Review

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Electrospinning: a facile technique for fabricating functional nanofibers for environmental applications

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Abstract: Over the last few decades, the excess exploitation of our planet and degradation of environment have gone up at an alarming rate. Environmental problems, especially air and water pollution, which takes a huge number of years to recover, have become the major concern affecting the progress of human society. The overwhelming threats have driven global research and innovation in the development of advanced technology and devices toward a cleaner environment. In this context, the generation of functional one-dimensional (1-D) nanomaterials has become an area of intense interest from both academia and industry due to their unique advantages for environmental applications. Electrospinning is recognized as the most powerful technique for producing 1-D composite nanofibers via facile incorporation of active ingredients in the solutions for electrospinning or by some posttreatment process. In this review, we give an overview on the latest research progress in the fabrication and utilization of functional polymer/ceramic/carbon nanofibers generated by electrospinning for air and water purification, as well as their applications as sensors for pollutant monitoring and control. We also present the perspectives and challenges of the current electrospinning technique for environmental applications.

Keywords: air purification; electrospinning; nanofibers; sensors; water treatment.

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1 Introduction

Environmental degradation is one of the most pressing challenges facing human development in the 21st century. Two indispensable elements critical to the survival of mankind, air and water resources, have been heavily contaminated with toxic materials and pollutants as a result of rapid industrialization. This has threatened humans and ecosystems with serious health risks. Water pollution is widely known to be a leading worldwide cause of deaths and diseases. Diarrheal diseases, caused by polluted water, poor sanitation and hygiene, result in more deaths a year compared to all forms of violence, including war [1]. There have been reports indicating that more than 80% of sewage in developing countries is discharged untreated [2, 3]. This affects the entire biosphere – plants and organisms living in these bodies of water. Air pollution refers to the presence of suspended particulate matter (PM) such as dusts, fumes, and smoke, or other gaseous pollutants in the form of gases and vapors, which can cause diseases and death to humans and living organisms. According to the Blacksmith Institute World's Worst Polluted Places report in 2008, urban air quality and indoor air pollution are listed as two of the world's worst toxic pollution problems [4]. Public awareness on the air quality problems have also been raised due to the increasing media reports over the PM2.5 issue. These airborne pollutants can often deposit back onto land and water bodies, sometimes at great distances from the source, contribute to the decline of both air and water quality. According to the 2014 World Health Organization report, air pollution caused the deaths of around 7 million people worldwide. Given the recognized threats to our world ecosystem, the focus has been directed toward driving global research to develop technology and devices for a cleaner environment.

Development of advanced functional nanostructured materials, using one-dimensional (1-D) nanostructures (nanofibers, nanowires, nanotubes) have been an area of intense interest from academic and industries for

environmental applications [5]. The attractiveness of 1-D nanostructures lies in their large aspect ratio and high specific surface area, which may greatly benefit their electrical and thermal transport characteristics, mechanical properties, and interactions with surrounding media. They are regarded as the most promising materials for a wide range of applications such as energy storage, sensing, tissue engineering, catalysis, and filtration. Electrospinning is recognized as the most powerful and facile technique for generating uniform nanofibers with controlled dimension and morphology from synthetic and natural polymers, polymer alloys, and polymers loaded with nanoparticles, active agents, as well as metals and ceramics [6]. The standard setup for electrospinning consists of a spinneret with a metallic needle, a syringe pump, a high-voltage power supply, and a grounded collector, as shown in Figure 1A. A solution of polymer, sol-gel, or composite is loaded into the syringe, and this viscous liquid is driven to the needle tip by a syringe pump, forming a droplet at the tip. When a high voltage is applied to the metallic needle, the droplet is first stretched into a structure called Taylor cone and finally into an electrified jet. The jet is then elongated and whipped continuously by electrostatic repulsion until it is deposited randomly onto the collector to form a nonwoven fibrous mat. The size of the fibers can be tuned from tens of nanometers to hundreds of micrometers depending on polymer solution properties and processing parameters. As shown in Figure 1B, aligned nanofibers could be obtained by using a rotating drum collector. In addition, by using a spinneret comprising two coaxial capillaries, uniform core-sheath hybrid nanofibers or hollow nanofibers can also be fabricated (Figure 1C).

Incorporation of functional materials (such as nanoparticles, nanosheets, nanotubes, active reagents, etc.) with electrospun fibers has emerged as one of most exciting research topics in the field of electrospinning [7–13]. Generally, two main strategies are employed for producing functional electrospun fibers. One is preparing the hybrid fibers after the electrospinning process, which is usually combined with other postprocessing methods, and the other is fabricating the composite nanofibers during the electrospinning process. The facile formation of 1-D composite nanomaterials by electrospinning cannot only endow the fibrous materials with multifunctional properties for various applications but also avoid aggregation of the active nano-components and facilitate the recycle and reuse of the materials. Moreover, electrospun fibers also have good air and water permeability, high surface-to-volume ratio to be functionalized easily. All these characteristics make them an excellent choice for air/water purification and sensor applications.

Many excellent review articles on the preparation and applications of electrospun fibers have been published. Most of them mainly summarized the exciting works emerging in a period of time, the preparation and applications of a specific kind of material, or discussed around particular applications [10, 14–18]. However, comprehensive review articles focused on recent advances of electrospun fibers for environmental applications are as yet not fully realized. Our research group has been actively engaged in the development of composite electrospun fibers for energy storage and biomedical applications over the past decade [7–13, 19–22]. With great interest in this area, we would like to give an overview on the latest research progress in the fabrication and utilization of functional electrospun polymer nanofibers, ceramic nanofibers, and carbon nanofibers for air and water purification, as well as their applications as sensors for pollutant monitoring and control. We also present the perspectives and

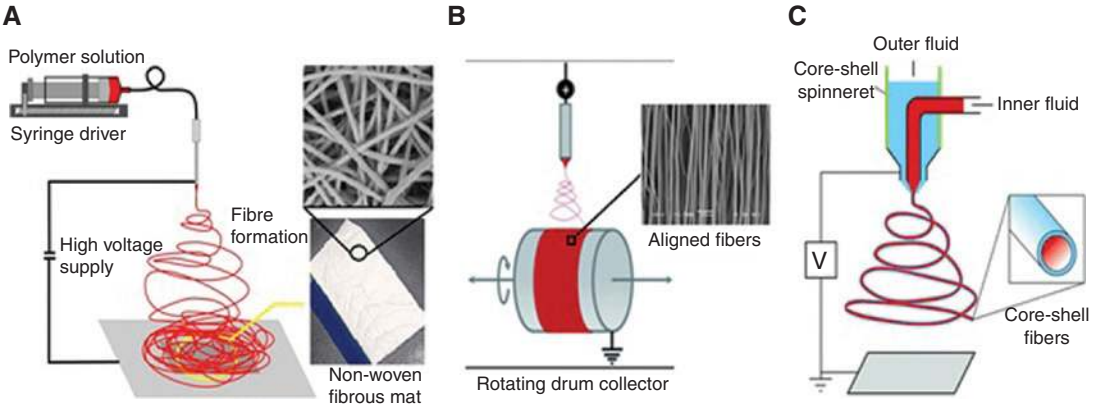

Figure 1: (A) Conventional electrospinning setup to obtain random nanofibers; (B) aligned fibers obtained by a rotating drum collector; (C) core-shell structured fibers generated by a core-shell spinneret.

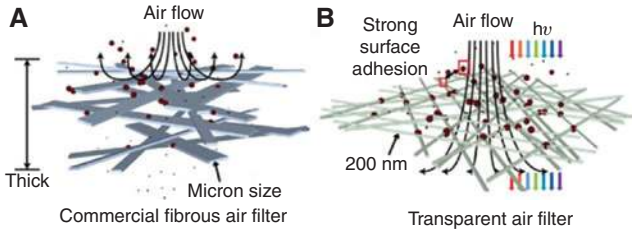

Figure 2: Schematics of (A) bulky fibrous air filter capturing PM particles by thick physical barrier and adhesion; (B) transparent air filters that capture PM particles by strong surface adhesion and allowing a high light and air penetration. For details, see Ref. [23]; reprinted with permission from Nature Publishing Group.

challenges of the current electrospinning technique for environmental applications.

2 Electrospun fibers for air purification

2.1 Filtration of nanoparticles in the air

Existing air filtration technology usually uses high efficiency particulate air (HEPA) filters made of micro-sized fiberglass to remove tiny particles in the atmosphere. However, the most penetrating particle size (between 0.1 and 0.5 μm), cannot be removed by the present nonwoven filter media because the size of pores formed with micron-scale fibers is considerably larger. To enhance the filtration efficiency of the filter media, it is necessary to make much thicker media for smaller pore sizes. However, thicker filter media can be difficult to use due to increased pressure drop and higher energy cost (Figure 2A). Existing technology would not meet the requirements of a transparent high-efficiency PM2.5 filter. Liu et al. have recently developed a transparent and lightweight air filter for high-efficiency PM2.5 captured using the electrospinning technique [23]. They have investigated electrospun membranes derived from various polymers (including polyacrylonitrile (PAN), polyvinylpyrrolidone (PVP), polystyrene (PS), poly(vinyl alcohol) (PVA), and polypropylene (PP)) with different fiber diameters and found that the surface chemistry and microstructure of the fibers were important for particulate capture. When the surface chemistry of the air filter was optimized to match that of PM particles, and the fiber diameter was decreased to nanoscale, the fiber capture ability was increased a lot, and the membrane filter could be reduced significantly to a transparent level to enable both transparency to sunlight and sufficient air flow (Figure 2B). Through PM chemical composition analysis, they found that polar functional groups such as C–O, C=O, and C–N were present at the outer surface of the PM particles, and therefore, polymers with higher dipole moment can have stronger dipole-dipole and induced-dipole intermolecular forces with the particles. Electrospun PAN nanofibers with diameters around 200 nm were demonstrated to be the most effective transparent PM filters (Figure 3A). In a field test conducted in Beijing, an electrospun PAN air filter with a transmittance of 75% can be used under a hazardous PM2.5 level for as long as 100 h with efficiency maintained at 95–100% (Figure 3B), showing the practical applicability of these transparent filters.

The preparation of electrospun fibrous air filters from recycled polyethylene terephthalate (PET) [24] and polyvinyl chloride (PVC)/polyurethane (PU) [25] were also reported. Besides the conventional fibrous structure, electrospun nanofibers with unique structures were also investigated. Wang et al. have fabricated porous fibrous membranes bead-on-string from poly(lactic acid) (PLA) [26]. Liu et al. have designed and fabricated the bio-based polyamide(PA)-56 membranes with bimodal structures,

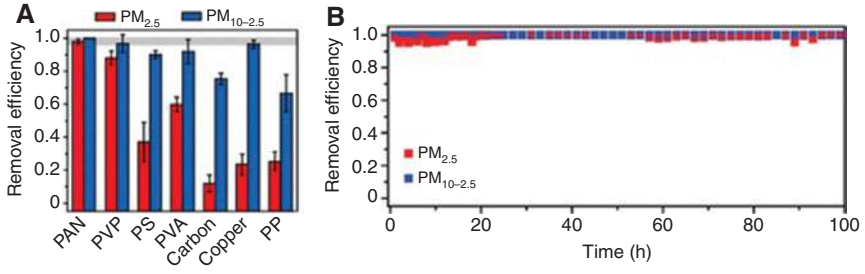

Figure 3: (A) Removal efficiency comparison between PAN, PVP, PS, PVA, PP carbon, and copper transparent filters with the same fiber diameter of ~200 nm and the same transmittance of ~70%. Error bar represents the standard deviation of three replicate measurements. (B) The long-term PM2.5 and PM10–2.5 removal efficiencies by PAN transparent filter of 70% transmittance under continuous hazardous level of PM pollution in a field test in Beijing. For details, see Ref. [23]; reprinted with permission from Nature Publishing Group.

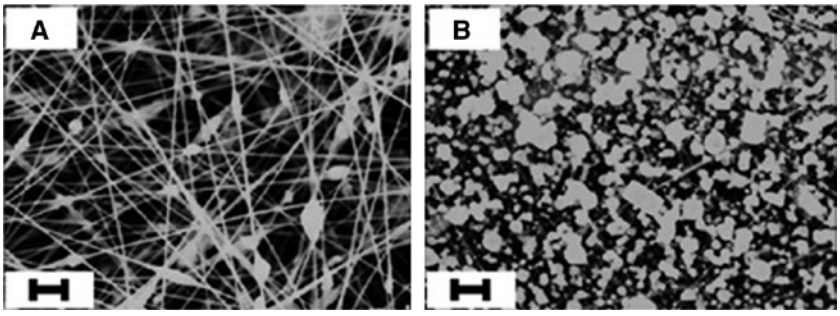

Figure 4: SEM images of 0.5 g/ft² PAN/TiO_2 hybrid nanofibers on the cellulose substrate (A) before and (B) after filtration testing. All scale bars are 3 mm. For details, see Ref. [29]; reprinted with permission from Elsevier.

including novel nanonets comprising of interlinked ultrathin nanowires (20 nm) and stable cavity structures built by the bonded scaffold fibers for air filtration via one-step electrospinning/netting [27]. To further enhance the filtration properties, electrets (like SiO_2) [28], metal oxide (like TiO_2) nanoparticles [29], which can strongly influence electrostatic interactions between dust particles and nanofibers, have been incorporated to the electrospun polymer membranes to trap electrostatically active nanoparticles more effectively (Figure 4).

2.2 Adsorption of volatile organic compounds (VOCs)/toxic gases

Toxic gases (such as NO_x, SO_x, H_2S, etc.) and VOCs (such as aldehyde, benzene, methanol, methane, etc.) have recently become a major concern to both human health and environment. Significant quantities of VOCs are emitted into the air, both indoors and outdoors, each year by various sources, including both deliberate and fugitive emissions from industrial plants, vehicles, and aircraft. Several methods are used to control the emission of such gases, including thermal oxidation, biofiltration, and absorption. Adsorption is the preferred technique for controlling gaseous pollutants at low concentration levels.

Over the past decade, porous carbon nanofibers have been studied extensively in the field of energy storage and catalysis due to their prominent properties such as high length-to-diameter ratio, nano-scale diameter, highly accessible surface areas, and plenitude of shallow pores compared with conventional porous carbon materials, such as activated carbon (AC) and activated carbon fibers (ACFs) [8, 11, 12, 19, 20]. Lee et al. have prepared ACFs with high nitrogen content and microporosity by stabilization, carbonization, and steam activation of electrospun PAN-based nanofibers (Figure 5) [30]. A remarkable amount of formaldehyde was adsorbed onto the pore surface of the PAN-based ACFs even at a low concentration (ca. 11 ppm), demonstrating more than twice as long as breakthrough time of formaldehyde adsorption compared to conventional thick ACFs. The superior adsorption capability of ACNFs is mainly ascribed to the rich nitrogen content and the shallow microporosity, which would enable faster and easier diffusions of not only the formaldehyde molecules from surrounding atmosphere to the adsorption sites.

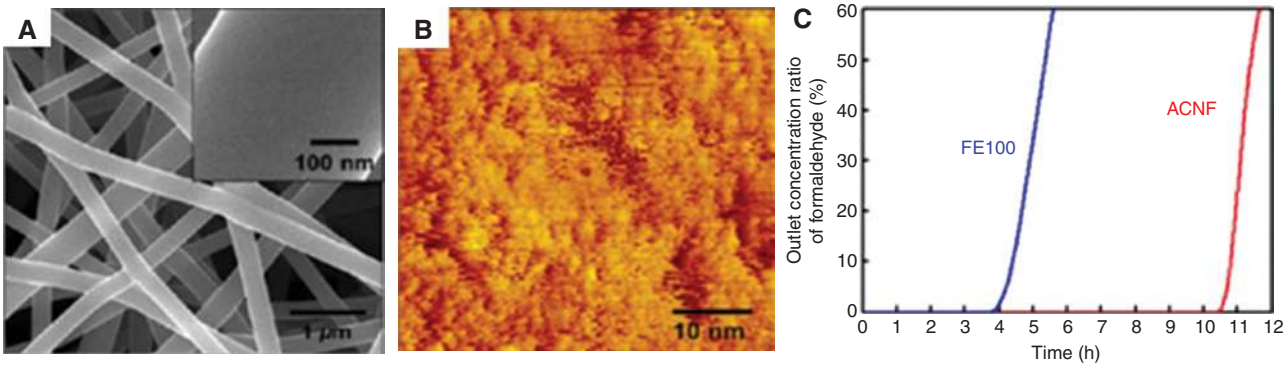

Figure 5: (A) SEM image and (B) STM image of PAN nanofiber carbonized at 600°C for 1 h under He atmosphere. (C) Breakthrough curves of formaldehyde (11 ppm) in dry condition for FE100 (conventional ACF) and PAN-based ACNF (activation conditions: 600°C, RH 90%, 1 h). For details, see Ref. [30]; reprinted with permission from Elsevier.

Katepalli et al. have developed a novel hierarchal carbon fabric, consisting of electrospun PAN-based nanofibers on an ACF substrate, with subsequent thermal stabilization by preoxidation at 250°C in air [31]. The prepared multiscale webs were shown to be effective in controlling major air pollutants, such as SO_2, NO, and toluene due to the presence of a large number of nitrile and amine surface functional groups and a large specific surface area.

Besides ACNFs, electrospun polymer (such as PU) nanofibers can also be used to prepare robust and elastic fibrous membranes with quick and high sorption capacities for VOCs [32]. These fibrous mats can be regenerated readily by desorption under ambient conditions via a simple purging process with nitrogen, which contrasts favorably with the harsh thermal treatments for regeneration of AC adsorbents. Cyclodextrins have the ability to form noncovalent host-guest inclusion complexes (CD-IC) with various molecules such as hazardous chemicals and polluting substances. They have been incorporated into poly(methyl methacrylate) (PMMA) and polyester (PE) electrospun fibers by Uyar et al. and demonstrated to be effective to trap VOCs such as aniline, styrene, and toluene [33, 34].

2.3 Catalytic oxidation/decomposition of VOCs/toxic gases

In addition to the traditional adsorption method, more and more efforts have been devoted to the catalytic conversion of VOCs or toxic gases to clean substances. Some investigations on the application of electrospun-derived carbon nanofibers in catalytic removal of NO_x have been accomplished. Huang and Kang et al. first studied the absorption and catalytic oxidation of NO to NO_2, which can be easily washed away by water, over PAN-based porous carbon nanofibers (PCNFs) fabricated via electrospinning, stabilization, carbonization, and activation with steam [35]. The ratio of NO removed by PCNFs is higher than 60% when the inlet NO concentration was 20 ppm with 0.10 g of sample, and NO_x ($NO+NO_2$) cannot be detected when the inlet NO concentration was 2 ppm within 24 h. To enhance the NO removal efficiency, they carried out further modifications to the electrospun carbon nanofibers, such as high-temperature graphitization and incorporation of reduced graphene oxide sheets (Figure 6), in order to increase the catalytically active sites [36–38].

Heterogeneous photocatalytic degradation over titania (TiO_2) or doped TiO_2 nanoparticles has become a promising technology for the treatment of environmental pollutants. Photocatalytic processes can convert a range

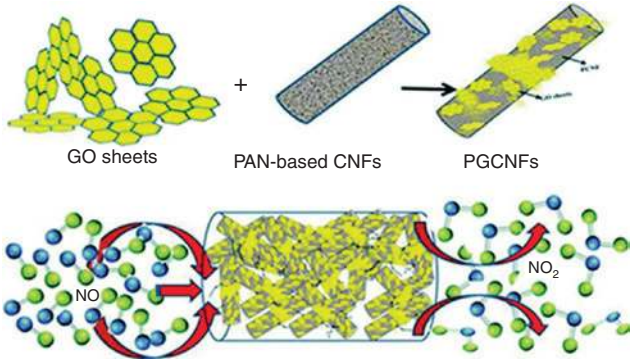

Figure 6: Schematic diagram of reduced graphene oxide (rGO) embedded in CNFs forming of graphene/PAN-based carbon nanofibers (PGCNFs) and the process of oxidation of NO to NO_2. For details, see Ref. [36]; reprinted with permission from Royal Society of Chemistry.

of organic pollutants to harmless CO_2 and H_2O via photocatalytic oxidation reactions with photo-produced superoxide ions and hydroxyl radicals. Chun et al. prepared iron-doped titania (Fe-TiO_2) nanoparticles and coupled them to PVP as polymer support to synthesize Fe-TiO_2 electrospun nanofibers for photocatalytic degradation of gaseous pollutants (benzene, toluene, ethyl benzene, and o-xylene) at environmental sub-ppm levels [39]. Zhan et al. reported mesoporous TiO_2 nanofibers with different SiO_2-doped ratio prepared using electrospinning technology combined with sol-gel methods [40]. Their photocatalytic performances were evaluated through degradation of gaseous toluene under UV light. In both of the two studies aforementioned, the embedding of the TiO_2 nanoparticles in the fibers causes a reduction in activity, as it reduces the total photoactivated surface compared with freestanding particles on the surface. Szatmáry et al. fabricated anatase TiO_2-coated electrospun polymeric nanofibers (polyamide 6 (PA6), PS, and PU) via heterogeneous nucleation in an acidic aqueous solution of titanium oxysulfate at low temperature (Figure 7) [41]. The functionalized PA6 and PS nanofibers were demonstrated to be effective materials for photocatalytic oxidation of NO_x pollutants in the air.

Compared to photocatalysis, which might require the use of UV light, room-temperature thermal catalytic oxidative decomposition of VOCs is a more favorable technique because it is energy saving and environmentally friendly. To date, various supported noble-metal catalysts have been developed for room temperature oxidation of HCHO to CO_2 and H_2O. Nie et al. have recently developed a mat-like hierarchically porous TiO_2 nanofibers (TF) decorated with Pt nanoparticles (NPs) (Figure 8) via dipping the electrospun TF mat into an H_2PtCl_6 solution followed

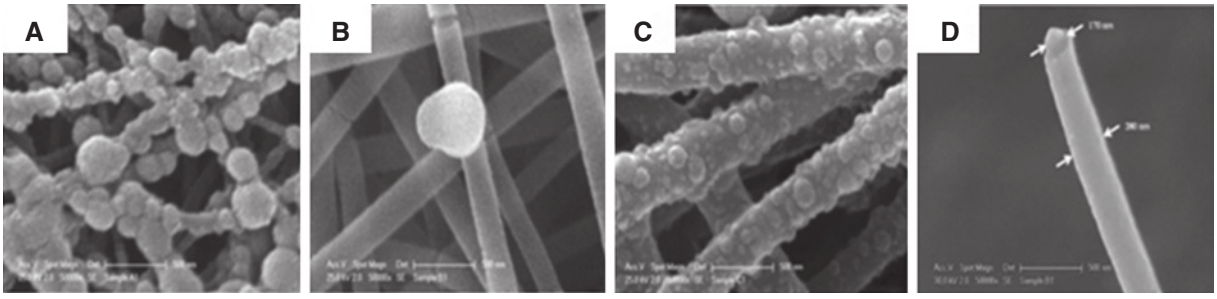

Figure 7: SEM observations of the prepared nanofibers: PA6 (A), PS (B), and PUR (C). A detailed view of one polystyrene fiber coated with anatase is presented in (D). For details, see Ref. [41]; reprinted with permission from Elsevier.

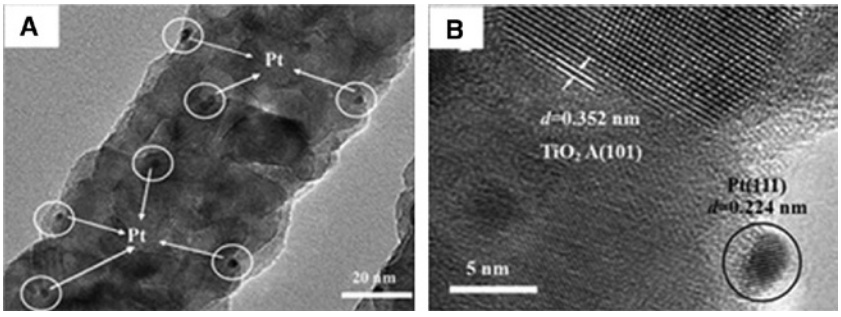

Figure 8: (A) TEM and (B) HRTEM images of the Pt/TF sample. For details, see Ref. [42]; reprinted with permission from Wiley.

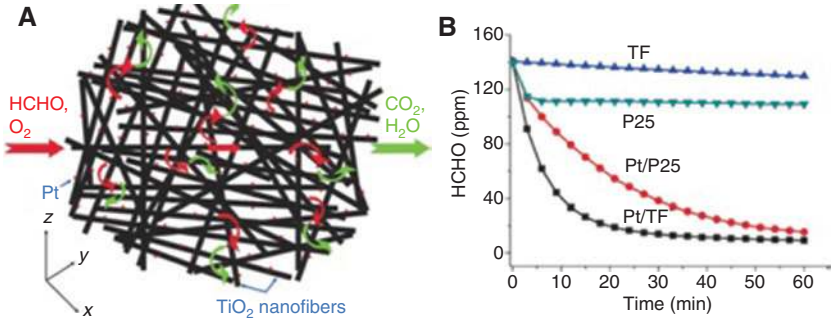

Figure 9: (A) Illustration of the fast diffusion of reactants (O_2 and HCHO) and products (CO_2 and H_2O) in the hierarchically porous channel of the Pt/TF catalyst. (B) Changes in formaldehyde concentration as a function of reaction time for the Pt/P25 and Pt/TF samples. For details, see Ref. [42]; reprinted with permission from Wiley.

by $NaBH_4$ reduction [42]. Compared to a commercial Pt-NP-decorated TiO_2 (P25) powder catalyst, such a mat-like catalyst, which can be used directly in air purification systems, showed enhanced catalytic activity in the decomposition of formaldehyde at room temperature (Figure 9) because of its hierarchical macro-/mesoporous structure that results in smaller air resistance and facilitates the diffusion of reactants and products.

2.4 Protective clothing

Increasing global competition in textiles has led to the development of high added-value products with multifunctional properties. Advanced textile materials that can provide multiple functionalities such as UV protection, disinfection, and pollutant-decomposing properties are greatly in demand by a more discerning and demanding consumer market and have many potential applications in apparel fabrics, household textiles, and technical textiles.

Electrospun fiber mats are promising barrier material for aerosol filtration. Unlike traditional filtration media that cannot simultaneously achieve high filtration efficiency and low pressure drop or high air permeability, electrospun fiber mats have small fiber diameters and large surface areas, and hence, they can significantly increase the filtration efficiency without sacrificing the

air permeability. Usually, the electrospun fiber mats are deposited on fabric substrates to combine advantages of both materials. Vitchuli et al. have deposited electrospun nylon 6 fiber mats onto 50/50 nylon/cotton fabric to prepare a protective clothing material against chemical and biological warfare agents [43]. Nylon 6 was chosen for the process ability. The filtration efficiency of the fabric was increased by a maximum of more than 250% after the deposition of electrospun fiber mats.

Metal oxide nanoparticles have also been incorporated into the electrospun polymer fibers to endow the fabrics with multifunctionalities. Lee et al. examined the application of electrospun polyurethane/zinc oxide nanocomposite fibers onto cotton fabrics for the purpose of imparting UV protection and antibacterial functions [44]. A very thin layer of composite fiber web significantly reduced the transmission of UV radiation and exhibited an ultraviolet protection factor of >50, indicating excellent UV protection. Layered fabric systems with zinc oxide nanocomposite fiber webs containing 5 wt% zinc oxide exhibited over 98% reduction in both *Staphylococcus aureus* and *Klebsiella pneumoniae*. The same research group has also prepared electrospun TiO_2/PVA nanocomposite fiber webs for application in multifunctional textiles [45]. Layered fabric systems with electrospun TiO_2 nanocomposite fiber webs were demonstrated to show UV-protective properties, antibacterial functions, formaldehyde decomposition ability, and ammonia deodorization efficiency, which exhibit high potential for the use in sports/outdoor textiles and technical textiles.

In addition to incorporation of functional substances in the solution before electrospinning, post-spin treatment of the fibers, such as surface modification or coating, can also endow the fibers with certain functions with maximized surface density of the reactive substances. Chen et al. have conducted surface oximation of electrospun PAN mats with excess hydroxylamine to form polyacrylamidoxime (PAAO), which enables the fiber mats to react with organophosphate pesticides or chemical warfare agents [46]. They have developed breathable chemical and biological detoxifying protective fabrics via functionalization of electrospun fiber mats using a layer-by-layer electrostatic assembly technique. The chemically reactive polyanion, poly(N-hydroxyacrylamide) or poly(hydroxamic acid) (PHA), and bactericidal polycation, poly(N-vinylguanidine) (PVG), were synthesized and assembled electrostatically to generate multifunctional coatings on prefabricated PAN fiber mats (Figure 10) [47].

2.5 Antimicrobial membranes

The incorporation of antimicrobial agents such as silver, chitosan into electrospun fibers has been demonstrated to impart antimicrobial properties to the filters. There are generally two approaches for introducing silver

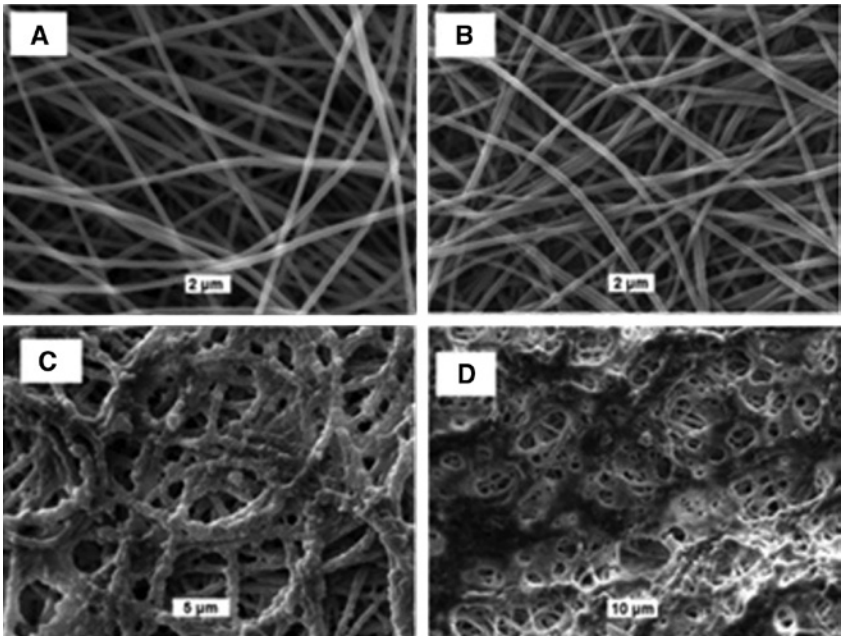

Figure 10: Typical SEM images of (A) prefabricated PAN fiber mat (scale bar: 2 μm); (B) functionalized PAN fiber mat $(PVG/PHA)_{10}$ (scale bar: 2 μm); (C) functionalized PAN fiber mat $(PVG/PHA)_{20}$ (scale bar: 5 μm); (D) functionalized PAN fiber mat $(PVG/PHA)_{30}$ (scale bar: 10 μm). For details, see Ref. [47]; reprinted with permission from American Chemical Society.

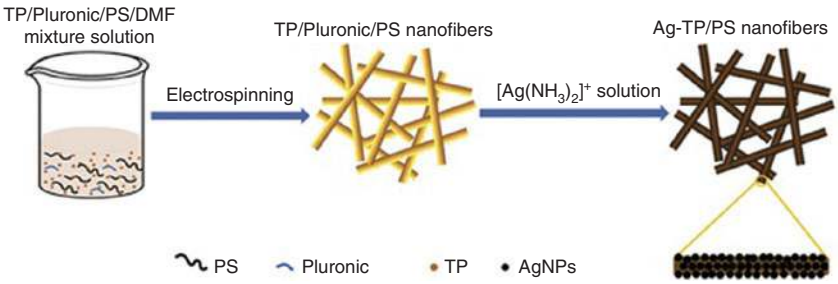

Figure 11: Schematic illustration of the preparation of Ag-TP/PS nanofiber membrane. For details, see Ref. [49]; reprinted with permission from Elsevier.

nanoparticles (AgNPs) in/onto nanofibers: one implies the inclusion of pre-synthesized AgNPs in polymer during the electrospinning process [48], and the other relies on the deposition of AgNPs on nanofibers via *in situ* reduction of silver ion during the posttreatment process. For example, Liu et al. has developed an efficient and environmentally friendly method to prepare AgNP-coated tea polyphenols/polystyrene (Ag-TP/PS) nanofiber membrane, which combines electrospinning and *in situ* reduction of $[Ag(NH_3)_2]^+$ using TP as the reductant and stabilizer (Figure 11) [49]. In this method, TP/pluronic/PS nanofiber membranes are fabricated by electrospinning and then immersed in the aqueous solution of $[Ag(NH_3)_2]^+$. While TP is being released from TP/pluronic/PS nanofibers, the surface of the nanofibers could function as reactive sites for reduction of $[Ag(NH_3)_2]^+$ without any extra reagents. The SEM image (Figure 12B) shows that AgNPs can be densely and uniformly coated on the surface of TP/pluronic/PS nanofibers. The antibacterial assays reveal that Ag-TP/PS nanofiber membrane possesses extraordinary antibacterial activity against both Gram-positive *Staphylococcus aureus* and Gram-negative *Escherichia coli* microorganisms. Chitosan is another widely used antimicrobial agent due to the interaction between the positively charged amine groups on the chitosan backbone and negatively charged components in the microbial cell membranes. Desai et al. have fabricated nanofibrous filter media by electrospinning of chitosan/PEO blend solutions onto a spun bonded nonwoven polypropylene substrate. Heavy metal binding, antimicrobial and physical filtration efficiencies of these chitosan-based filter media were studied [50].

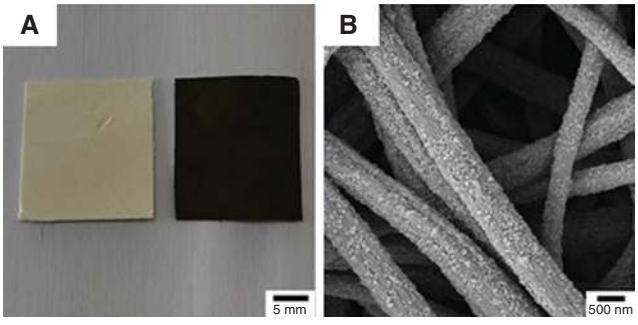

Figure 12: (A) Digital photo of TP/pluronic/PS membrane (left) and Ag-TP/PS membrane (right); (B) SEM images of Ag-TP/PS membrane. For details, see Ref. [49]; reprinted with permission from Elsevier.

3 Electrospun fibers for water purification

3.1 Filtration of suspended pollutant particles

Microfiltration and ultrafiltration membranes have drawn increasing attention to provide low-energy cost strategies for wastewater treatment. Electrospun nanofiber membranes (ENMs) are potential candidates for filtration membranes as they possess high porosity and tunable pore sizes. Based on size exclusion, they can be used to remove suspended pollutant particles, chemicals, or bacterial in the solution. Suspended micro-sized particles such as flocs and dusts are the most common pollutants in water, which are removed using microfiltration membranes with micro- or submicro-sized pores (0.1 μm–10 μm). Comparisons between ENMs and commercial microfiltration membranes, both composed of poly(vinylidene) fluoride (PVDF), have been made by Kaur and coworkers. ENMs and commercial microfiltration PVDF membranes were plasma treated and grafted with methacrylic acid to render them the same pore size (about 0.5 μm) and surface hydrophilicity. The grafted ENMs display higher porosity and shows better filtration performance with higher water flux density [51]. To demonstrate the use of ENMs in practical application, Shirazi et al. tested the performance of electrospun PS membrane for the treatment of wastewater

from biodiesel industries by physical filtration and found it to be (>90%) highly effective in removing the total solid and total dissolved solid in the wastewater [52].

Even though, performance of ENMs with more than 95% efficiency have been reported in removing particle size of 3–10 μm, they are insufficient for rejecting nano-sized particles smaller than 0.1 μm from an aqueous solution [53]. Hence, the use of ENMs can only be limited in the pretreatment process. To improve the separation efficiency of smaller molecules, further decrease in the pore size of ENMs or incorporation with other materials is necessary. Elbahri et al. reported a bio-hybrid membrane, which could be used to remove metal NPs (such as Au NPs) from water with efficiency as high as 97% [54]. These membranes were fabricated by using electrospun nanofibers composed of poly (acrylonitrile-co-glycidyl methacrylate) (PANGMA) with epoxy groups. Subsequently, bovine serum albumin (BSA) proteins were immobilized on these nanofibers through conventional amine-epoxy reaction. The wetting during the filtration process gave rise to conformational change of BSA proteins. The swollen proteins conferred the membranes' smaller pore sizes, leading to more steric hindrance (Figure 13). In addition, the exposed functional groups of BSA during the conformational change were able to capture metal NPs via protein-metal interactions such as Van der Waals and hydrophilic interactions [54]. Thus, these bio-hybrid membranes have a good performance in the removal of Au NPs with a diameter smaller than 100 nm.

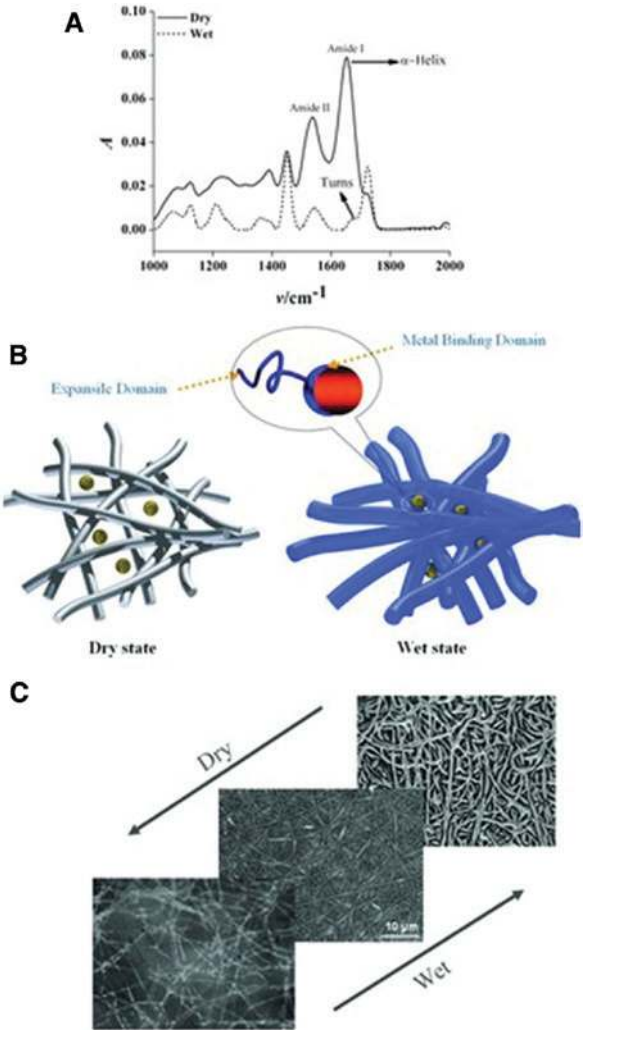

Figure 13: (A) Fourier transform infrared spectroscopy spectra of the BSA/PANGMA ENMs as dry (the solid upper line) and wet (the dashed lower line). (B) The sketch illustrates how the swollen functionalized nanofibers capture the nanoparticles. (C) The optical images show morphological change of the membrane and the reversible swelling of the functionalized nanofibers in wet and dry states implying a smart-performing membrane. For details, see Ref. [54]; reprinted with permission from Wiley.

3.2 Removal of organic compounds

3.2.1 Oil

Organic compounds such as oil, proteins, and chemicals pose health hazards and have to be removed from drinking water. Modification or functionalization of ENMs could serve as a promising solution for the removal of the organic compounds in water compared to physical retention. Oil is an organic compound commonly encountered in wastewater due to the industrial manufacturing. The removal of oil in water has been achieved using porous membranes with hierarchical structure [55]. As shown in Figure 14, the membrane consisted of three layers: (1) the bottom layer is a conventional porous nonwoven mat based on micro-sized PET fibers, (2) the middle layer is a water-resistant electrospun PVA mat followed cross-linking with glutaraldehyde, and (3) the hydrophilic top layer is fabricated by incorporating a cross-linked PVA layer with surface-oxidized multiwalled carbon nanotube (MWCNT). In this

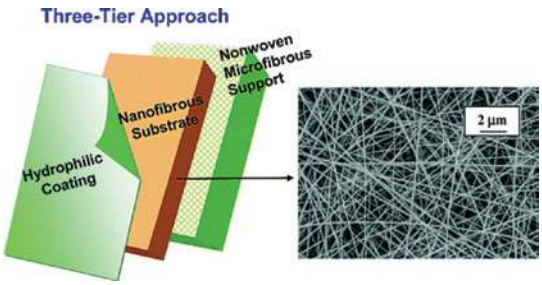

Figure 14: Three-tier approach to fabricate high flux membranes. For details, see Ref. [55]; reprinted with permission from American Chemical Society.

case, PVA is chosen to fabricate the membrane due to its excellent chemical stability, biocompatibility, processibility, and high water permeability. However, one drawback of the electrospun PVA membrane is that its mechanical strength is not strong enough for practical application. To overcome this problem, PVA nanofibers are cross-linked with glutaraldehyde and also incorporated with MWCNT to significantly improve the mechanical property. Compared to the conventional microfiltration membrane with porosity of about 34% [56], the three-tier membranes possess much higher porosity (about 80%), leading to high flux during filtration process. The incorporation of surface-oxidized MWCNT in the top layer of cross-linked PVA is believed to provide effective hydrophilic nano-sized channels for water to pass through, which ensures the high separation rate and low fouling for oil/water separation. Oil/water emulsion tests showed that this three-layer filtration membrane showed high flux rate (about 330 l/m^2h at an inlet pressure of 100 psi) and excellent rejection rate (99.8%).

PAN, which has good hydrophobicity and mechanical property, is suitable to be used as a material for filtration membranes used in water treatment. Yoon et al. has prepared another kind of three-tier filtration membrane for oil/water separation based on electrospun PAN nanofibers [56]. In this case, electrospun PAN nanofibers were deposited on the surface of PET mat to achieve high porosity of the resulting membranes. To support the uniform coating of the top layer of chitosan, an asymmetric structure of PAN layers was constructed. Electrospun PAN nanofibers with a diameter of about 700 nm were deposit onto the PET substrate to form a coarse PAN layer. Subsequently, a fine PAN layer with a diameter of about 120 nm was coated on top of the coarse layer by changing the concentration of PAN electrospinning solution (Figure 15). Finally, chitosan was impregnated in the fine PAN layer to coat on the PAN nanofibers uniformly. As the fouling rate is mostly related to the surface characteristic of the membrane, the hydrophilic chitosan coating on PAN nanofibers allows water to pass through the membrane without losing much flow rate, minimizing the fouling concern. Thus, this three-tier membrane showed a flux rate, which is an order of magnitude higher than the commercial membranes in the oil/water emulsion test.

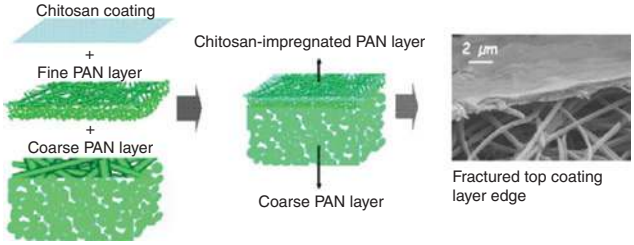

Figure 15: Fabrication schematics of the electrospun scaffold with a coating layer. SEM image represents the fractured composite membrane containing PAN nanofibrous scaffold (with 4~12 wt% sequential electrospinning) and chitosan coating. For details, see Ref. [56]; reprinted with permission from Elsevier.

3.2.2 Proteins

Protein is another commonly encountered organic compound, particularly in wastewater treatment. Even low concentration (1%) of proteins in the river could use up the dissolved oxygen, leading to no survival of aquatic life in the river. Functionalization of ENMs with effective moieties that have strong affinity to proteins could be employed to remove the protein in water. Zhang et al. have shown that electrospun PAN membranes can serve as substrate to remove bromelain protein in water [57]. The hydrophobic surface of PAN nanofibers is not suitable for the immobilization of ligand Cibacron Blue F3GA (CB), which has good affinity to bind with bromelain. Thus, chitosan was used as a linker to adsorb on the surface of PAN nanofibers and bind with CB via covalent bond. The resulting membranes showed high performance in the adsorption of bromelian (up to 370 μmol/g membrane), which is five times higher than the untreated PAN membranes.

The previously mentioned bio-hybrid PANGMA ENMs can also be employed to remove proteins in water [58]. After functionalization with BSA or Candida Antarctica Lipase (Cal-B), the resulting PANGMA ENMs exhibit good separation rate for rejecting BSA (88%) or Cal-B (81%) in the retention test. It is believed that this promising result is attributed to the small pores in the ENMs due to the swelling of the proteins as well as the exposed functional groups of BSA or Cal-B on the nanofibers, which are able to capture the biomolecules during filtration process.

3.2.3 Dye

Wastewater discharge from textile, paper, and plastic industries often generate a significant amount of reactive azo dye [59, 60]. Once these dyes enter into environment, they can be toxic and carcinogenic to aquatic living organisms. Thus, they are considered as one of the major sources of water pollution, which need to be addressed.

One common example of azo dye is Methyl Orange (MO). MO is water soluble and is suspected to be carcinogenic and harmful to humans as well as aquatic life.

Novel magnetic α-Fe_2O_3 nanofibers are prepared via electrospinning of PVA solution containing ferric nitrate, followed by calcination of polymer nanofibers at 800°C. Ten milligrams of α-Fe_2O_3 was demonstrated to be effective in degrading and decolorizing 80 mg/l of MO dye over 10 cycles. The decolorization effect is due to the Fe^{3+} species on the surface of the nanofiber that reacts with hydrogen peroxide and leads to the formation of hydroxyl and perhydroxyl radicals, which decompose the azo dye. The results also show that the nanofiber structures possess much higher efficiency than mesoporous Fe_2O_3-SiO_2 composites or core-shell Fe-Fe_2O_3 nanostructures [61]. Furthermore, α-Fe_2O_3 also possesses good magnetic properties and can be separated from water easily by the use of an external magnetic source after removal of the dye. Similar dye removal can also be achieved using the photocatalytic effect of TiO_2 and ZnO nanofibers, which will be addressed in the latter section [62, 63].

Malachite green is another example of an organic compound, which has emerged as a controversial agent in aquaculture [64]. Vinyl-modified mesoporous PAA with SiO_2 composite ENMs can also be used for the adsorption of malachite green with an absorption capacity of 240.49 mg/g [65]. The mechanisms of malachite green adsorption on the PAA/SiO_2 fibers membranes are due to the electrostatic interaction between the negative-charged silica surface and positive-charged malachite green molecule. As the specific surface area and high energy of the silica surface is large, it might have a physical adsorption effect. The third reason is due to the conjugation effect between the delocalized π-bond of the dye molecule and the vinyl group of the membrane surface [65].

Another approach to the adsorption of the dye is to functionalize the fiber membrane. Teng et al. demonstrated using PVA/SiO_2 ENMs functionalized with cyclodextrin groups for absorbent of indigo carmine dye [66]. The adsorption capacity was 495 mg/g and can be achieved in <40 min. Methyl blue removed by hollow silver-doped carbon fiber with efficiency up to 85% has also been reported [67].

3.3 Removal of organic compounds by catalytic degradation

An alternative to treat polluted wastewater is through catalytic degradation. Ultraviolet light is employed to activate the inorganic catalysts such as TiO_2. TiO_2 is a preferred choice as it is cheap, abundant, chemically stable, non-photodegradable, and most importantly, it can be activated by natural sunlight [68]. An et al. fabricated two different types of TiO_2 fiber membranes by batch process and continuous process as depicted in Figure 16. Batch process is a two-step fabrication approach to

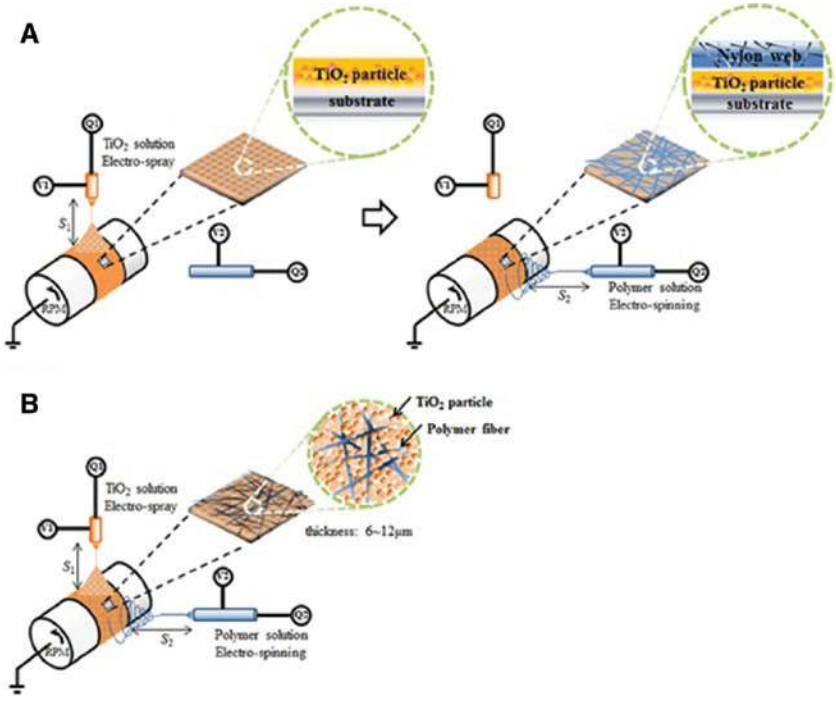

Figure 16: Schematics show the fabrication methodology to produce titania fiber membrane by (A) batch process and (B) continuous process. For details, see Ref. [68]; reprinted with permission from Elsevier.

electrospray TiO_2 NPs followed by electrospinning of polymer fibers onto the substrate. The resulting structure is a 2-D structure. On the other hand, continuous process refers to electrospraying of TiO_2 NPs and the polymer solution simultaneously to have the TiO_2 NPs embedded within the membrane. Based on the Methylene blue degradation test, the latter method was more efficient than the 2-D layered structure. It is also believed that this method of fabrication is also superior compared to the electrospun polymer solution containing TiO_2 NPs. Electrospun nylon fibers with TiO_2 NPs are also shown to significantly reduce the toxicity of 2,4-dichlorophenol and 2,4,6-trichloro-phenol when tested against *Daphnia magna* [68].

In_2S_3 is another promising photocatalyst as it can be easily activated using visible light. However, the usage of In_2S_3 photocatalyst is limited by its recombination rate. A promising combination is to use carbon fiber with In_2S_3 due to the excellent electron conductivity of carbon [69]. Carbon fiber integrated with In_2S_3 fiber was fabricated by Gao and co-workers and demonstrated high efficiency to remove *E. coli* cells under visible light irradiation.

3.4 Removal of heavy metal ions

Heavy metal (lead, zinc, copper, cadmium, mercury, and chromium) contamination in wastewater has been a growing concern due to the toxicity effect to living organisms. Excessive lead (Pb) ions results in severe damage to kidneys, liver, brain, and nerve system resulting in acute lead poisoning. Chitosan-based ENMs have excellent adsorption characteristics for heavy metal due to its high hydrophilicity, flexible structure of polymer chain, large number of functional group such as the amino and hydroxyl group, which act as chelation sites [70]. Chitosan cross-linked with glutaraldehyde can be used for zinc ion adsorption [70]. Yan Li and coworkers electrospun chitosan solution with Pb(II) as template and cross-linked with glutaraldehyde, showing improvement in the adsorption capacity of Pb(II) ions by two to five times [71]. Similar improvements in Pb absorption was also achieved with Pb(II) ion-imprinted chelating compounds imprinted in the nanofibers [72]. Silica fiber membrane can also be used for heavy metal adsorptions. Recently, ENMs constructed by nonporous SiO_2 cores and mesoporous shells have been reported to be a more efficient and convenient way for the removal of heavy metal ions [73].

Beside chitosan and silica, other electrospun materials have also shown adsorption capacity for heavy metals. Rad et al. demonstrated the adsorption of Ni and Cd ions by using zeolite nanofiber [74]. PMMA fibers with rhodamine show high adsorption capacity for Ag and Pb ions [75]. Carbon materials with MnO_2 can also be employed to remove heavy metals from water. Carbon/MnO_2 fibers can be formed by anodic electrodeposition of MnO_2 onto the carbon fiber. The specific capacitance was reported to have a value of 387 F/g, which is comparable to many other reports [76]. Magnetic materials such as Fe_3O_4 can also be incorporated into carbon fibers as shown in Figure 17. The C/Fe_3O_4 nanocomposites demonstrate high capability to remove Rhodamine B dye and Cu^{2+} ions from aqueous solution [77].

3.5 Removal of sodium chloride

Producing fresh water from brackish water and/or even seawater is an inevitable step to solve the water crisis that brings negative impact to the environment, health, and economy. Techniques such as electrodialysis, multistage flash distillation, and reverse osmosis have been used to produce purified fresh water [78]. Recently, capacitive deionization (CDI) has drawn attention as a new strategy to desalinate brackish water due to their low cost and high energy efficiency [79]. To achieve high electrosorption capability, carbon materials are highly promising as electrode materials in CDI [80].

Electrospinnng of ACF can be fabricated directly from PAN, followed by chemical activation with CO_2 at 750°C–900°C. The ACF demonstrates improvement for the removal of salt ions using capacitive deionization [81]. Increasing porosity and conductivity leads to high performance of ACF. Porous ACF can be fabricated by co-electrospinning of PAN/dimethyl sulfone (PAN/$DMSO_2$). After carbonization under N_2, $DMSO_2$ evaporated, and nano-sized pores formed in the ACF [14]. Embedding CNTs in ACF can increase both conductivity and porosity of the resulting fibers to achieve good desalination capacity of 6.4 mg/g [82]. Dong et al. have prepared ENMs, which are fabricated by co-electrospinning of ACF and reduced graphene oxide (rGO) [83]. After activation by using CO_2, the electrospun rGO/ACF membranes were employed as high-performance electrodes with adsorption capacity as high as 7.2 mg/g (Figure 18). Besides carbon materials, metals can be incorporated into ACF to get an excellent performance. Liu et al. have incorporated Zn into PAN-based ACFs to show high adsorption (10.52 mg/g) of NaCl in water [84]. With higher concentration of Zn, adsorption performance of ACFs is better (Figure 19).

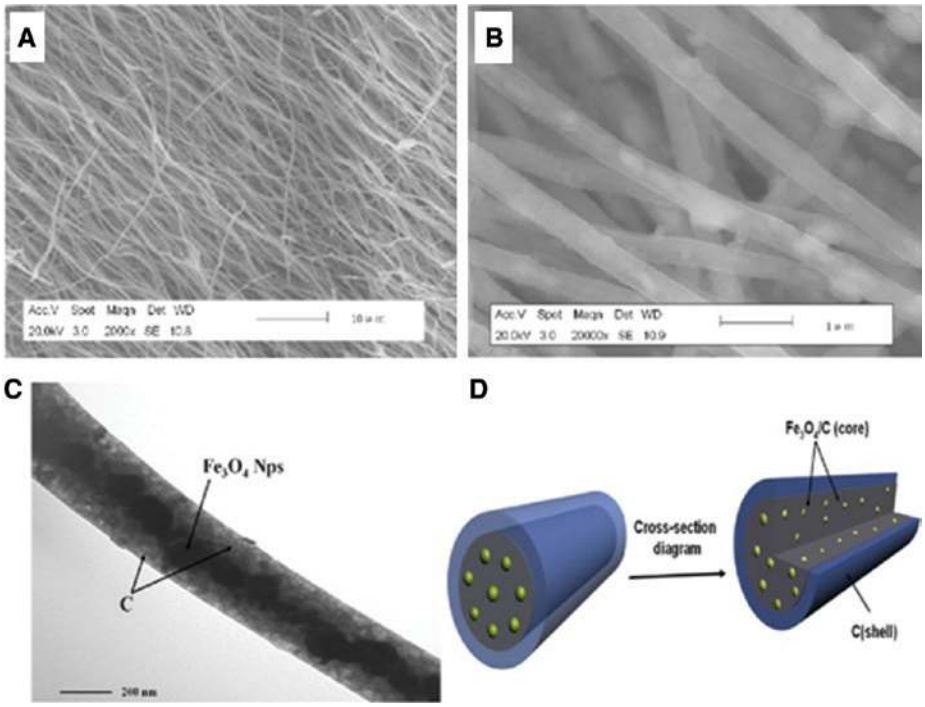

Figure 17: (A, B) shows the FESEM images of [C/Fe_3O_4]/@C coaxial nanocables (C) TEM image, (D) structural schematic diagram of [C/Fe_3O_4]/@C coaxial nanocables. For details, see Ref. [77]; reprinted with permission from Springer.

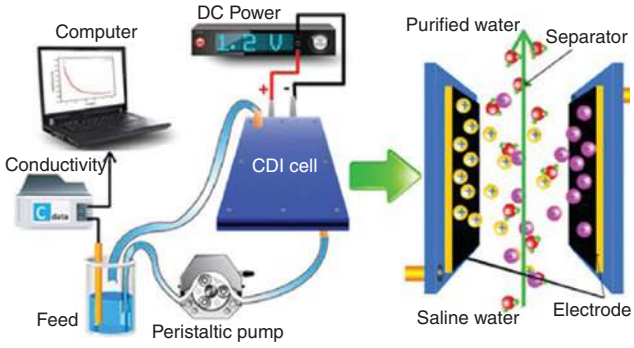

Figure 18: Schematic of the CDI setup. For details, see Ref. [83]; reprinted with permission from Elsevier.

3.6 Removal of other chemicals

As mentioned previously, ENMs incorporated with functional ligands on their surface can serve as promising filters to remove specific kinds of metal NPs or proteins. This strategy is also applicable in removing other organic chemicals with small molecular weight. Propranolol is a common chemical that has practical relevance in environmental analysis. The detection of propranolol residue in surface water is able to show leaking sewers [85]. Yoshimatsu et al. have reported that molecularly imprinted ENMs show selective adsorption to propranolol molecules

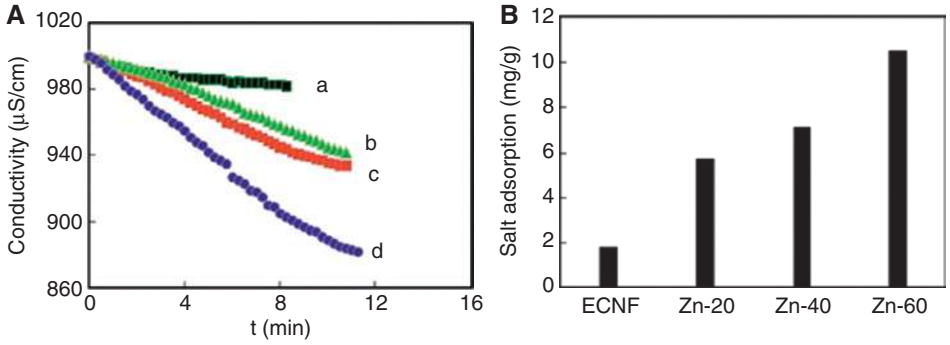

Figure 19: (A) Ionic adsorption behavior of PAN-based ACF (a) and Zn-ACF (b–d) electrodes in CDI cell in 500 mg/l of NaCl solution. Curves b–d correspond to Zn-20, Zn-40, and Zn-60, respectively. (B) The salt adsorption per cycle on different electrodes derived from the average of five charging-discharging cycles. For details, see Ref. [84]; reprinted with permission from Elsevier.

in water, and the adsorbed propranolol could be collected from ENMs via solvent extraction [86]. The molecularly imprinted ENMs were fabricated by electrospinning of the mixture of PET polymers and polymeric NPs composed of racemic propranolol (Figure 20A). To test the adsorption capability, the ENMs were soaked in the propranolol water solution within 1 h to ensure the full adsorption of propranolol on ENMs. The adsorbed propranolol molecules on ENMs can be recovered by treating with a mixture of acetonitrile, water, and acetic acid, which gave the highest propranolol recovery. These imprinted ENMs could be used for solid phase extraction of propranolol from water. These imprinted ENMs are stable, and the propranolol recovery remained constant after several cycles. Compared to the non-imprinted ENMs, which were prepared under the same condition but without imprinted propranolol, imprinted ENMs showed significantly higher elution recovery of β-antagonists including propranolol, pindolol, acebutolol, etc. (Figure 20). With the high sensitivity to propranolol (2–4 ng ml^{-1}), the imprinted ENMs are suitable to be used to detect trace propranolol in tap water.

The molecularly imprinted ENMs can also be applied in the separation of chiral molecules. Sueyoshi et al. have reported that imprinted ENMs based on CA are employed to separate D-glutamic acid (D-Glu) or L-glutamic acid (L-Glu) in the filtration test [87]. The imprinting molecules N-α-benzyloxycarbonyl-D-glutamic acid (Z-D-Glu) or N-α-benzyloxycarbonyl-lglutamic acid (Z-L-Glu) were dissolved in N,N-dimethylformamide (DMF) and mixed with CA DMF solution. These mixtures were then eletrospun to form two types of fibrous membranes imprinted by Z-D-Glu or Z-L-Glu. These imprinted ENMs exhibited adsorption selectivity, i.e. chiral recognition ability. ENMs imprinted by Z-D-Glu adsorbed more D-Glu molecules, while ENMs imprinted by Z-L-Glu adsorbed more L-isomers. In this case, although the chiral separation rate of imprinted ENMs is not high, these ENMs with high surface area and porosity are promising candidates to improve both chiral selectivity and flux for practical application.

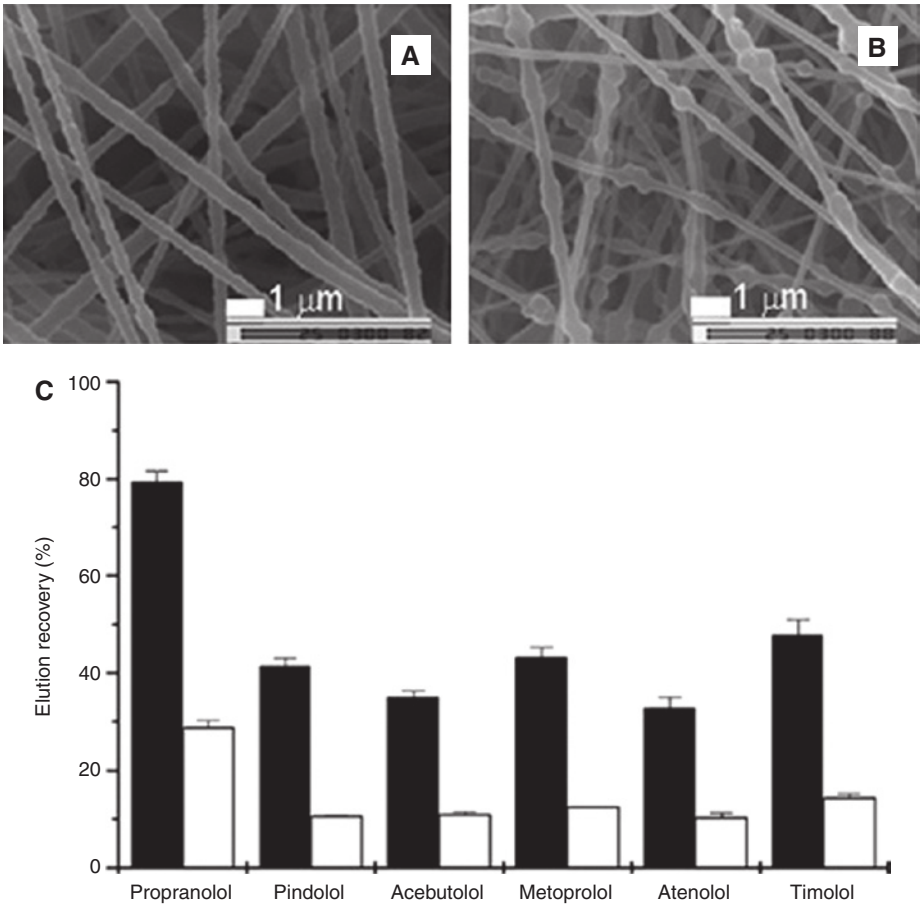

Figure 20: 2SEM images of electrospun nanofiber membranes containing (A) 50% of imprinted nanoparticles, (B) 50% of non-imprinted nanoparticles. (C) Selectivity of nanofiber-based SPE. Recovery of β-antagonists at the elution step from the imprinted (solid) and the non-imprinted nanofiber(open). For details, see Ref. [86]; reprinted with permission from Elsevier.

4 Sensors for environmental applications

4.1 Gas sensors

Gas sensor is used to detect the presence of different gases in an area, especially those that might be harmful to humans or animals. The development of gas sensor technology has received considerable attention in recent years for monitoring environmental pollution. Potential materials such as conductive polymers, semiconductors, and carbon composites have been used as sensing materials to detect the targeted gases based on various sensing techniques such as acoustic wave, conductivity, photoelectric, and optical techniques. It is worth noting that because the surface reactions/interactions between the gas molecules and sensing materials largely depend on the active centers and the defects existing on the surface layer of the materials, the sensor response is usually determined by the surface-to-volume ratio of materials. To satisfy this requirement, researchers have developed 1-D electrospun nanofibers as highly sensitive gas sensors because of the ultrahigh surface-to-volume ratio and high gas accessibility. So far, many attempts have been carried out to prepare ultrasensitive gas sensors to detect vapors of NH_3, H_2S, H_2, O_2, NO, NO_2, moisture, and VOCs (such as methanol, ethanol, acetone, formaldehyde, benzene, aniline, etc.) with improved detection limits using ENMs as sensing structures.

Various kinds of conducting polymers, such as polyaniline (PAni), poly(3,4-ethylenedioxythiophene):poly(styrene sulfonate) (PEDOT:PSS), etc., are currently used as gas sensors [88, 89]. The conductivity of such polymers results in the existence of charge carriers and from the ability of those charge carriers to move along the bonds of the polymer chains. These conducting polymers show chemical selectivity, which allows them to act as excellent materials for the immobilization of gas molecules and exhibit highly reversible redox behavior with a distinguishable chemical memory. PAni doped with (+)-camphor-10-sulfonic acid (HCSA) represents one of the most studied classes of electrically conductive polymers and is particularly suitable for application as gas sensor due to the excellent tunable electrical conductivity. The activity of the dopant can be switched reversibly between oxidation and reduction states simply by exposure to acidic and basic gases, respectively. However, PAni is relatively hard to process into fibers, due to its rigid backbone and relatively low molecular weight. To overcome this challenge, Zhang et al. have recently reported the successful production of continuous fibers of pure PAni doped with HCSA by coaxial electrospinning and subsequent removal of the shell polymer PMMA by dissolution [88]. These fibers were shown to exhibit electrical conductivities as high as 130 S cm^{-1} when fully doped and, thus, present a broader range of tunable conductivity with which to work during gas sensing than most of the similar systems reported. These electrospun PAni fiber sensors exhibit high sensitivities and fast response times to both NH_3 and NO_2 gases. In addition to conductive polymers, many researchers have studied polymer composites incorporated with conductive nanocarbon (such as graphene, CNTs) as chemical vapor sensors because they can amalgamate both the selectivity of the nanocarbon materials and the polymer matrix [90, 91]. For example, rGO sheets were self-assembled onto the surface of electrospun positively charged PVA/PEI composite nanofibers to form an ultrathin coating [90]. These rGO/polymer composite nanofibers were used to fabricate NO_2 sensor and exhibited a high sensitivity of 1.03 ppm^{-1} with excellent selectivity and good reversibility.

Besides conducting polymer composites, semiconducting metal oxides such as SnO_2, TiO_2, ZnO, Fe_2O_3, In_2O_3, and other wide band gap metal oxides are widely used to detect trace concentrations of various gases in air via charge transfer interactions between the sensor and chemisorbed species that change the sensor's resistance. Sensing characteristics can be enhanced by loading of noble-metal catalysts (Pd, Pt, Au, etc.) [92–94] or by the formation of hetero-nanostructured composites between oxide additives/catalysts [95–97]. These ceramic nanofibers are mostly fabricated via a combination of sol-gel and electrospinning process followed by thermal treatment in the air. Promising results of the gas-sensing performance of semiconductor-based nanofibers have been reported. Wang et al. have prepared Pd-loaded SnO_2 nanofibers via electrospinning, calcination followed by *in situ* reduction. The nanofiber gas sensors have been found to have superior characteristics in terms of time and selectivity compared with thin-film structures of the same materials. By adjusting the Pd-loaded levels, high sensing performance such as high response, low detection limit (20 ppb), fast response (4–13 s) and recovery (3–9 s), and high selectivity toward H_2 can be obtained at room temperature [92]. Liang et al. prepared CuO-loaded In_2O_3 nanofibers as ultrasensitive and ultraselective H_2S sensors via electrospinning the solution of PVA mixed with both the two metal precursors followed by calcinations [95]. The prepared CuO-loaded In_2O_3 nanofibers combine the advantages of high gas accessibility of nanofibrous structures and the distinctive chemical interaction between CuO and H_2S. The loading

of CuO on In_2O_3 nanofibers significantly enhanced the gas response toward 5 ppm H_2S from 515 to 1.16×10^5 at 150°C and a high response of 9.17×10^3 (toward 5 ppm H_2S) at room temperature. Figure 21 presents the morphology of various doped ceramic electrospun fibers for application as gas sensors.

4.2 Detection of explosives

Given the extensive applications of explosives in mass destruction weapons as well as their environmental toxicity, explosive detection is very important for applications in homeland safety, industrial process safety control, and daily life. Fluorescent sensing is an effective and extensively applied method for the detection of explosives because of its short response time, excellent sensitivity, simplicity, and cost effectiveness compared to the currently widely used analytical methods, such as chromatography, ion mobility spectrometry, Raman spectroscopy, and X-ray diffraction, that are expensive, complex, and lack portability. The performance of most fluorescent sensory materials is limited by film thickness due to the fact that diffusion of analyte vapor in dense films is slow. Electrospinning is a powerful technique to produce nanofibrous sensing films with large surface-to-volume ratio, inherent high porosity, and easy accessibility of sensing materials.

Fluorescent-conjugated polymers, which exhibit sensitive and selective fluorescence quenching to nitro compounds, have been applied as film-sensing materials for the detection of explosives because of their efficient exciton migration along the polymer chains. Sun et al. have prepared electrospun fluorescent pyrene-polyethersulfone (Py-PES) nanofibrous films with ultrafine fiber diameters <100 nm (Figure 22) [98]. The Py-PES nanofibers were applied for highly sensitive detection of explosives, such as picric acid (PA), 2,4,6-trinitrotoluene (TNT), 2,4-dinitrotoluene (DNT), and 1,3,5-trinitroperhydro-1,3,5-triazine (RDX) in aqueous phase with limits of detection (S/N=3) of 23, 160, 400, and 980 nM, respectively. A similar work was done by Xue et al., who developed a highly sensitive, low-cost nanofibrous sensing film toward nitrocompounds via doping small fluorophores into low-cost polyethylene oxide followed by electrospinning [99].

4.3 Detection of heavy metal ions

Among the many causes of water pollution, those generated by heavy-metal ions pose a serious threat to mankind and have been a topic of concern for decades now. Various detection techniques have been devised, of which, fluorescent-based sensors have been identified as an efficient sensing platform with regard to their simple visual detection of metal ions in the environmental

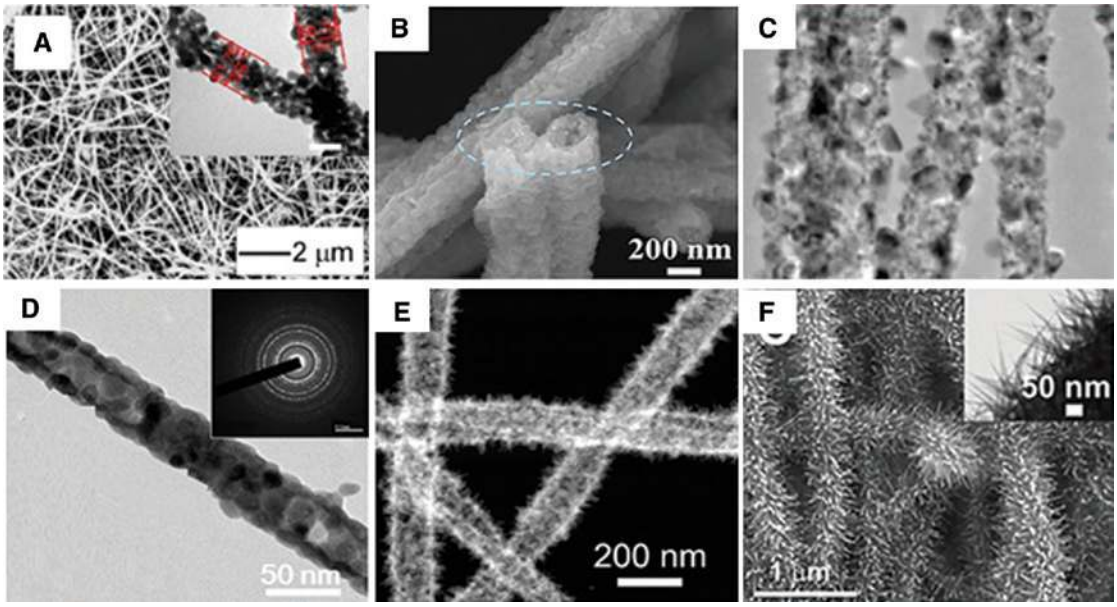

Figure 21: SEM or TEM images of different electrospun metal oxide nanofibers for gas sensing: (A) Pd-loaded SnO_2 fibers for sensing hydrogen; (B) hollow Au/V_2O_5 fibers for sensing ethanol; (C) Pt-loaded NiO fibers for sensing ethanol; (D) CuO-loaded In_2O_3 nanofibers for sensing H_2S; (E) SnO_2-doped α-Fe_2O_3 nanotubes for sensing ethanol and acetone; (F) $ZnSnO_3$ nanoneedle/TiO_2 nanofiber heterojunctions for sensing humidity. For details, see Refs. [92–97]; reprinted with permission from American Chemical Society, Elsevier, Royal Society of Chemistry.

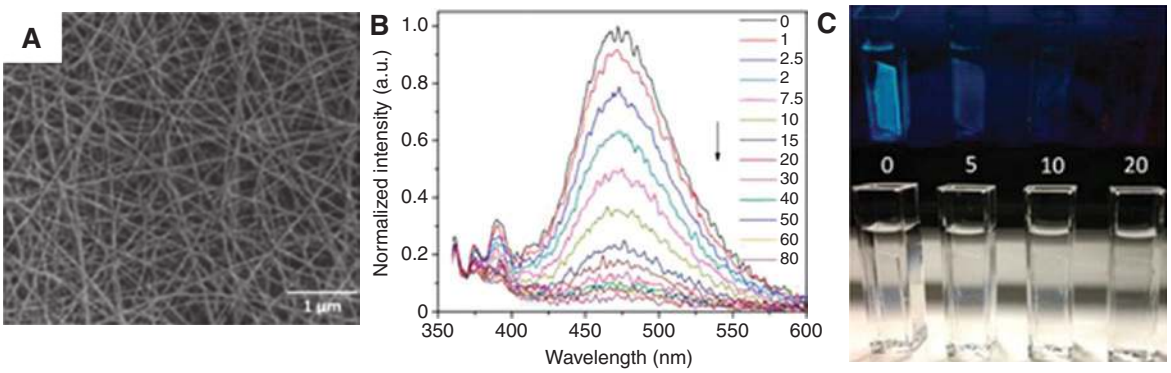

Figure 22: (A) SEM image of the Py-PES nanofibrous film using 4% PES concentration at a fixed Py concentration of 0.1 M and DMF/THF ratio of 4:6; (C) concentration-dependent fluorescence quenching of Py-PES nanofiber film upon the addition of different concentrations (μM) of TNT in DI water. (B) Photographs of Py-PES fluorescent nanofiber films in cuvette under UV light (254 nm, upper panel) and visible light (bottom panel) in the presence of various TNT concentrations (0, 5, 10, and 20 μM). For details, see Ref. [98]; reprinted with permission from American Chemical Society.

samples. Uyar et al. have effectively integrated fluorescent gold nanoclusters (AuNC) into electrospun polyvinyl alcohol nanofibers [100]. The resulting freestanding composite nanofibrous membranes (AuNC*NFM) could retain the fluorescence properties of AuNC over extended periods of time up to 6 months in an applicable environment involving temperatures up to 100°C. Upon coordination with Hg^{2+} in aqueous solution, the color change of the composite membrane can be easily observed by the naked eye (Figure 23). The AuNC*NFM hybrid system has a high sensitivity to Hg^{2+} down to 1 ppb, and its selectivity has been demonstrated by its response to other common metal interferences (Pb^{2+}, Mn^{2+}, Cu^{2+}, Ni^{2+}, Zn^{2+}, Cd^{2+}). The same group later developed a fluorescent gold nanocluster decorated polycaprolactone (PCL) nanofibers for real-time visual monitoring of Hg^{2+} detection at a even higher sensitivity down to ppt level in water [101].

Recently, some approaches have been developed for simultaneous detection and removal of metal ions. Li et al. has reported an intriguing and economic pyromelliticdianhydride(PMDA)-grafted deacetylated cellulose acetate (DCA-PMDA) electrospun nanofibrous membrane with dual functions, the adsorption (through filtration) and colorimetric detection (through the Na_2S color-producing reaction) of lead(II) ion (Pb^{2+}) in polluted water (Figure 24) [102]. PMDA performs very well as a grafting agent for adsorbents because it can readily react with hydroxyl or amide groups and simultaneously introduce large amounts of carboxyl groups on the adsorbents, which can improve the adsorption capacity for Pb^{2+}. The color of the DCA-PMDA changes from white to dark yellow-brown due to the formation of PbS, which can be leveraged for the colorimetric detection of Pb^{2+} by the naked eye with a detection limit of 0.048 mM and a maximum adsorption

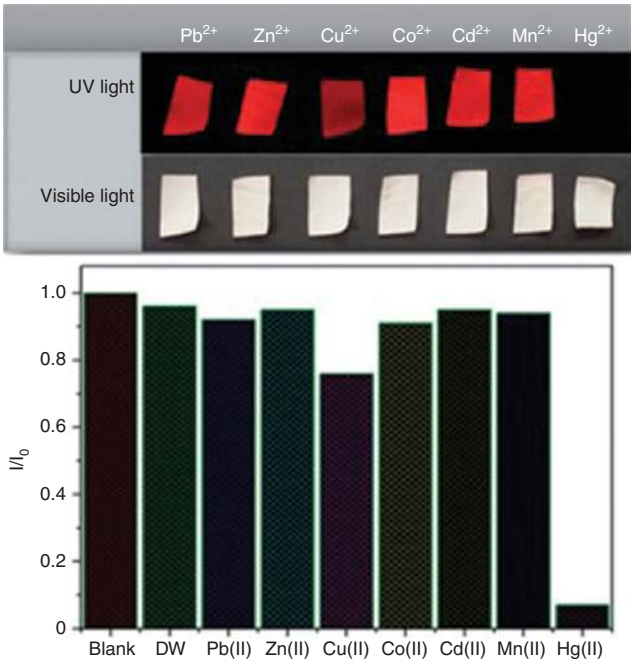

Figure 23: Sensing performance of AuNC*NFM upon exposure to different metal ions in water. The concentration of all metal ions was fixed at 10 ppm. Photographs were taken under UV and white light. For details, see Ref. [100]; reprinted with permission from Royal Society of Chemistry.

capacity up to 326.80 mg g^{-1}. Furthermore, the membrane could be regenerated via extraction of Pb^{2+} with HNO_3 and reused over many cycles without losing functionality. Wei et al. have also developed two kinds of poly(vinyl alcohol) electrospun nanofibrous (PVANF) membranes modified with spirolactam-rhodamineine derivatives (PVANF-SRD) and sulfo-spirolactam-rhodamine derivatives (PVANF-SSRD), which exhibited high selectivity and sensitivity

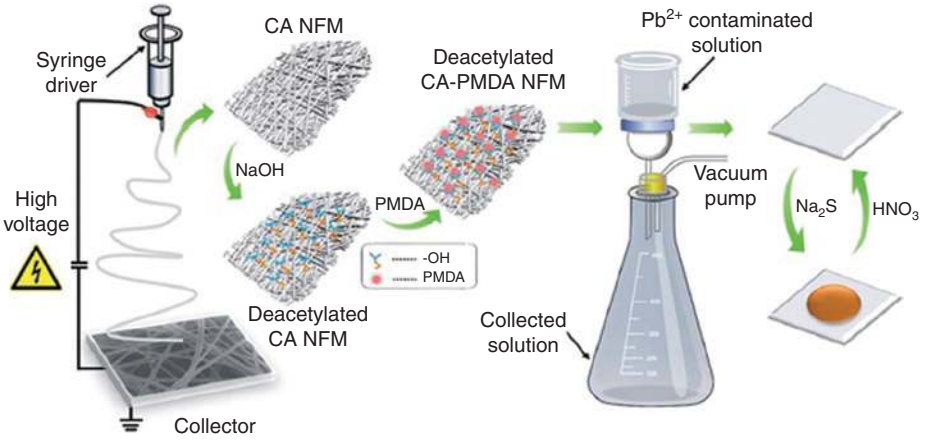

Figure 24: Schematic illustration of the fabrication procedure of DCA-PMDA NFM and simultaneous colorimetric detection and enrichment of target Pb^{2+} by DCA-PMDA NFM. For details, see Ref. [102]; reprinted with permission from Royal Society of Chemistry.

toward Fe^{3+}/Cr^{3+} and Hg^{2+}, respectively [103]. These two membranes could display real-time sensing by the naked eye based on ring-opening reaction of spirolactam-rhodamine derivatives induced by corresponding metals.

5 Conclusions and future perspectives

Air and water pollution is the most significant environmental concern in the 21st century, especially in developing countries. The emerging clean environment technologies provide enormous opportunities for the creation of high value-added products and associated business development. The past decade years have witnessed significant progresses of electrospinnning technique to fabricate functional nanofibrous materials for various applications. Current advances in electrospinning technology provide important evidence of its potential roles in water treatment, air purification, and environmental monitoring and control. The next-generation electrospun air and water filters will combine multifunctionalities and be able to convert hazards to nontoxic substances other than simple absorption and filtration. Therefore, intense interest in electrospinning technology has arisen from not only academic research laboratories but also from companies worldwide such as Dupont, eSpin, Donaldson, Esfil Techno, SPUR nanotechnologies, etc. Though electrospinning has become a versatile technique for generating 1-D nanostructures, the industrial exploration is still young, and many challenges have to be faced. One of the problems is that most electrospun polymer nanofibers and carbon nanofibers are brittle, not suitable for practical applications. Therefore, in the pursuit of functionality and performance, it is also important to achieve good mechanical strength of the fibrous membranes to increase their reusability. The common methods include (i) blending the functional material with a strong carrier polymer [104], (ii) deposition of fragile electrospun nanofibers on micron-sized fibrous substrates [31], and (iii) formation of core-shell structured electrospun fibers with a flexible and self-standing material as the core [105]. Another drawback is the relatively low production rate. Hence, the major task after success in laboratories is to scale up the apparatus and optimization of the process to increase the productivity. The most relevant technological advances that have, to date, been explored to increase the volume of production are mainly based on the modification of the polymer injection system and consist of (i) the introduction of multi-spinneret components that allows parallel multiprocessing and (ii) the development of free surface electrospinning methods. Also, due to the high added value of uniaxially aligned nanofiber yarns in many applications, various modifications of the electrospinning collector geometry have been made, specifically aimed to improve and control the nanofiber orientation when scaling-up the electrospinning production capability [106]. Finally, to make the technology more favorable for industrial application, it is essential to avoid the use of expensive feedstocks and corrosive, toxic solvents, which may cause damage to the environment. Developing the electrospinning process using abundant and renewable raw materials in aqueous solutions will pave the way for large-scale production. Furthermore, melt-electrospinning technique, which spins molten polymer in electric field without using any solvents would be another environmentally friendly approach for producing fibers at industrial scale.

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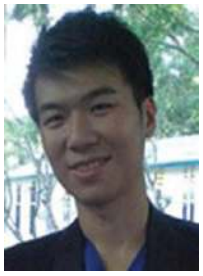

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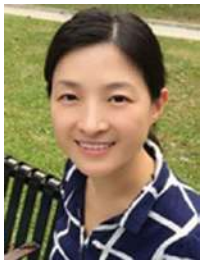

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