non-governmental Ho Leung Ho Lee Foundation, and many others.



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intensification; physical-chemical treatment of process water and wastewater.

commonly used solvents, a good chemical resistance and thermal stability. In the light of these advantages, KANFs have been widely used as advanced composite materials for aircrafts, automotive manufacturing, radiation shielding, ballistic protection, protective clothing and water purification.^{18,19} Typically, Kevlar fabrics can be dissolved into aramid nanofiber solutions by breaking the strong inter-chain interactions, deprotonation of amide groups or amide hydrolysis into small nanofibers, which enable further incorporation of other components. Due to these characteristics, KANFs are promising candidates for synthesizing advanced membranes. Their properties and structure give the KANFs their high membrane performance, even in harsh environments.²⁰ Moreover, their tunable structure, dispersibility, physical and chemical stability, controllable hydrophobicity and hydrophilicity and chemical reactivity allow for specific tuning of the KANFs through structural design or the introduction of various functional materials for different kinds of membranes and applications in different processes. These intrinsic properties of KANFs have motivated scientists to further explore the synthesis of KANF-based membranes suitable for separation in additional fields, making KANF-based membranes a current hot topic in organic membrane separation technology and energy areas.

In the past five years, the research on KANF-based membranes ranged from water treatment to organic solvent separation and has influenced the fields of environmental science, energy technology and biological science. However, no comprehensive review has so far covered this topic. In this review, research on KANF-based membranes in separation processes and energy application is evaluated, highlighting

important lessons that may apply to future work on design and preparation of KANFs in pressure-driven membranes, electro-driven membranes, concentration-driven membranes and temperature-driven membranes. First, the development of Kevlar fabric dissolving methods and the tunable structure of KANFs including physical dispersion, blending, hybridization, network interpenetration, and metal-organic framework (MOF) and covalent organic framework (COF) controlling is discussed. The key properties of KANFs including chemical reaction, stability, hydrophobicity/hydrophilicity conductivity and selectivity of KANFs are then summarized. Next, rational design strategies of KANF-based membranes are addressed, including the blending method, chemical reaction, network interpenetration and interfacial polymerization. Then, the applications of KANF-based membranes in water treatment (including oil/water separation, water purification and desalination, emulsion separation and dye wastewater separation), organic solvent treatment, ion separation, antibacterial applications, separation of battery and proton exchange membrane fuel cells are discussed. Finally, the physicochemical properties that arise from the controlled formulation of structures or properties of KANFs are highlighted, as well as their influence on the use of KANF-based membranes for further development in this area.

2. Processing

Different kinds of KANF-based membranes are distinguished by the structure and properties of KANFs. Due to their one-dimensional nanofiber structure with large specific surface area and intermolecular bonding interactions, KANF-based

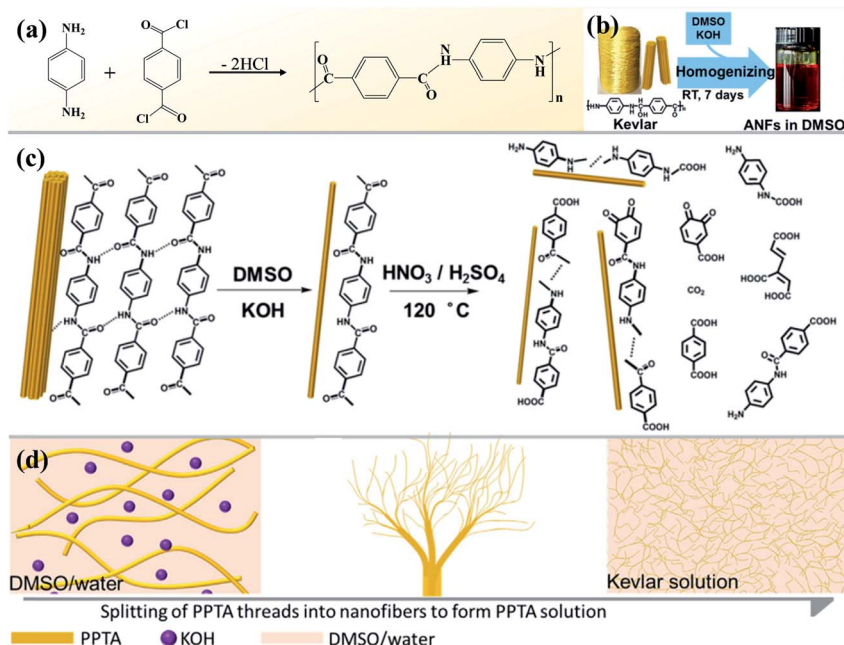


Fig. 1 Reaction scheme showing synthesis of PPTA from *p*-phenylene and diaminerephthaloyl chloride (a); homogenizing Kevlar fibers in DMSO saturated with KOH (b) and the synthesis mechanism of KANFs (c), reprinted with permission from ref. 17. Copyright 2017 American Chemical Society; schematic illustration of Kevlar threads in DMSO-KOH/water (volume 40 : 1); then splitting of Kevlar threads into nanofibers by breaking the hydrogen bonds via KOH and DMSO/water and the formation of Kevlar dope solution containing KANFs (d), ref. 21. Copyright 2019 Elsevier.

membranes have expanded into fields which necessitate efficient and precise separations. From a rational design point of view, breaking these strong intermolecular and aramid bonds is a fundamental obstacle. In order to obtain the basic features of KANFs in KANF-based membranes, the key point is to tune the structure to recombine these interactions and aramid bonds.²¹ Thus, the main focus of the study of these membranes is on additive substances, which give varying functional properties to different separation membranes. In several separation applications, conductivity, hydrophobicity/hydrophilicity and other properties are also important. Following the view of practical application, ideal KANF-based membranes with highly efficient separation ability and long-term operation capacity have been proposed.

2.1 Dissolving and properties of KANFs

It has been proven that raw Kevlar fabrics can be directly dissolved in fuming sulfuric acid (>98%) to prepare composite materials.²² However, the low efficiency, scalability and uncontrollable method limited the KANFs into specific structures and functions. KANFs can be formed using PPTA molecules with strong interchain interactions. In an overview article by Jassal & Ghosh,²³ PPTA molecules were synthesized using benzene-1,4-dicarbonyl dichloride and benzene-1,4-diamine *via* low-temperature anhydrous polycondensation (see Fig. 1a).^{16,24}

A facile, controllable and direct liquid exfoliation of KANFs was developed by Kotov *et al.*²⁵ Commercial Kevlar fabrics were dissolved in dimethyl sulfoxide (DMSO) saturated with KOH under constant magnetic stirring for 1–15 days at room temperature. In this method, the concentration of KANFs was adjusted from 0.1 to 2.0 wt%; the solutions change to a dark red color and turn into sticky homogeneous solutions. In order to speed up the above processes, some studies report the dissolution of commercial Kevlar fabrics in DMSO saturated with KOH and water, with a volume ratio 40 : 1 (DMSO/water), resulting in a viscous KANF homogeneous solution (see Fig. 1d). Some reports used NaOH instead of KOH and obtained a viscous KANF solution. All these methods mainly split the strong bonding interactions between molecular chains, which are hydrogen bonding, π - π stacking bonds and van der Waals forces. In order to obtain a full splitting of the fibers from the KANFs, a constant stirring is needed for several months at room temperature.

With the above methods, the obtained viscous KANFs are exfoliated in liquid solution into nanofibers with diameters of 20–30 nm. The obtained nanofibers have a highly ordered, asymmetric, alternate structure of benzene rings and aramid groups, which is poly(*p*-phenylene terephthalamide) (PPTA) (Fig. 1b).

A further study was conducted in Van der Bruggen's group,²⁶ in which the temperature was maintained at 70–90 °C for dissolving Kevlar fabric based on Kotov's method. In this process, not only the strong bonding interactions between molecular chains are quickly split, but also some amide chemical bonds are broken and the final KANF solutions that are obtained have short PPTA polymer chains. These short PPTA polymer chains

will provide more $-\text{NH}_2$ groups and $-\text{COOH}$ groups, which may be used to react with other functional groups (Fig. 1c). In addition, the concentration of KANFs can be adjusted to values as high as 6.0 wt%. Therefore, the dissolving methods of KANFs for membrane preparation and application are shown in Table 1.

2.2 Tunable structure

The membrane structure, which can be dense or porous, often affects the membrane separation efficiency.⁴² Single PPTA polymer chains easily form a dense structure after phase inversion and drying, due to the easy regeneration of the hydrogen bonding. The structure of KANFs, especially the pore size, is primarily derived from the geometry and connectivity of the interactions. With the strong interactions in the one-dimensional nanofibers of KANF-based membranes, the low flux limits the application of separation areas. Hence, adjusting the structure while maintaining the basic properties of KANFs is the key to designing KANF-based membranes with highly efficient separation performance. Several strategies have been reported to achieve a tunable structure in KANF-based membranes:

2.2.1 Physical dispersion. The typical physical methods are electrospinning, layer-by-layer (LBL) assembly, interfacial polymerization and wet-spinning. Electrospinning is an efficient and advanced technology to construct nanofibers with pore structures of certain diameters, which has been widely applied for the synthesis of polymeric nanofibers (see Fig. 2a).^{20,43} It provides an ideal strategy for design and fabrication of nanofibers.⁴⁴ However, this method is not suitable for changing the structure of KANFs. LBL assembly is a potential method for the preparation of KANF-based membranes (*e.g.*, KANF network LBL assembly with poly(ethylene oxide)) (see Fig. 2b).^{28,40} In particular, these KANFs avoid the 'weak links' when the porosity of the KANF-based membranes is smaller than the growth area of the dendrites, which may yield ultrastrong membranes. However, the requirements for materials in LbL assembly are very rigorous, as it requires a combination of hydrophilic and hydrophobic blocks. Interfacial polymerization is a convenient method for preparation of solid porous materials but cannot change the structure of KANFs (see Fig. 2c). The wet-spinning approach is a facile method for fabricating KANF aerogels (see Fig. 2d).⁴¹ This advantageous technology leads to a high specific surface area and thermal stability of final KANF aerogels in a wide temperature range.

2.2.2 Blending. Blending is a common design strategy for changing the structure of KANFs and has been intensively investigated. The conventional additive of this method involves nanoparticles, nanosheets, nanowires, and organic monomers and polymers.⁴⁵ Inorganic nanoparticles are used as a universal modification additive; examples are ZnO and TiO₂. They are used to obtain KANFs with enlarged specific surface and the superoleophobicity or superhydrophilicity.⁴⁶ Graphene oxide (GO), a typical 2-dimension nanosheet structure material, is introduced into the structure of KANFs through π - π stacking interactions, leading to an enhanced hydrophilicity and

Table 1 Dissolving methods of KANFs for membrane preparation and application

Year	Dissolving methods	Temperature	Structure control methods	Applications	Ref.
1980	Dissolving in sulfuric acid or sulfuric acid containing varying amounts of sulfurtrioxide	Below 60 °C	—	Solvent resistant ultrafiltration membrane	22
2011	1 g Kevlar + 1.5 g KOH + 500 mL DMSO	Room temperature	Layer-by-layer assembly	—	27
2017	Immersing in 30 H ₃ PO ₄	40 °C	Self-assembly process	Provide a green dissolving method	28
2017	Kevlar + NaOH + DMSO	Room temperature	Blending	Nanofiltration membranes	17
2018	3.0 g Kevlar + 1.5 g KOH + 500 mL DMSO	25 °C	Blending and network interpenetrating process	Oil/water separation	29
2018	0.1 g Kevlar + 2.5 mmol NaOH + 20 mL DMSO	Room temperature	Blending	Emulsion separation treatment	30
2018	1 g Kevlar + 2.0 g KOH + 500 mL DMSO	Room temperature	Blending	—	31
2018	1 g Kevlar + 1.5 g KOH + 500 mL DMSO	Room temperature	Vacuum-assisted suction method	Water treatment membranes	32
2019	0.2 wt% Kevlar + 5 wt% phosphotungstic acid DMF solution in a ratio of 1 : 4	Room temperature ultrasonic treatment	Blending	proton exchange membrane	33
2019	1 g Kevlar + 1 g KOH + 100 mL DMSO	Room temperature	Blending	Nanofluidic osmotic power generators	34
2019	(1.0 to 3.0%) Kevlar + 6.0 g (3.0%) KOH + 200 mL DMSO	Room temperature	Blending	Organic solvent nanofiltration	35
2019	2.0 g Kevlar + 2.0 g KOH + DMSO/water (volume ration, 40 : 1)	Room temperature	—	Organic solvent nanofiltration	21
2019	1.0 g Kevlar + 1.5 g KOH + 500 mL DMSO	25 °C	Blending	Electrical-conductivity membranes	36
2019	2.0% Kevlar + 3.0% KOH + 95% DMSO	Room temperature	Network interpenetrating and amide condensation reaction	Cation exchange membrane	37
2019	3% Kevlar + 4.5% KOH + 92.5% DMSO	70 °C	Amide condensation reaction	Cation exchange membrane	26
2019	4.0 g Kevlar + 6.0 g KOH + 200 mL DMSO	Room temperature	Interfacial polymerization	Water desalination	38
2019	4.0 g Kevlar + 6.0 g KOH + 200 mL DMSO	Room temperature	Interfacial polymerization	Organic solvent nanofiltration	39
2019	1.0 g Kevlar + 1.5 g KOH + 500 mL DMSO	Room temperature	Layer-by-layer assembly	Electrodes	40
2019	5.0 g Kevlar + 2.5 g KOH + 500 mL DMSO	Room temperature	Network interpenetrating	Proton exchange membrane fuel cells	18
2019	(0.5, 1.0, 1.5, and 2.0 wt%) Kevlar + KOH + DMSO	Room temperature	Freeze-drying process	Highly efficient infrared stealth	19
2019	(0.1 to 2.0 wt%) Kevlar + KOH + DMSO	Room temperature	Wet-spinning process	Thermal insulation	41

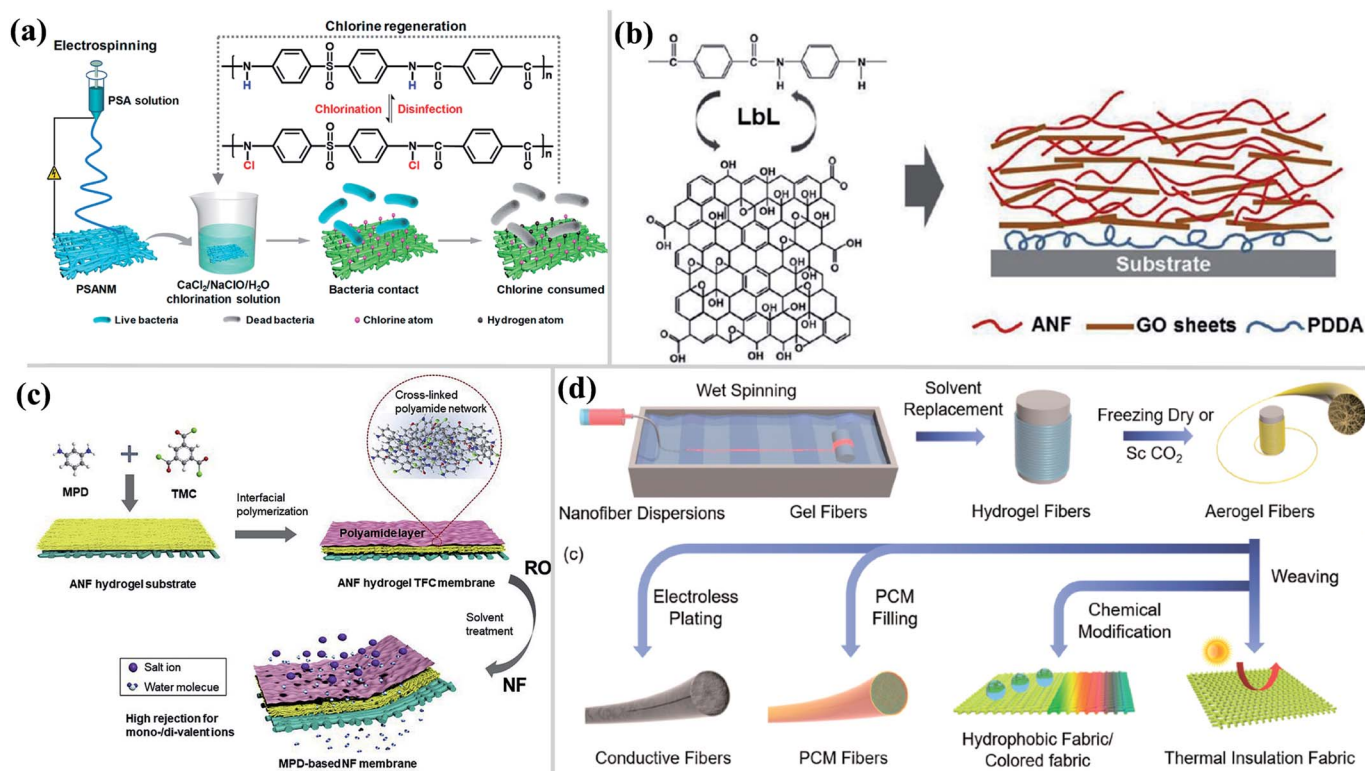


Fig. 2 Schematic illustration of the design and fabrication of the KANF-based membrane by electrospinning, and the bactericidal procedure (a), reprinted with permission from ref. 42. Copyright 2019 American Chemical Society; layer-by-layer assembly of KANFs and GO sheets (b), ref. 39. Copyright 2017 American Chemical Society; Fabrication of the composite polyamide/KANF membrane (c), ref. 37. Copyright 2019 Elsevier; fabrication of the KANF aerogel and its various application images (d), ref. 40. Copyright 2019 American Chemical Society.

mechanical strength of KANFs.^{31,47,48} Nanowires include inorganic nanowires (*e.g.*, hydroxyapatite nanowires) and organic nanowires (*e.g.*, cellulose triacetate) and can be used to twist or interweave with KANFs that reinforced the mechanical properties and constituted a special skeleton.^{17,27} Organic monomers or polymers can interact with KANFs through non-covalent interactions to enlarge the size between PPTA and enhance the flux (Fig. 3).⁴⁹

2.2.3 Hybridization. The hybridization technology is an efficient method to develop excellent properties of materials.⁵⁰ The organic-inorganic hybridization is an efficient way to synthesize high composite materials, such as oligomeric silsesquioxane (POSS) incorporated into the structure of KANFs.³² Biomimetic hybridization is a method that controls the structure of KANFs in combination with the outstanding biocompatibility, biodegradability and sustainability of natural biomaterials, such as silk fibroin, hemp and mussels-dopamine. Hybridization with other artificial synthetic materials to change the KANF structures is also studied. For example, the tribological properties of hybrid polytetrafluoroethylene in KANFs are of interest.

2.2.4 Network interpenetrating. The viscous KANF solution easily forms a hydrogel material. With the evaporation of water, hydrogen bonds are induced and generated, and a 3-dimensional interconnected hydrogel structure network of KANFs is formed, with high porosity and specific surface area. Through

controlling interfacial polymerization of small monomers (*e.g.*, amphiprotic millimeter scale collagen) or incorporating phase-change materials (*e.g.*, polyethylene glycol), they are fabricated on the nanofibrous hydrogel support materials and control the structure. This method is only used to control the structure between the KANFs; it is difficult to change the structure of the KANFs in this way.

2.2.5 MOF and COF controlling. Metal-organic frameworks (MOFs) (see Fig. 4a) and covalent organic frameworks (COFs) (see Fig. 4b) are a new class of crystalline porous materials, which are especially interesting due to their tunable pore size and structure.⁵¹⁻⁵⁴ The formation of a stable dispersion of MOFs or COFs between the KANFs is promising in controlling the structure, in view of a tunable pore size and other essential features. For example, zeolite imidazolate framework-8 (ZIF-8) can be uniformly distributed on KANFs to yield outstanding characteristics, such as superhydrophobicity (Fig. 4c).³⁰

2.3 Key properties of KANFs

2.3.1 Chemical reaction. Kevlar fabrics can be dissolved and form a PPTA nanochain solution, which offers a possibility to react with other functional components. Because the long PPTA polymer chains are split into small nanofibers *via* an amide hydrolysis reaction, the amount of $-\text{NH}_2$ and $-\text{COOH}$ groups can be used to react with various monomers or polymers *via* the amide condensation reaction or substitution reactions.³⁷

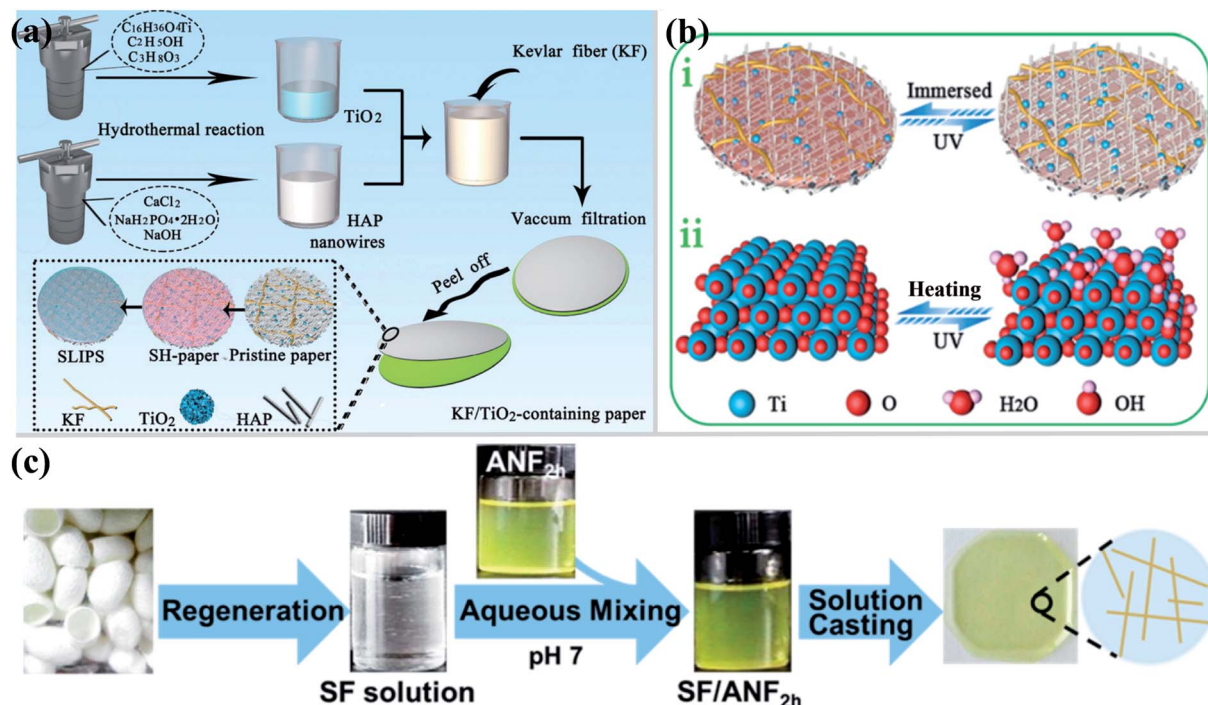


Fig. 3 Schematic of the preparation procedure of KANF@TiO₂@HAP paper via the hydrothermal process and vacuum-assisted suction filtration (blending) (a); the KANF@TiO₂ membrane and the wettability conversion mechanism: (i) photocatalysis of TiO₂ degrades the STA on the surface; (ii) UV irradiation results in the formation of vacancies and the adsorption of the hydroxyl group and water molecule (b), reprinted with permission from ref. 40. Copyright 2019 Royal Society of Chemistry; the three-step procedure followed to prepare SF/ANF_{2h} films, *i.e.*, SF regeneration, aqueously mixing SF with ANF_{2h}, and solution casting (c), ref. 17. Copyright 2017 American Chemical Society.

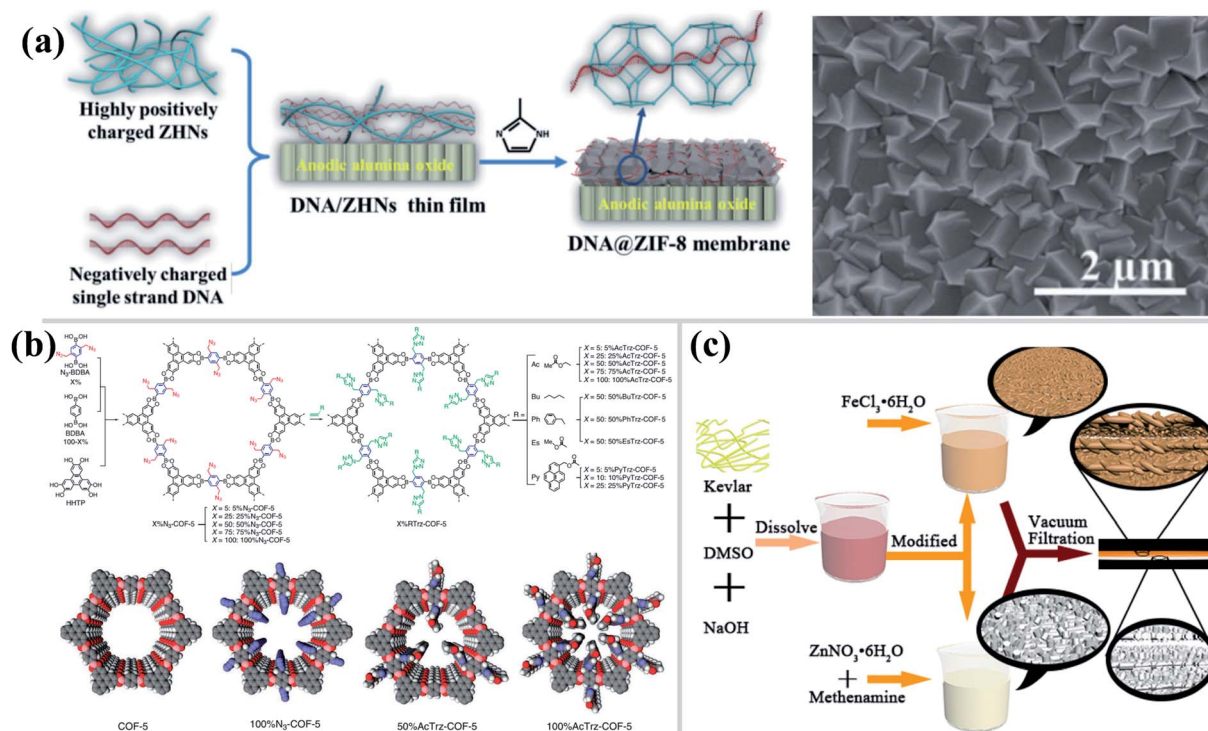


Fig. 4 Illustration of the synthesis process of the MOF-based membrane and the surface SEM image (a), reprinted with permission from ref. 52. Copyright 2019 John Wiley & Sons; synthetic functional groups to adjust the pore size of COFs (b), ref. 53. Copyright 2017 Spring Nature; fabrication of the MOF modified KANF-based membrane for separation of oil/water emulsions (c), ref. 29. Copyright 2019 Elsevier.

Because the small PPTA chains can be easily recombined *via* immersion into water and the formation of new hydrogen bonds, the final KANFs can have an excellent performance. This chemical reaction makes the KANFs applicable in many separation fields. By hydrogen bonding self-assembly, the KANFs also can self-immobilize with inorganic materials such as phosphotungstic acid, FeOOH, ZnO and synthesized composite materials.^{33,44}

2.3.2 Stability. Generally, the physical and chemical stabilities of KANFs are needed to analyze by combining with their chemical structures. Kevlar fabrics with sufficient amide bonds in PPTA polymer chains and hydrogen bonds between the KANFs have an outstanding physical stability (*e.g.*, mechanical properties and thermostability) and chemical stability (*e.g.*, resistance to organic solvents).^{55,56} Furthermore, stable and uniform dispersions of KANFs can also be prepared by mixing with physically or chemically stable polymers, such as methoxypolyethylene glycol (mPEG).⁴⁶

2.3.3 Hydrophilicity or hydrophobicity. The hydrophilicity or hydrophobicity of KANFs is mainly determined by the presence of amide chemical bonds. Therefore, the hydrophilicity or hydrophobicity of the final nanofibers is decided by mixing or chemical reaction with other compounds.⁵⁵ The hydrophilicity of KANF-based membranes can be obtained by the benefits of the introduced compounds, such as adding hydrophilic chitin nanofibrils and chemical reacting with 4-aminobenzenesulfonic acid monomers. On the other hand, the hydrophobicity is needed for organic solvent treatment and for pervaporation. For example, the KANFs are mixed in a matrix of polyvinylidene fluoride (PVDF) or poly(dimethylsiloxane) (PDMS) to prepare a superhydrophobic membrane for oil/water separation and oil absorption.⁵⁷

2.3.4 Conductivity. Compared to metallic or carbon nanofibers, KANFs have a much lower electrical conductivity. The zeta potential of KANFs in water is typically low and negative. Therefore, it is possible to control the electrical conductivity of KANFs by combining with other conducting polymers, nanocrystals and monomers. In this way, it is possible to obtain an excellent electrical conductivity in combination with robustness, flexibility, stability and endurance to temperature and organic solvents, which is in sharp contrast with other inorganic conductive nanomaterials. Furthermore, the KANFs can be designed with negative charge, such as reaction with 2,5-diaminobenzenesulfonic acid, cadmium telluride (CdTe) nanocrystals and phosphoric acid (PA) spin grafted on the KANFs.^{18,26} These methods have paved the way for obtaining a good electrical conductivity with excellent mechanical properties.

2.3.5 Selectivity. Selectivity between small molecules, or between monovalent and multivalent anions or cations, is crucial for resource recycling and for zero emission targets in industry. This has driven most scientists to develop various suitable materials and applications. Naturally, the size sieving effect between the target molecules/ions and the membrane structure is the most efficient way to obtain selective separation. Due to the KANFs with a strong interaction and dense structure, it is easy to control the structure (as explained above) in order to

selectively separate molecules or ions. In addition, the electrostatic repulsion effect between the molecules/ions and the charged membrane surface also contributes to the separation.

3. Design strategies of KANF-based membranes

3.1 Key principles

The rational design strategy of the KANF-based membrane for separation has been successful in recent years, due to the combination of the continuing improved KANF dissolution methods and synthesis routes. It is a key principle to design KANF-based membranes that use the features of KANFs for precise and rapid membrane separation.

3.2 Blending

The blending method is a common and simple approach to fabricate KANF-based membranes. Compared to the pure KANF membrane, these design strategies not only adjust the structure of KANFs to obtain a high flux or selectivity, but also endow it with new active functions. In this method, two key principles for blending need to be considered.

Firstly, a good dispersibility of the blending materials and an excellent compatibility in KANF solutions are needed. The current KANF membranes with strong interaction (resulting in a dense structure) generally suffer from a high mass transfer resistance and a low pore density, which provides interstitial spaces or channels for accelerated mass transport. Several nanomaterials, such as SiO₂ nanoparticles, graphene nanosheets and molybdenum disulfide nanosheets with a specific size and structure, have been explored for the construction of nanofluidic channels. With facile dispersibility and compatibility, these inorganic nanomaterials endow the KANFs with a great superiority for advanced separations. Zhang *et al.* used the HF etching method to prepare 2-dimensional Ti₃AlC₂ nanosheets and Mxene, and then blended these in the KANF solutions to fabricate the Mxene/nanofiber composite membranes (see Fig. 5a).³⁴ Driven by the ionic concentration gradient, these KANF-based composite membranes, with large specific surfaces, have a high-performance nanofluidic osmotic power, charge-governed ion transport and outstanding cation selectivity properties. From the interior structure, it can be seen that most of them are connected through π - π stacking interactions or van der Waals forces.

Thus, the long-term stability of the resulting KANFs should be the second key factor. Li *et al.* chose polyethyleneimine (PEI) as the blending material and *in situ* KANF solutions to form PEI microspheres, so that the structure of KANFs could be controlled (see Fig. 5b).³⁵ With the incorporation of PEI microspheres, the resulting KANF-based membranes not only have a high permeation and a sufficient solute rejection, but can be also operated for a long time. Li *et al.* concluded that oligomers or organic blends of monomers mix sufficiently with KANFs mainly *via* a reactive blending technology of *in situ* polymerization.⁵⁸ Compared to the conventional solution blending methods, the novel *in situ* polymerization methods solve the

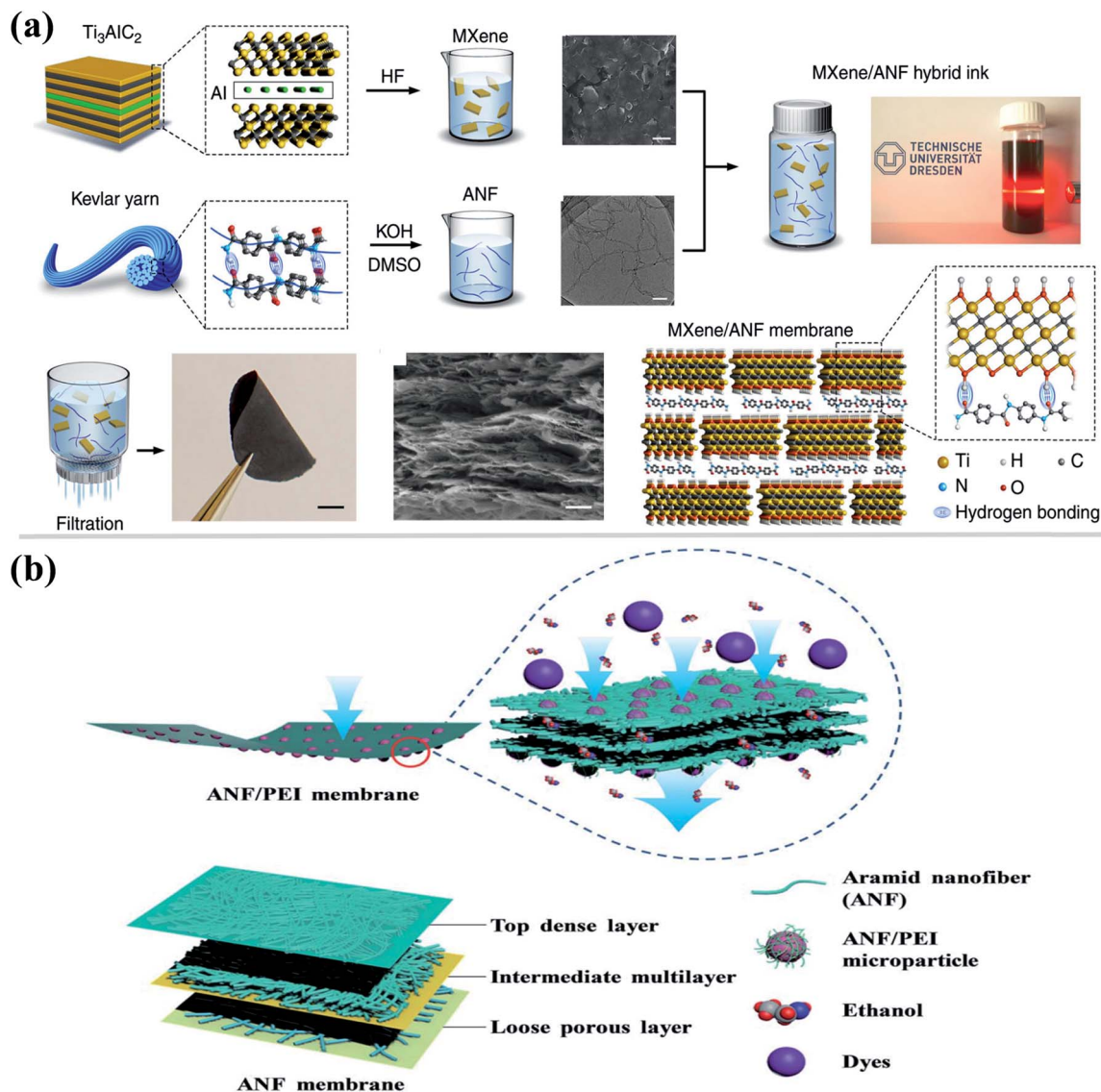


Fig. 5 Fabrication of a MXene/nanofiber composite membrane (a), reprinted with permission from ref. 33. Copyright 2019 Spring Nature; fabrication of the KANF/PEI composite membrane (b), ref. 34. Copyright 2019 Royal Society of Chemistry.

mixing issues, and the resulting KANF-based membranes have an outstanding performance with a high structural stability. The high performance was ascribed to the compatibility between the KANFs and blending materials, and the *in situ* polycondensation in the blending method was demonstrated to be a promising method to obtain compatible KANF-based separation membranes.

3.3 Chemical reaction

A chemical reaction is a common methodology for membrane fabrication, which has been used to design homogeneous membranes with special functions. Currently, three important chemical reaction methods, amide hydrolysis, amide condensation and substitution reaction, were designed and developed to synthesize functional KANFs for homogeneous composite membranes. Due to the synergetic combination of the amide

hydrolysis reaction and the Kevlar fabric dissolving process, KANFs can be split into small PPTA chains by controlling the temperature in the dissolving process, and the carboxyl groups ($-\text{COOH}$) and amino groups ($-\text{NH}_2$) on the side of different nanoscale PPTA polymer chains can provide reactive sites for other materials.

Zhao *et al.*³⁷ successfully fabricated a KANF-based cation exchange membrane by using 4-aminobenzenesulfonic acid (ABS) as the negatively charged functional monomer *via* an amide condensation reaction (see Fig. 6a). The synthesized membranes not only inherited excellent performances of KANFs, but also achieved advanced electrochemical properties (excellent ion exchange capacity, low membrane surface electrical resistance and high membrane limiting current density), having potential for application in electrodialysis. In this process, the amide condensation reaction is often at the

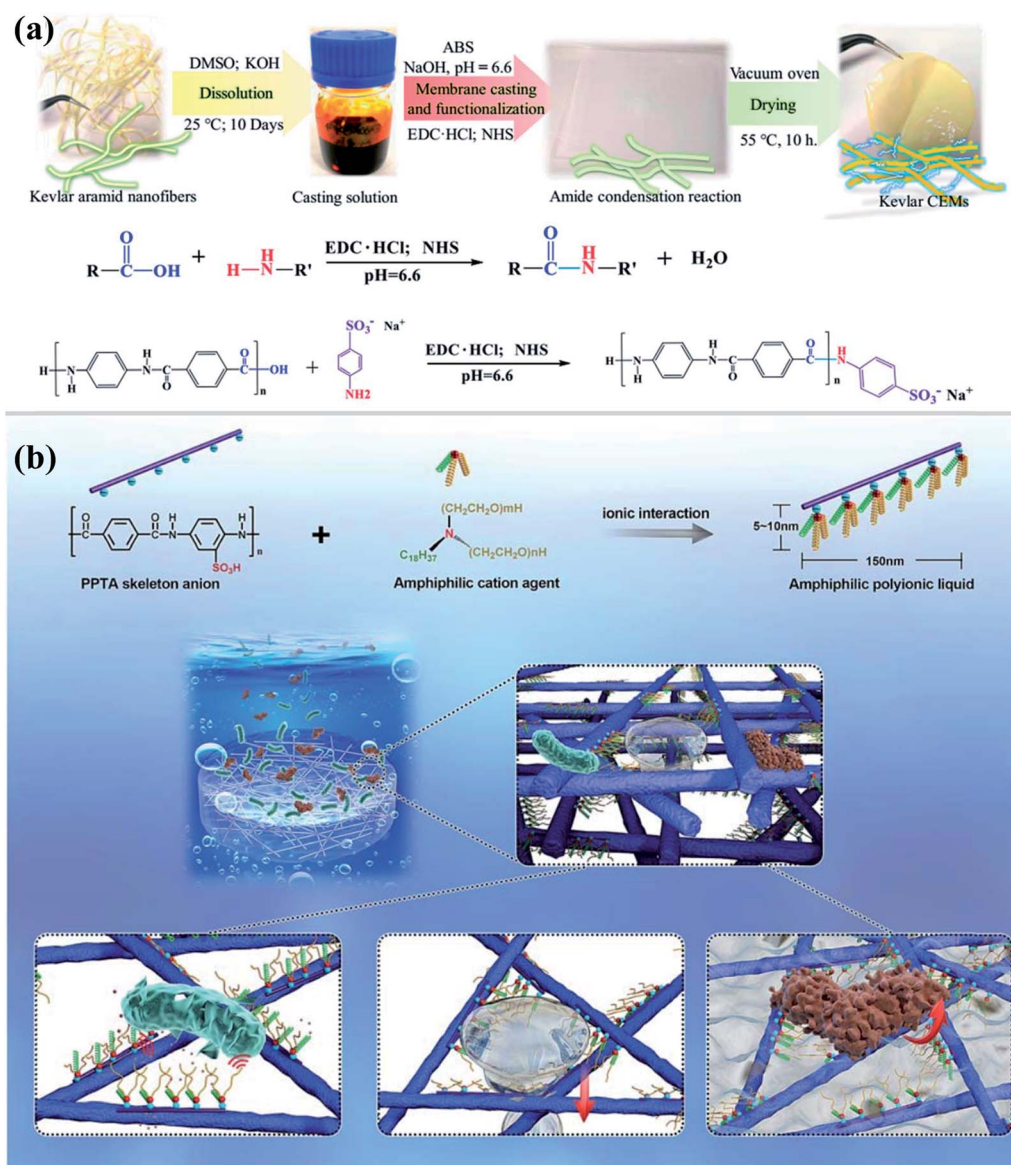


Fig. 6 The process of preparation of KANF-based cation exchange membranes and the process of the amide condensation (a); chemical structure of f-PPTA and illustration of the nanofiber structure and the modified membrane filtration performance and antibacterial activity (b). Reprinted with permission from ref. 36 and ref. 58 Copyright 2019 Royal Society of Chemistry, respectively.

expense of many $-\text{NH}_2$ groups or $-\text{COOH}$ groups in the KANFs to obtain the target performances.

With the alternate structure of benzene rings and aramid groups in PPTA, it is possible to graft functional groups on these benzene rings and aramid groups *via* substitution reaction. Wang *et al.*²⁴ chose the 2,5-diaminobenzenesulfonic acid and terephthaloyl chloride to obtain a series of flexible poly(*p*-phenyleneterephthalamide) (f-PPTA) materials through substitution reactions on benzene rings and a “grafting to” strategy. The established property–structure of state-of-the-art materials was further applied by Chen *et al.*⁵⁹ who prepared a self-supporting hydrophilic KANF-based membrane (see Fig. 6b). With these negatively/positively charged or hydrophilic groups, the resulting PPTA chains had a large effect on the diameter and pore size

of the KANF-based membrane. In addition, it can be used to enhance the antifouling or antibacterial properties of the resulting membranes.

3.4 Network interpenetrating

The KANF casting solution forms a gel material by generating hydrogen bonds, π – π stacking bonds and van der Waals forces through phase inversion in water. The gel KANF-based material, such as a gel KANF-based membrane with high porosity, low density and large specific surface area, is a promising network structure for further generation of multi-performance KANF-based membranes. The formation of an interpenetrating network is the most common and efficient method to endow a network structure with target functions. Usually, small

crystals, molecules or polymers are added into the KANF-based network gel to fabricate a composite membrane for energy storage or separation processes.

Xu *et al.*⁶⁰ fabricated an electrolyte in an all-solid-state cell (Li₂S–LiI solid solution was the cathode and lithium metal was the anode) by using Li₃PS₄ glass solid electrolyte and interpenetrating into the KANF-based network structure, as shown in Fig. 7a. In this process (see Fig. 7b), the predation of thin electrolyte layers played a critical role in enabling all-solid-state batteries, which determined the cell-level energy densities. In a thin KANF-based network, the Li₃PS₄ suspension in toluene was dropped into the network and dried. With the excellent thermodynamically stability and mechanical strength ability of KANFs, Li₃PS₄ with high ionic conductivity was added into the KANF-based network structure and resulted in an excellent interfacial stability of the electrolyte in the Li–Li₂S cell (with the stable voltage profiles at 0.2 mA cm⁻²).

In order to solve the drawbacks of applications of perfluoro sulfonic acid membranes as proton exchange membranes, such as their poor thermostability and organic solvent resistance, Liu *et al.*¹⁸ used cadmium telluride (CdTe) nanocrystals and phosphoric acid (PA) molecules interpenetrated into a KANF-based network membrane *via* spin coating to prepare (Kevlar–CdTe–PA)₄ membranes (see Fig. 7c). The networking interpenetrating structure of the resulting membranes showed a high structural

stability and a high hindrance to permeation of fuels in the organic solvent. Due to the interpenetrated CdTe nanocrystals and PA molecules, the (Kevlar–CdTe–PA)₄ membranes also have a low resistance to proton conduction.

The network interpenetrating method is an easy to control technology. The resulting networks usually have complementary advantages of the KANFs and interpenetrated materials. The most important factor is the interpenetrated materials, which should connect well with the KANF-based network and even form interaction bonds.

3.5 Interfacial polymerization bonding

Interfacial polymerization is a classical method to generate a thin active film layer (*e.g.*, thin film composite (TFC) polyamide membranes) with high porosity and uniform small pore size on a porous support construction in view of a precise permeability. Especially the interfacial polymerization reaction between two monomers, such as trimesoylchloride (TMC), *m*-phenylenediamine (MPD) and piperazine (PIP), has been widely used to synthesize nanofiltration and reverse osmosis membranes. Due to the tunability of the dense KANF structure and the excellent physical/chemical properties, KANFs can be interfacially polymerized as an ideal porous material embedded in the active layer for separation. Although the incorporation of the KANFs should be complemented by adding the blend

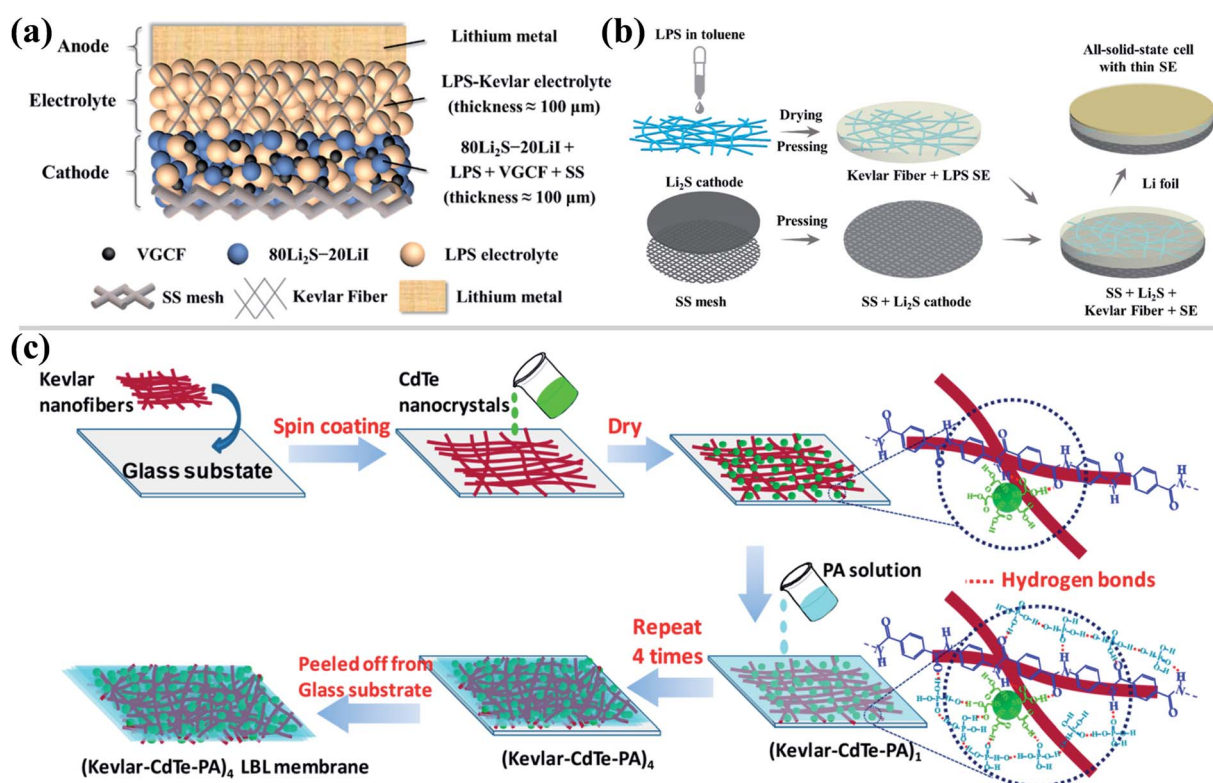


Fig. 7 Schematic representation of the cathode-supported all-solid-state Li–Li₂S cell (a) and its fabrication of proves (b), which reprinted with permission from ref. 59, Copyright 2019 American Chemical Society; the (Kevlar–CdTe–PA)₄ membrane preparation process (c). Reprinted with permission from ref. 18 Copyright 2019 American Chemical Society.

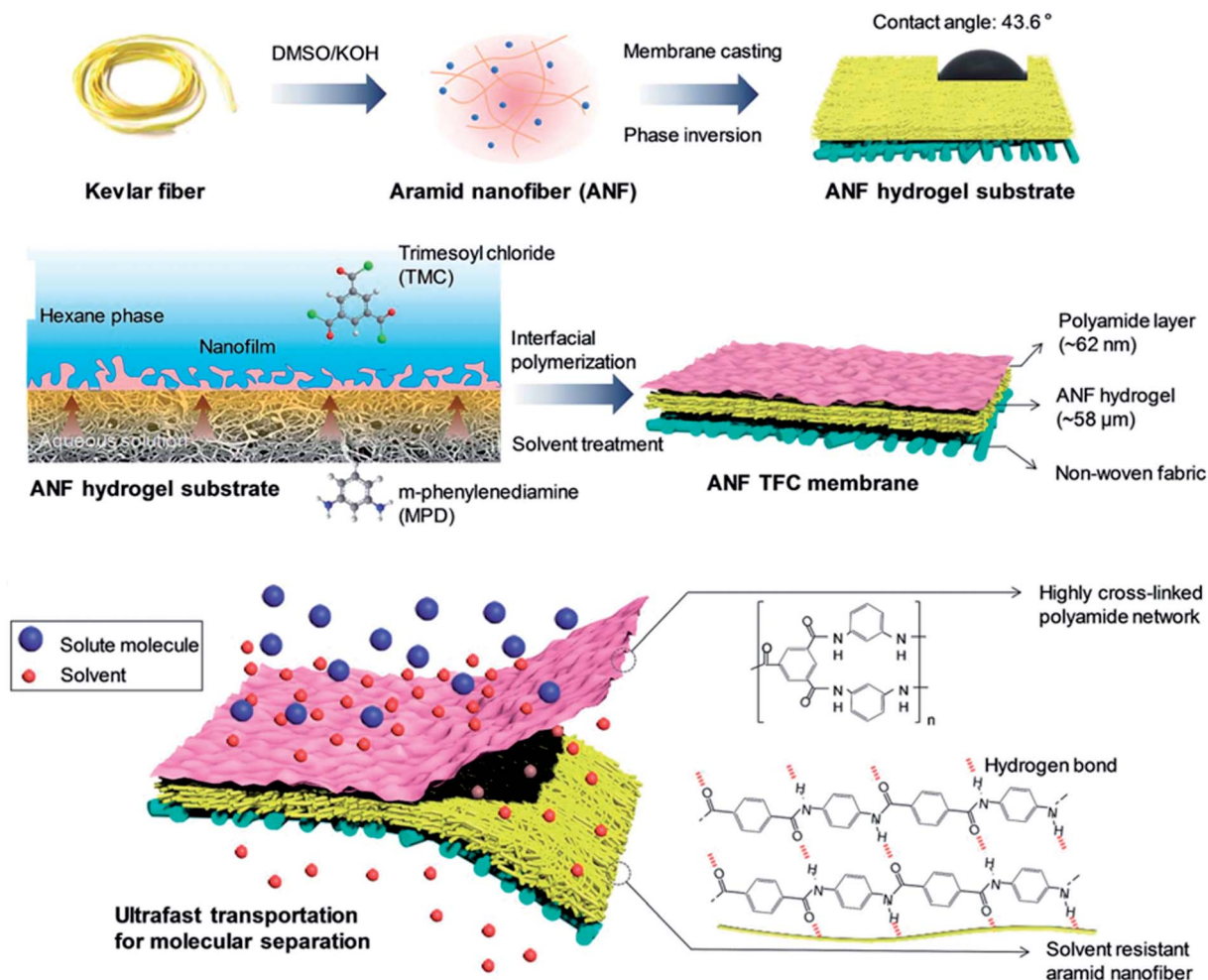


Fig. 8 Fabrication of a KANF TFC membrane via interfacial polymerization for molecular separation in organic solvents. Reprinted with permission from ref. 38 Copyright 2019 Royal Society of Chemistry.

materials, it cannot be classified as a classical blending method, due to the interfacial reaction between the aqueous phase and the organic phase. Similarly, a KANF-based network with a network porous structure can be used as a porous support, bonding a thin active film layer on its surface via interfacial polymerization. This process also cannot be classified as a network interpenetrating method, because of the interfacial polymerization reaction on its surface.

Shi *et al.*⁶¹ fabricated a new TFC layer on the surface of PPTA and polysulfone blended substrates. Due to the similar chemical structures, the PPTA produces *in situ* a polysulfone substrate and serves as an anchor to enhance between the TFC layer (fabricated by interfacial polymerization) and substrate, due to the amide–amide interactions. However, this work had to synthesize the PPTA polymers from the monomers. Li *et al.*³⁹ fabricated a TFC polyamide layer via interfacial polymerization on the surface of the prepared KANF-based membrane (shown in Fig. 8). The KANF solution was cast on the support fabric and yielded a KANF-based hydrogen network membrane via non-solvent phase inversion in water. MPD and TMC were chosen to form a polyamide layer through interfacial polymerization in

a short reaction time (about 20 s) at room temperature. The resulting membrane was then dried. This easy and fast preparation method combined with the advantages of KANFs promoted the KANF-based membrane application in molecular separation, solvent recovery, water treatment and water desalination.

3.6 Other design strategies

KANF-based membranes are intended for specific design strategies, with a targeted structure, in order to obtain enhanced properties that allow their use in new environments. Blending, chemical reaction, network interpenetrating and interfacial polymerization routes are relatively mature design strategies that have been applied as highly efficient methods in the synthesis of different kinds of KANF-based membranes. Apart from these methods, some innovative technologies including physical design strategies have been developed to prepare KANF-based membranes for specific applications. For example, Lyu *et al.*¹⁹ used the KANF solution through spin-coating or blade-coating, sol–gel processing, and subsequent freeze-drying to fabricate flexible and highly porous aerogel membranes,

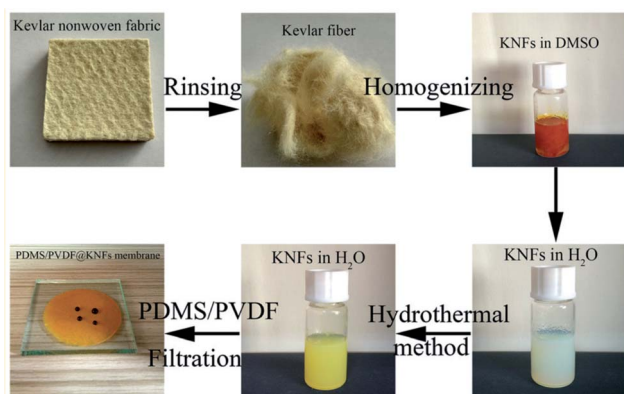


Fig. 9 Schematic illustration of the fabrication process of a superhydrophobic PDMS/PVDF@KNF membrane. Reprinted with permission from ref. 56 Copyright 2019 Royal Society of Chemistry.

followed by the incorporation of a phase-change material (PCM) to obtain the final KNA/PCM composite membranes. These composite membranes showed a high thermal capability, infrared emissivity of 0.94 and ultralow infrared transmittance of a wide waveband, which had a promising application for KANFs in infrared thermal stealth.

Combining mature design methods is also a trend to fabricate novel membranes. Li *et al.*²⁹ synthesized a robust superhydrophobic membrane *via* blending and network interpenetrating and obtained a high performance KANF-based membrane (see Fig. 9). Zhao *et al.*²⁶ controlled the temperature in the dissolution process, so that the long KANFs are split into small PPTA chains based on the amide hydrolysis reaction process. Then, symmetrically recombined with 2,5-diaminobenzenesulfonic acid (DSA) monomers *via* blending in the KANF solution and amide condensation reaction in water, the prepared homogeneous membranes exhibited a high thermal stability and excellent electrochemical properties.

4. Application of KANF based membranes

According to the pore size, as shown in Fig. 10, separation membranes may attract interest towards KANF-based

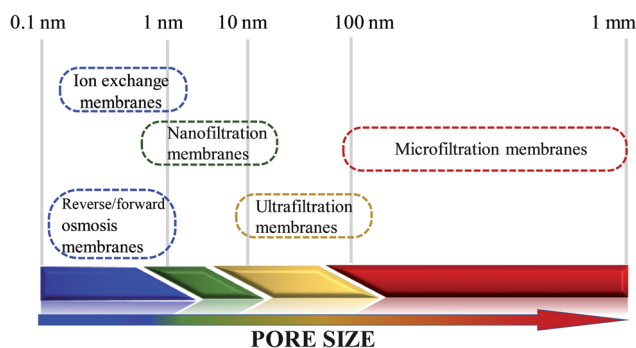


Fig. 10 The separation membranes are classified by pore size.

membranes, including ion exchange membranes (anion exchange membranes, cation exchange membranes and bipolar membranes and proton exchange membranes), reverse/forward osmosis membranes, nanofiltration membranes, ultrafiltration membranes and microfiltration membranes. Due to the tunable structure, adjustable composition and potential applications in the industry of KANF-based membranes, there is strong interest in developing such membranes for water treatment, organic solvent separation and fuel cells. These application fields are highlighted and discussed in this section.

4.1 Water treatment

In order to fulfill complex separation requirements in water treatment, many novel membrane materials have been developed. KANF-based membranes were designed for oil/water separation, desalination (producing pure water), viscous emulsion separation and dye separation.

4.1.1 Oil/water separation. Oily wastewater generated from oil spills is a global issue and has an extremely negative impact on the aquatic ecosystem. Membrane technology with superhydrophobic surfaces is of high interest for oil/water separation. Superhydrophobic surfaces obtained by designing KANF-based membranes have been broadly explored in recent years.

For example, by intertwining the KANFs and hydroxyapatite nanowires (HAPNWs), Li *et al.* prepared a multifunctional membrane through hydrothermal reaction and vacuum filtration approaches.⁶² TiO₂ nanoparticles were added into this intertwined structure, yielding a KF@TiO₂@HAPNW superhydrophobic membrane to efficiently separate oil/water mixed solutions. As shown in Fig. 11a, a 1,2-dichloroethane/water mixture (with methylene blue) and an *n*-hexane/water mixture were used to evaluate the efficiency in oil/water separation. The results indicated a rapid and highly efficient oil/water separation when KANFs with a superhydrophobic structure and nanopores.

4.1.2 Water purification. Lv *et al.* designed homogeneous hybrid membranes for wastewater treatment by vacuum-filtering of a mixture of silk fibroin (SF) and KANFs (Fig. 11b).¹⁷ With increasing the KANF content, the mechanical strength of the membrane was enhanced. The excellent ultimate stress and toughness were 52.4 MPa and 143.2 MJ m⁻³, respectively. In the pressure-driven filtration process, the water flux of a KANF-based membrane (thickness of 18 ± 3 μm) with 50 wt% of KANFs was much higher than that of any other membranes. Simultaneously, the rejections of dyes (Rhodamine B and Congo red) and Au nanoparticles (~6 nm) were all above 96%. This kind of KANF-based membrane with a dense nanopore structure and separation performance allows its potential applications in water purification and desalination.

4.1.3 Emulsion separation. The separation mechanism of pressure-driven membranes is mainly based on the size sieving, *i.e.*, selectively rejecting ions, molecules and particles. This mechanism is also suitable for emulsion separation. However, the emulsion may trigger the pore blocking of the membrane, which limits its separation performance. In addition, due to the trade-off between the separation efficiency and the flux, it is

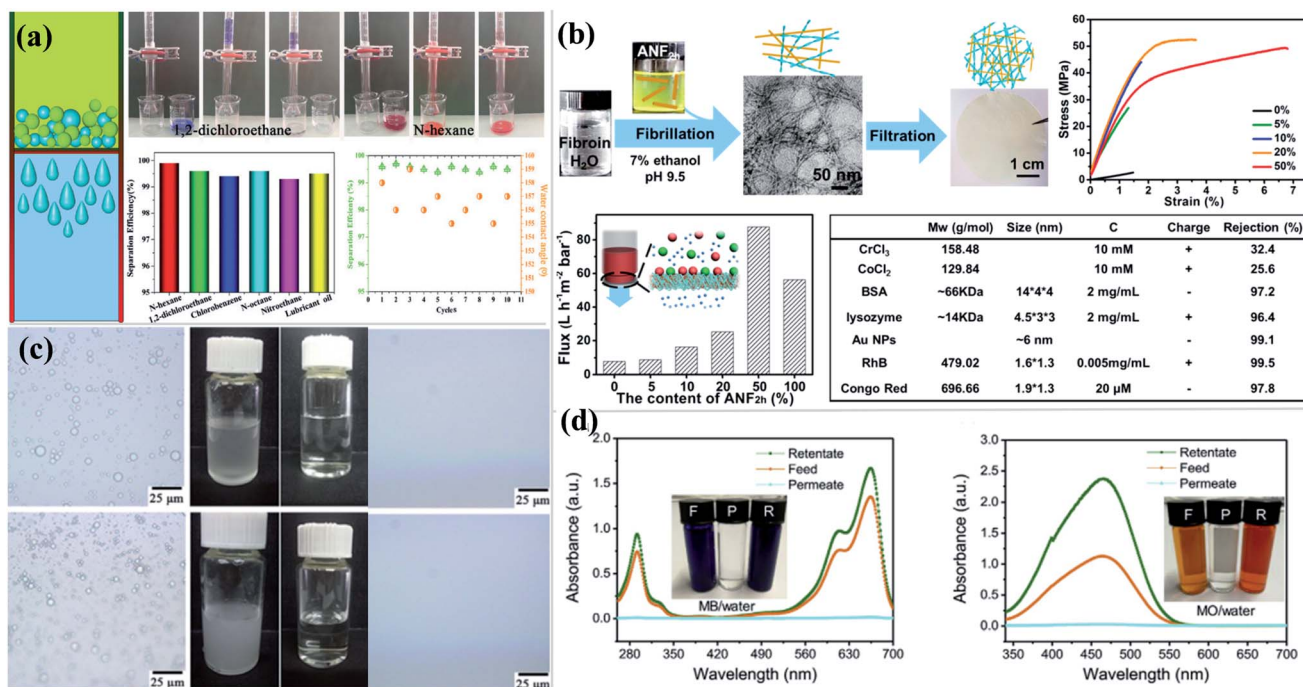


Fig. 11 Schematic illustration of the oil/water separation and the separation efficiency (a), reprinted with permission from ref. 61. Copyright 2019 Royal Society of Chemistry; desalination (b), ref. 17. Copyright 2017 American Chemical Society; viscous emulsion separation (c), ref. 29. Copyright 2019 Elsevier; dye wastewater separation (d), ref. 37. Copyright 2019 Elsevier.

a critical challenge to design a membrane with an excellent separation ability for emulsions. Some pioneering studies have been carried out to meet these challenges. For example, Yang *et al.*³⁰ prepared a composite KANF-based membrane *via* hydrothermal reaction, followed by modification with FeOOH and ZnO nanoparticles. The resulting KANF-based membrane showed an excellent hydrophilicity and hydrophobicity. In addition, the membrane was found to have a high separation efficiency for oil-in-water and water-in-oil emulsions (Fig. 11c). Ye *et al.*⁶³ designed an amphiprotic millimeter scale collagen nanofiber-based (MCN) membrane for efficiently separating a variety of viscous emulsions (77.3 to 200.0 mPa s). The flux of the obtained membrane was higher than $1582 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ with a rejection of 99.97%. This strategy may be used to develop highly efficient membranes for separation of viscous emulsions.

4.1.4 Dye wastewater separation. The discharge of wastewater containing organic dyes inevitably causes a serious ecological problem and a public health risk. Several technologies were developed for dye decontamination from wastewater. Among them, membrane separation has been widely studied for the removal of dyes. Li *et al.*³⁸ prepared a KANF-based thin-film composite (TFC) nanofiltration membrane *via* interfacial polymerization on a KANF hydrogel substrate. Several organic dyes, such as methylene blue (MB, a positively charged dye) and methyl orange (MO, a negatively charged dye), were successfully separated from water with this KANF-based membrane (Fig. 11d). Nearly 100% rejection for both organic dyes could be achieved, along with a satisfactory flux of $8.4 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for the MO solution and $7.2 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for the MB

solution. More importantly, the KANF-based membranes showed a good separation performance of dyes in organic solvents. The rejection of rose bengal (1017 g mol^{-1}), eosin Y (EY, 648 g mol^{-1}), Sudan black B (SBB, 457 g mol^{-1}), MO (327 g mol^{-1}) and Disperse orange 3 (DO3, 242 g mol^{-1}) in ethanol was 98.9%, 99.4%, 99.2%, 99.2% and 64.5%, respectively.

4.2 Organic solvent separation

Considering the important role of organic solvents in industrial production, the purification of organic solvents using the membrane process is a challenging but critically desired area.⁵⁶ Due to the strengthened hydrogen bonding, π - π stacking bonds and van der Waals forces between KANFs, KANF-based membranes may be applied for separations in organic solvents.

Li *et al.*³⁹ constructed KANFs with a three-dimensional interconnected hydrogel structure and fabricated a KANF-based TFC nanofiltration membrane *via* interfacial polymerization. The prepared KANF-TFC membranes were applied in organic solvents (both polar protic and polar aprotic harsh organic solvents). With the KANF-based membrane structure and 62 nm thickness of polyamide layer, the designed KANF-TFC membranes exhibited a high pure solvent permeance for polar organic solvents, which was $54.0 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for methanol and $13.6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ for ethanol. A high pure solvent permeance for harsh organic solvents was achieved: $13.6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ of acetone and $13.6 \text{ L m}^{-2} \text{ h}^{-1} \text{ bar}^{-1}$ of *N,N*-dimethylformamide. Furthermore, the nanofiltration experiments showed that the methyl orange rejection was higher than 90% and the rejection of rose Bengal was nearly 100%. This kind of

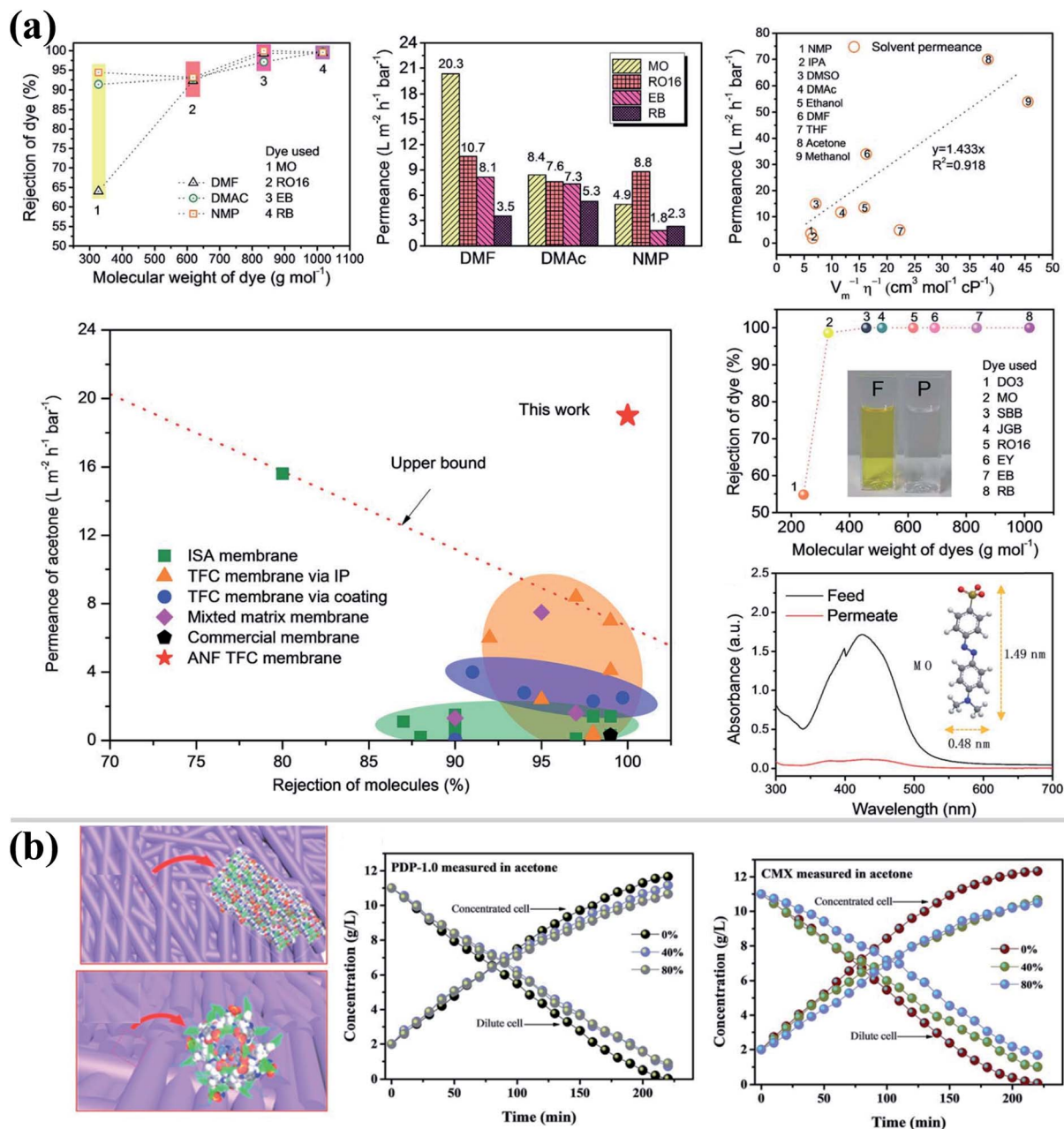


Fig. 12 KANF-TFC membrane with ultrafast transport performance for molecular separation in organic solvents (a); electrodialysis in organic solvent solutions (b). Reprinted with permission from ref. 38 and ref. 25. Copyright 2019 Royal Society of Chemistry, respectively.

the KANF-based membrane therefore has great potential for application in organic solvent purification, solvent recovery, solute concentration and catalytic processes in organic solvents. In another work, Zhao *et al.*²⁶ symmetrically recombined KANFs using 2,5-diaminobenzenesulfonic acid (DSA) and prepared a new class of KANF-based cation exchange membranes, denoted as PPTA-DSA-PPTA (PDP) membranes. Acetone, a common polar organic solvent, was chosen to evaluate the separation of ions in electrodialysis. After treatment in 40% and 80% acetone aqueous solutions for 24 hours, the separation performance (for separation of ions) of the PDP-1.0 membrane in both dilute and concentrated cells was similar to that of the

original PDP-1.0 membrane (see Fig. 12b). Compared with a commercial polymeric cation exchange membrane (CMX), the PDP-1.0 membrane had a strong resistance to organic solvents, which extremely extends the application area of electrodialysis to organic solvents.

4.3 Separation of ions

Electro-driven membranes, which can be cation exchange membranes, anion exchange membranes or bipolar membranes, show a unique advantage in separating/extracting target ions, which stimulates the development of various high performance materials for electro-membrane separation.

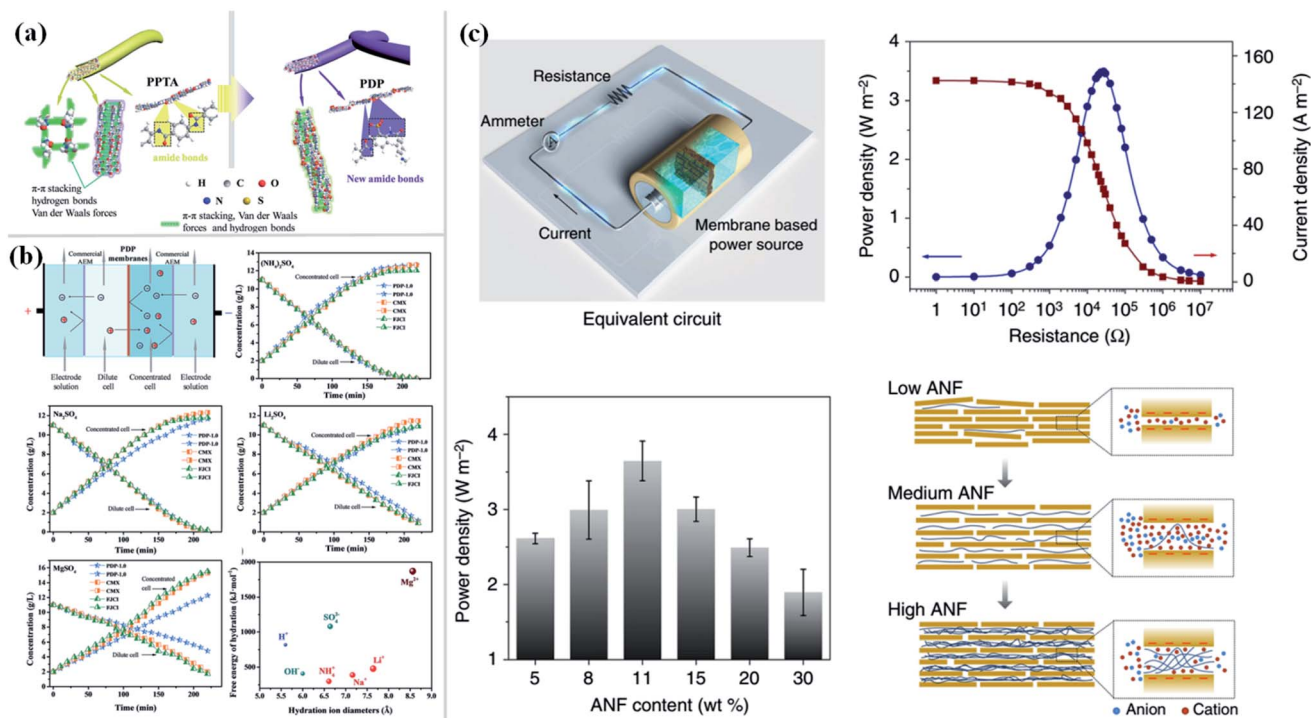


Fig. 13 The chemical structure of KANFs and KANF-based cation exchange membranes (a) and cation separation behaviors in the ED process (b), reprinted with permission from ref. 25. Copyright 2019 Royal Society of Chemistry; osmotic energy conversion behavior (c), ref. 33. Copyright 2019 Spring Nature.

Additionally, the reverse electro dialysis process through specific membranes may generate energy for industrial applications; reverse electro dialysis and osmotic power generators have been considered as green technologies in recent years. The chemically and physically advanced properties of KANF-based membranes suggested as a promising potential application in this area.

Zhao *et al.*²⁶ prepared a KANF-based cation exchange membrane (PDP-1.0, Fig. 13a) which showed a high performance for ion separation in electro dialysis. In electro dialysis with a constant voltage of 15.0 V, the desalination efficiency of Na_2SO_4 was as high as 99.7% after 220 min (Fig. 13b). NH_4^+ , Li^+ , Na^+ and Mg^{2+} were chosen to explore the relationship between the KANF-based membrane and its separation performance. Due to the strong interaction and dense structure of KANFs in PDP membranes, the relative desalting efficiencies for NH_4^+ , Li^+ , Na^+ and Mg^{2+} were different, *i.e.*, $\text{NH}_4^+ > \text{Na}^+ > \text{Li}^+ > \text{Mg}^{2+}$. This was explained by the size-sieving effects and electrostatic repulsion. Thus, this KANF-based membrane not only could be used as the ion exchange membrane for anion/cation separation, but also had high potential in selective separation of target ions.

Zhang *et al.*³⁴ fabricated MXene/KANF-based membranes as high performance nanofluidic osmotic power generators in a river-sea water system. As shown in Fig. 13c, in pressure retarded osmosis, power is generated. With a KANF content of 11 wt%, the maximum power density generated by the MXene/KANF-based membrane was 4.1 W m^{-2} . This highlighted that KANF-based membranes can be applied for ion separation in energy conversion technologies. With their excellent

mechanical strength and outstanding stability, KANF-based membranes were found suitable for energy conversion technologies.

4.4 Antibacterial applications

Bacterial fouling in pressure-driven membranes may result in a decrease of the water flux and can deteriorate the water quality. Therefore, creating membrane materials with antibacterial activity is important, especially in producing drinking water. Chen *et al.*⁵⁹ mixed sulfonated poly(*p*-phenylene terephthalamide) (f-PPTA) with poly(vinylidene fluoride) (PVDF) to obtain a hydrophilic nanofibrous membrane *via* an electro-spinning process. The as-prepared KANF-based ultrafiltration membrane with desirable porosity exhibited an excellent antibacterial behavior against *E. coli* (see Fig. 14). Additionally, this membrane showed a high pure water flux in a bacterium-containing aqueous environment.

4.5 Battery separators

Cathodes, anodes and ion conducting membranes (separators) are the three key components for batteries. The capacity and discharge rate of batteries are the most important indicators for a battery. Therefore, it is important to improve the performance of cathodes and anodes. In addition, using advanced membranes as the separators is equally crucial for achieving high capacity and discharge rate ion batteries.

Tung *et al.*⁶⁴ combined KANFs with poly(ethylene oxide) (PEO) by a layer-by-layer assembled strategy to fabricate KANF-

based membranes with high ionic conductivity and a good thermal stability. With KANF-based membranes having 30–50 PEO/ANF layers, a high capacity of suppression for hard copper and soft lithium dendrites could be obtained. Moreover, the ionic conductivity was as high as $1.7 \times 10^{-4} \text{ S cm}^{-1}$, which made a breakthrough between high ionic conductance. Li *et al.*⁶⁵ dispersed the KANFs and methoxy polyethylene glycol (mPEG) *via* vacuum assisted filtration to assemble into batteries as the separator. By integrating the advantages of KANFs and mPEG, the KANF-based membrane was found to have a high electrolyte wettability and ionic conductivity, and a high mechanical and thermal stability, thus enhancing the safety of lithium ion batteries. The cycling property at 0.5 C-rates by using the KANF-based membrane separator was almost

comparable to the polypropylene (PP) separator, which is one of the most widely used separators in lithium ion batteries (Fig. 15a). This work illustrates that the KANF-based membranes can be prepared with better retention properties with mPEG. Similarly, Han *et al.*³⁶ combined conducting polymers with KANFs to obtain core-shell KANFs through *in situ* polymerization. The presence of polypyrrole shells yields electrical conductivity for the KANF-based membranes (see Fig. 15b). When the content of polypyrrole became 67%, the membrane conductivity became more than 25 S m^{-1} . The membrane conductivity only decreased by about 2% after 5000 bending cycles and remained high during 40 000 cycles of rubbing. Furthermore, these membranes showed a high resistance for various frequently used organic solvents.

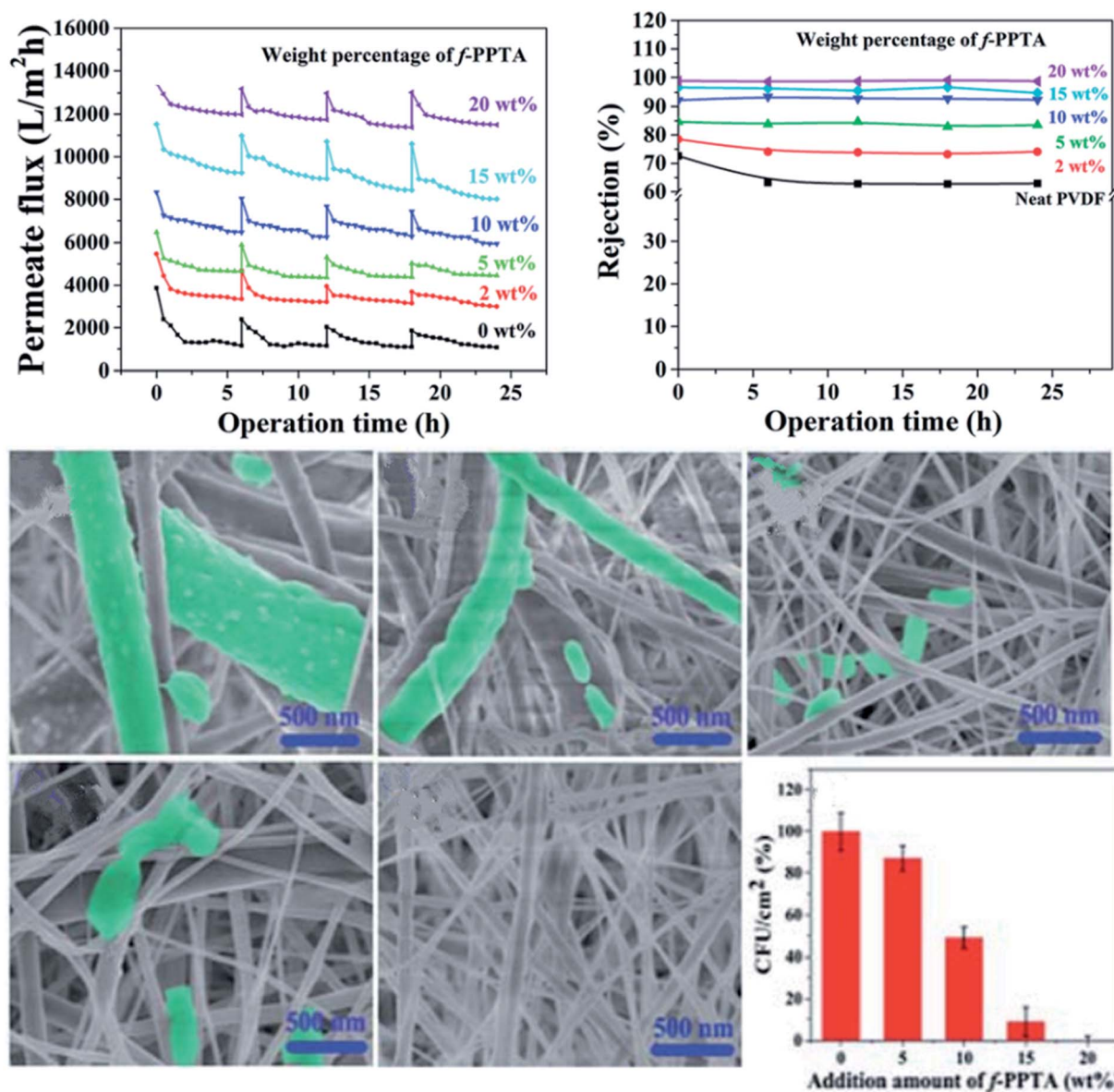


Fig. 14 Rechargeable antibacterial KANF-based membranes for bioprotective applications. Reprinted with permission from ref. 58. Copyright 2019 Royal Society of Chemistry.

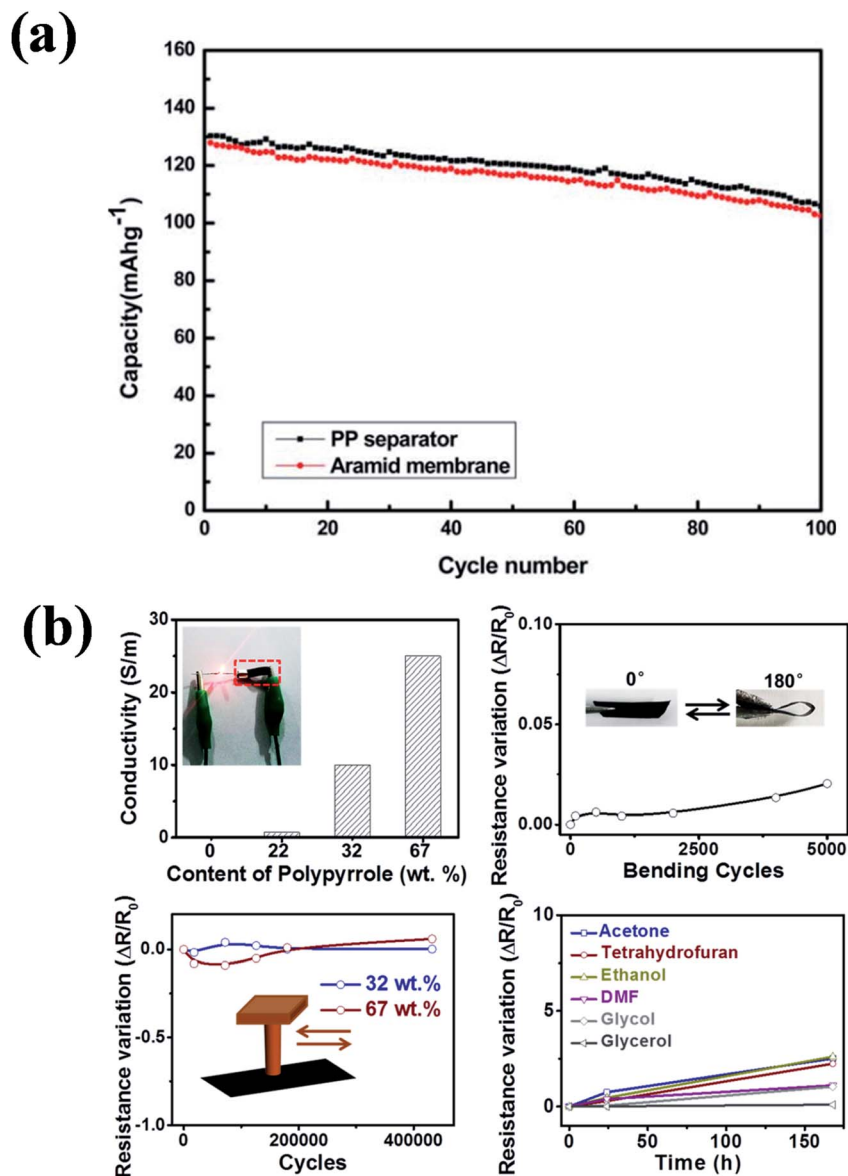


Fig. 15 KANF-based membrane for the separator of lithium ion batteries (a), ref. 64. Copyright 2019 Elsevier; membranes of core-shell ANFs (b), ref. 35. Copyright 2019 American Chemical Society.

4.6 Proton exchange membranes

With the advantages of a high-power density, a highly efficient energy conversion efficiency and low emission of pollutants, novel energy conversion batteries, such as vanadium redox flow battery and fuel cells, have attracted increasing attention. Proton exchange membranes are the core part of these energy conversion batteries: they lead the transport of protons from anodes to cathodes and hindering fuel penetration, which has an influence on the proton conductivity.

Yang *et al.*³³ constructed phosphotungstic acid (PWA) self-immobilized fibers and KANFs *via* self-assembly (see Fig. 16a). With the strong interaction of hydrogen bonds inside the structure, KANF-based composite membranes were prepared by incorporating the obtained composite into a Nafion matrix *via* a solution-casting method to fabricate Nafion-(NKFs@PWA)

membranes. The proton conductivities of Nafion-(NKFs@PWA)-10 wt%, Nafion-(NKFs@PWA)-20 wt%, Nafion-(NKFs@PWA)-30 wt% and Nafion-(NKFs@PWA)-40 wt% membranes were 0.066, 0.064, 0.061 and 0.053 S cm⁻¹, respectively.

Liu *et al.*¹⁸ accumulated the KANFs, cadmium telluride (CdTe) nanocrystals and phosphoric acid (PA) molecules to prepare a multilayered (Kevlar-CdTe-PA)₄ membrane *via* spin coating. The (Kevlar-CdTe-PA)₄ membrane was obtained by intermolecular hydrogen bonds in the structure. The obtained membrane showed a sufficient structural stability, a high hindrance to permeation of fuels and a low resistance to proton conduction, which is crucial for their use as proton exchange membranes in fuel cells. The proton conductivity of the (Kevlar-CdTe-PA)₄ membrane was tested to evaluate the efficiency of a proton exchange membrane fuel cell. Without humidification,

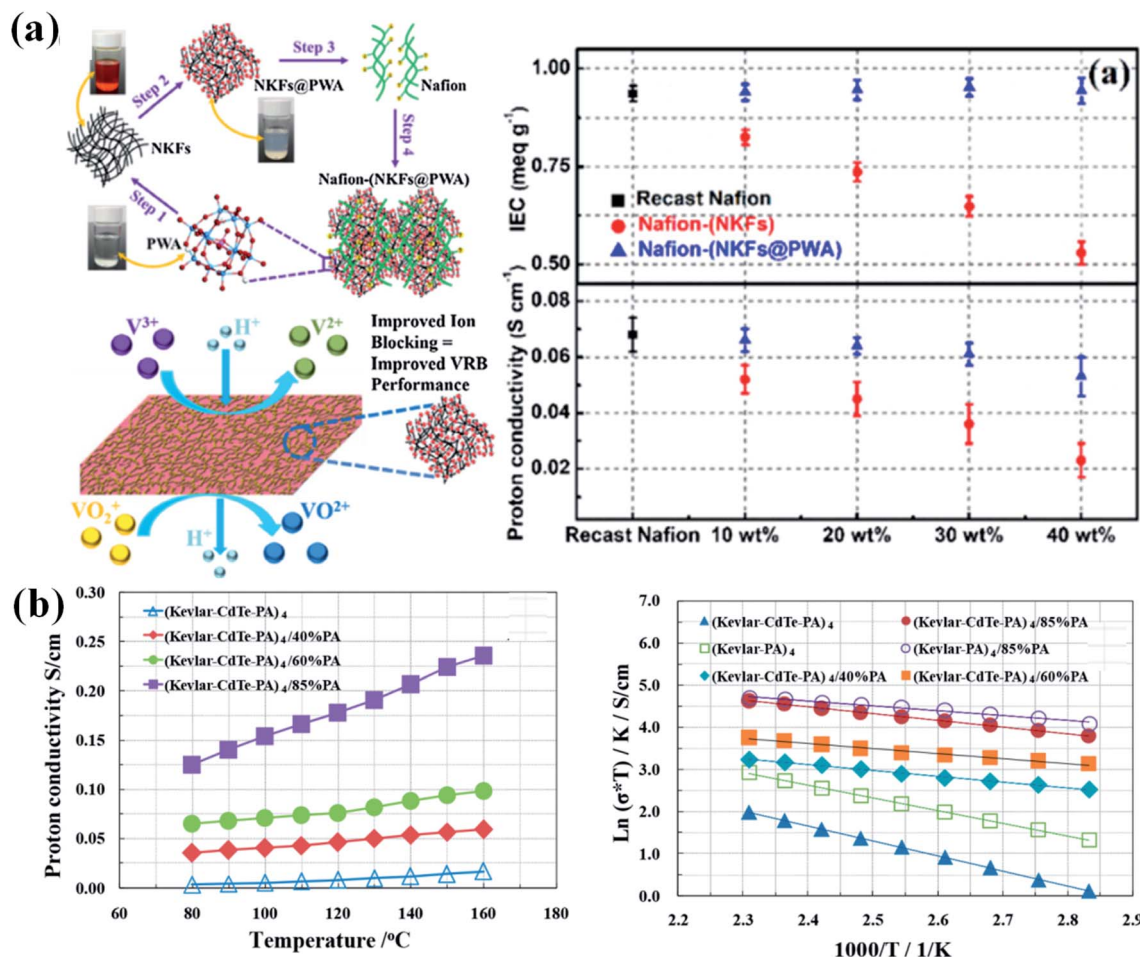


Fig. 16 KANF composite membrane vanadium redox flow battery (a); KANF-based membrane for high-temperature proton exchange membrane fuel cells (b). Reprinted with permission from ref. 32. Copyright 2019 Elsevier and ref. 18. Copyright 2019 American Chemical Society, respectively.

the proton conductivity of the (Kevlar-CdTe-PA)₄ membrane and the (Kevlar-CdTe-PA)₄/PA membrane increased with temperature. The proton conductivity of the (Kevlar-CdTe-PA)₄/85% PA membrane was 0.235 S cm⁻¹ at 160 °C (see Fig. 16b). In addition, the activation energy of the (Kevlar-CdTe-PA)₄/60% PA membrane was 9.94 kJ mol⁻¹. The high proton conductivity and mechanical properties of KANF-based membranes suggest practical application as the proton exchange membrane for fuel cells.

5. Conclusion and outlook

Kevlar aramid nanofibers are among the strongest polymeric materials with superior mechanical performance, extremely high thermostability, and a high resistance to organic solvents. They have been widely used as advanced composites for aircrafts, and automobiles, radiation shielding, ballistic protection, protective clothing, *etc.* Since a facile and controllable dissolving method was developed by Kotov's group, the field of KANF-based membranes in separation and energy conversion developed quickly. Especially in the last three years,

the development of Kevlar aramid nanofiber composite membranes has accelerated, due to the fundamental understanding of the dissolution methods, tunable structure, key properties and design strategies of KANFs. KANFs are one-dimensional organic nanomaterials and consist of the nano-scale version of poly(paraphenylene terephthalamide) (PPTA) made up of highly ordered and asymmetric alternating benzene rings and aramid bonds. The successful development of KANF-based membranes for separation and energy conversion has a strong relationship with the material's capacity for hydrogen bonding, π - π stacking bonds and van der Waals forces. Understanding the tunable structure (including electrospinning, layer-by-layer assembly, phase separation, wet-spinning, blending, hybridization, network interpenetrating, *etc.*) and the material's key properties (chemical reaction, stability, hydrophilicity/hydrophobicity, conductivity, selectivity, *etc.*) is the basis for preparation of the KANF-based membranes. Based on this knowledge, many new designs and strategies (blending method, chemical reaction method, network interpenetrating, interfacial polymerization, *etc.*) for fabricating and applying KANF-based membranes have emerged.

In the past years, the successful synthesis of KANF-based membranes has been applied in oil/water separation, water purification and desalination, emulsion separation, dye wastewater separation, organic solvent treatment, ion exchange and separation, antibacterial applications, separators in battery application and proton exchange. The combination of KANFs with other components to prepare novel structures and multi-functional composites may further increase applications of membranes for separation. Further energy and separation challenges will trigger more exploration of design and fabrication of KANF-based membranes.

Challenges remain in the use of KANFs and KANF-based membranes in the academic and industrial sectors. The potential health hazard of the KANFs during the grinding process has drawn attention.⁶⁶ Furthermore, the current dissolving methods still take several days and this limits the application of KANF-based membranes.⁶⁷ The length of the KANFs after dissolving and pore size of the resulting membranes are also difficult to control.⁶⁸ Moreover, the application of KANF-based membranes remains to be explored in other areas, such as gas separation. Therefore, KANFs show promise in academic and industry fields due to their potential for combination with other novel materials.

Conflicts of interest

There are no conflicts to declare.

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