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Intelligent Environmental Nanomaterials

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Abstract

Due to the inherent complexity of environmental problems, especially water and air pollution, the utility of single-function environmental nanomaterials used in conventional and unconventional environmental treatment technologies are gradually reaching their limits. Intelligent nanomaterials with environmentally-responsive functionalities have shown potential to improve the performance of existing and new environmental technologies. By rational design of their structures and functionalities, intelligent nanomaterials can perform different tasks in response to varying application scenarios for the purpose of achieving the best performance. This review offers a critical analysis of the design concepts and latest progresses on the intelligent environmental nanomaterials in filtration membranes with responsive gates, materials with switchable wettability for selective and on-demand oil/water separation, environmental materials with self-healing capability, and emerging nanofibrous air filters for PM2.5 removal. We hope that this review will inspire further research efforts to develop intelligent environmental nanomaterials for the enhancement of the overall quality of environmental or human health.

Environmental Significance

Conventional environmental nanomaterials perform relatively simple and fixed tasks and they are unable to adapt or may even loss their original functionalities as the environmental conditions change. On the other hand, the design of intelligent environmental nanomaterials endows the nanomaterials with proactive functionalities so they can self-adjust their properties and thus achieve satisfactory performances under changing environmental conditions. The design of the intelligent environmental nanomaterials may offer some disruptive technologies and has a potential of reforming the landscape of the future of environmental engineering.

1. Introduction

As reported by World Health Organization (WHO) in 2017, about 270,000 children die every year during their first month of life mainly due to the environmental pollution induced prematurity, including lack access to clean water and air pollution.¹ Meanwhile, with the nonrenewable and pollutant-laden fossil fuels dominating the global energy supply, air pollution is worsening in many parts of the world especially where economy is heavily dominated by low-tech manufacturing. 4.2 million deaths and 103.1 million disability in 2015 was attributable to

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ambient particulate matter (PM), especially PM with diameters smaller than 2.5 micrometer, infamously known as PM_{2.5}.² Thus, the ability to remove contaminants from these environments to a safe level and doing it rapidly, efficiently, and with reasonable costs is important. On the other hand, these alarming facts insinuate that conventional water and air treatment technologies, which made critical contributions to sustaining human society in the past centuries, have lagged behind the ever-increasing and tougher demands at new times.

In general, conventional environmental treatment technologies, such as adsorption,^{3,4} chemical treatment,⁵⁻⁷ membrane-based separation,⁸⁻¹⁰ and biological treatment,^{11,12} are designed on the basis of bulk chemistry of the materials and water. Research efforts to improve the performance of conventional treatment technologies now include nanotechnology-based solutions. For many nanomaterials, interfacial properties rather than bulk properties control their behaviors. These interfacial properties can depend on size, and therefore can be tuned to afford the desired properties. Innovations in nanomaterials have fueled advances in environmental engineering and this has been the case in the development of nano-adsorbents, environmental catalytic materials, water purification and desalination membranes, environmental sensors, *etc.*^{10,13-17}

It is now a popular belief that many of the solutions to the existing and even future environmental challenges are most likely to come from nanotechnology and especially novel nanomaterials with increased affinity, capacity, and selectivity for environmental contaminants. The field of rational design of nanomaterials for environmental engineering has experienced a significant growth in the past two decades.^{15,18-23}

Since 1990s, nanomaterials with multiple, synergistic, and proactive functionalities have started to first emerge in many 'non-environmental' applications from shape-memory materials,^{24,25} artificial muscles,^{26,27} nanoscale motors,^{28,29} and biosensors,³⁰⁻³² to new drug-delivery devices,^{33,34} *etc.* These nanomaterials work as 'nanomachines' which, based on their environmental conditions, make self-adjustments for the purpose of maximizing their possibility to achieve their desired goals.³⁵ These nanomaterials are popularly named as 'intelligent' nanomaterials. The key to the design of intelligent nanomaterials is entrusting the nanomaterials with proactive,³⁶ instead of reactive, functionality, which thus leads to their change-oriented and self-initiated behaviors. Given the inherent complexity and stochastic nature of environmental problems, environmental nanomaterials can greatly benefit from an "intelligent" design, i.e. the ability to change its properties depending on the environmental conditions.

The development and application of intelligent nanomaterials in environmental field is comparatively sluggish and still at a very nascent stage, although its popularity is growing. However, over the years, there are indeed some exciting exploratory works done in the intelligent environmental nanomaterials, many of which seemingly offer innovative and disruptive technologies.

For example, the self-propelled nanomotors that were able to autonomously travel through polluted samples with their own power and to penetrate inaccessible locations,³⁷⁻³⁹ have potential applications to water-quality screening,⁴⁰⁻⁴⁵ removal and degradation of pollutants,⁴⁶⁻⁵⁰ removal of spilled oil,⁵¹⁻⁵³ and CO₂ scrubbing.⁵⁴ Conventional filtration membranes were imparted with responsive gates that could self-regulate their permeation and species selectivity, which offer certain hope toward differential water quality or fit-for-purpose separation using the same separation membranes.⁵⁵ A number of photothermal materials, when combined with membrane distillation (MD), harvested solar energy, generated heat locally only at the membrane and bulk

water interface, and thus led to considerably improved energy efficiency when compared with the conventional bulk water heating scheme of the conventional MD processes.⁵⁶⁻⁶⁰ The photothermal based MD might offer a new paradigm of the next-generation MD based water desalination.

Moreover, the materials were made to switch their oil and water wettability between two opposite sides in response to external stimuli and were used for self-controlled, on-demand, and selective oil-water separation. In the case of spilled oil cleanup, the materials would allow for the recovery of the collected oils as well as the reuse of the separating materials, which the conventional materials largely fail to.^{61, 62} Self-healing materials were made to self-recover their physical damages, self-restore their lost functions and self-clean their contaminated surfaces, which have been preliminarily extended to water filtration membranes and to fouling resistance of oil/water separation materials with confirmed results at lab scales.⁶³⁻⁶⁶ Given the frequent PM2.5 induced severe air quality incidents these years, the nanofibrous membrane air filters were created with high filtration capacity and even self-powering capability, which have an eminent application as personal protective equipment.⁶⁷

Nevertheless, one has to be cautious with only limited optimism toward the future of the intelligent environmental nanomaterials. Without any exception, all of the previous works, although conceptually stimulating, were conducted at lab bench-scale and with simplified testing conditions. Thus the technical hurdles in pushing these new concepts into real world practical applications with cost-effectiveness are expectedly enormous.

The design of intelligent environmental nanomaterials is meant to create things new. Therefore, it is expected that new designs of intelligent environmental nanomaterials will continue to arrive. The purpose of this article is to provide a comprehensive review of the state-of-the-art of intelligent environmental nanomaterials, with a particular focus on the design concepts and responsiveness of the materials. However, the review is not intended to be exhaustive and instead it aims to give a focused and critical review of this burgeoning field using a limited number of selected examples. It is for this purpose that some topics, for example, intelligent nanomotors, molecularly imprinted nanomaterials, although interesting and relevant, are not included in the review. The review covers the following topics: (1) designing filtration membranes with responsive gates; (2) switchable wettability materials for controllable oil/water separation; (3) self-healing materials for environmental applications; (4) emerging nanofibrous air filters for PM2.5 removal; and (5) concluding remarks.

2. Designing filtration membranes with responsive gates

Membrane technology is a key component of an integrated water treatment and reuse paradigm.¹⁰ In membrane separation, both permeate and retentate can be collected and utilized, which has a special meaning nowadays in wastewater treatment as there is a growing interest in recovering from municipal and industrial wastewaters valuable resources, including water, nutrient, energy, *etc.* By employing membranes with different pore sizes or separation mechanisms, membrane separation is able to provide differential water quality and fit-for-purpose products at the lowest energy cost. All these advantages make membranes essential tools to the current and future water sectors.

The performance of conventional membranes largely bears an inherent trade-off between solvent

permeability and solute selectivity or rejection, both of which cannot be tuned during their operations.^{10, 68} Based on the cutoff size of membrane separation, filtration membrane can be classified into microfiltration (MF), ultrafiltration (UF), nanofiltration (NF) and reverse osmosis (RO).¹⁰ Over the years, membrane separation has been an important playground of innovative nano-designs, which enable many conventional membranes to steadily improve their separation performances.^{10, 17, 69}

Inspired by cell membrane whose ion channels can be switched on and off on demand,^{70, 71} intelligent gating membranes have emerged since 1960s when the stimuli-responsive behaviors of some polymers were first revealed by Heskins and Guillet.⁷² These intelligent gating membranes show distinct performances responsive to environmental triggers, perform more complex tasks, and have gradually been extended to water filtration.^{56, 73-76}

Generally, membrane pore size modulation by external triggers heavily dominates the intelligent membrane research thus far.⁷⁷⁻⁷⁹ However, news designs and concepts are emerging in combining responsive chemistry with membranes toward better membrane performance. For example, stimuli responsive materials have been combined with RO membranes to improve their antifouling properties and been incorporated into the membranes to endow the membrane with self-healing capability.⁸⁰⁻⁸⁶ In addition, there is increasing interest in combining MD with photothermal materials, which, in response to solar light, generates heat locally with high energy efficiency.⁵⁹ All-in-one membrane has been reported to integrate chemical reactions and physical separation in one system, where the trigger-initiated sequential reactions selectively and on-demand degraded and separated water pollutants.⁸⁷

The chapter reviews the state-of-the-art of the intelligent gating membranes for environmental separation and is organized according to the type of environmental triggers, namely, temperature (i.e., heat), pH, and light. Intelligent gating membranes based on ions/molecules and redox triggers, although interesting, are not covered here due to the space limitation.

The general design principle of intelligent gating membranes is to incorporate stimuli-responsive materials, dominantly polymers, into the pores of membranes. These stimuli responsive polymers, in response to appropriate external triggers (e.g., temperature, pH, and light), change their conformations or chemistry, leading to modulation of permeability and selectivity of the membranes (Figure 1).^{55, 88}

Figure 1 Schematic representation of the different gating states of intelligent gating membrane in response to appropriate triggers.

Post modification of existing porous membranes is the most popular method to fabricate polymer-based stimuli-responsive gating membranes and the polymeric species are bound onto the pore surface via covalent bonding,⁸⁹⁻⁹² *van der Waals*' forces,⁷⁸ electrostatic interaction,^{93, 94} and so on. In literature, various existing membranes, organic and inorganic ones, have been utilized as matrix to fabricate intelligent gating membranes. The organic ones include polypropylene (PP),^{95, 96} polycarbonate (PC),^{93, 97-99} polyethylene (PE),^{90, 91, 100} polytetrafluoroethylene (PTFE),¹⁰¹⁻¹⁰³ Nylon-6,¹⁰⁴⁻¹⁰⁶ polyvinylidene fluoride (PVDF),^{87, 92, 104, 107-110} polyimide (PI),¹¹¹ polyamide (PA),^{80, 81, 112} poly(ethylene terephthalate) (PET),¹¹³⁻¹¹⁵ polysulfone,¹¹⁶ poly(vinyl chloride) (PVC),¹¹⁷ polyethersulfone (PES),¹¹⁸⁻¹²⁰ while the inorganic membranes mainly include anodic aluminum oxide (AAO),^{121, 122} nanoporous silica,¹²³ and nanoporous silicon nitride membranes.¹²⁴ Although one-step formation of stimuli-responsive gating membranes by phase inversion method have also been reported in literature, it is applicable to only a small group of responsive polymers.^{79, 119, 125, 126}

2.1 Temperature

Thermoresponsive polymer typically changes its conformation around a critical solution temperature. For lower critical solution temperature (LCST) response mode, the polymer takes an extended and stretched conformation in solution at temperatures below its LCST while a phase-separated and contracted polymeric conformation above the LCST.^{127, 128} On the contrary, upper critical solution temperature (UCST) response mode polymers conform to the opposite temperature dependence relationship. Due to the unsuitable UCST values (>100 or <0 °C) for most polymers,¹²⁹ the UCST response mode polymers have been employed to a much limited extent when compared with the LCST ones in environmental separation,¹³⁰ and thus are not reviewed in this chapter.

Polymers with typical LCST thermal responsiveness include poly(N-isopropylacrylamide) (PNIPAM),^{72, 131} poly(N-vinylcaprolactam) (PVCL),^{78, 132-135} poly[2-(dimethylamino)ethyl methacrylate] (PDMAEMA),¹³⁶⁻¹³⁸ poly-(MEO₂MA-*co*-OEGMA),⁷³ poly(L-lactic acid)-poly(ethylene glycol)-poly(L-lactic acid) (PLLA-PEG-PLLA) triblock copolymers,¹³⁹ poly(vinylalcohol-*co*-vinylacetal)¹⁴⁰ and poly(ethylene oxide)-poly(-propylene oxide)-poly(ethylene oxide) (PEO-PPO-PEO) copolymers.¹⁴¹ Without any doubt, PNIPAM is the most popularly investigated thermoresponsive polymer in intelligent gating membrane due to its easy synthesis, low cost, and appropriate LCST (typically 32 °C).¹⁴² Below its LCST, water is a good solvent to PNIPAM due to the abundant water-PNIPAM hydrogen bonds. Above the LCST, water is a poor solvent and PNIPAM breaks its hydrogen bonds with water. In this case, the hydrogen bonds within and among its own polymeric chains are enhanced, leading to the polymer having a contracted and coiled conformation (Figure 2) and an increased pore size of the gating membranes.¹²⁸

Figure 2 The structural scheme of PNIPAM at different temperatures. The polymer forms hydrogen bonds with water and presents an expanded state at a temperature below LCST. At a temperature above LCST, PNIPAM forms hydrogen bonds among itself and thus presents a collapsed state.

It was 1986 when the first intelligent thermoresponsive gating membrane was constructed. The membrane was made by grafting PNIPAM onto a nylon membrane and the modified membrane regulated its water flux by changing water temperature below and above the LCST of PNIPAM.¹⁴³ Ever since, there had been an explosive growth of using PNIPAM or PINPAM copolymers on different porous substrates for intelligent gating membranes.^{90, 91, 95, 97, 101, 107, 115, 144-147} In addition, valuable efforts were made to increase (e.g., to 40 °C) and decrease (e.g., to 17 °C) the LCST by introducing hydrophilic or hydrophobic moieties into PNIPAM copolymers, respectively,¹⁰⁴ which offers more flexibility in applying intelligent gating membranes to environmental separations.

However, directly changing the temperature of a bulk water during continuous separation is not trivial and more importantly is considered as energy-inefficient. Instead of changing the bulk water temperature so to induce the membrane pore size change, in 2014, Gajda *et al.* reported an *in situ* local heat generation scheme using an external magnetic field to excite Fe₃O₄ nanoparticles co-embedded into the membrane pore along with PNIPAM.¹⁴⁸ The pore size and water flux of the membrane could be tuned between 290 nm, 42 L m⁻² h⁻¹ and >400 nm, 240 L m⁻² h⁻¹ in the absence and presence of the magnetic field, respectively.

In 2013, Chu *et al.* modified the pores of nylon-6 membrane with a copolymeric poly(N-isopropylacrylamide-coacryloylamidobenzo-18-crown-6) chains that selectively detected and removed Pb²⁺ from wastewater.¹⁴⁹

Besides PNIPAM, other thermoresponsive polymers with suitable LCST were also introduced in intelligent gating membranes recently. PVCL, with a LCST around 32~35 °C, was physically coated on hollow-fiber membranes for controllable MF and UF.⁷⁸ In 2016, Jin *et al.* grafted pyrene-terminated poly-(MEO₂MA-co-OEGMA) (LCST~32 °C) onto single-wall carbon nanotubes (SWCNTs) membrane.⁷³ The membrane's pore size varied between 12 to 14 nm when the water temperature was changed between 25 to 40 °C, leading to a stable flux variation between 3730 and 6430 L m⁻² h⁻¹ over several cycles.

Inspired by the stomatal closure feature of plant leaves at relatively high temperature, in 2017, Zhao *et al.* constructed a negative temperature-response nano-gating membrane by covalently grafting PNIPAM chains on GO sheets.¹⁵⁰ Such membrane was capable of separating multiple molecules with different sizes by regulating the temperature. The water permeance of this membrane was 12.4 L m⁻² h⁻¹ bar⁻¹ at 25 °C and 1.8 L m⁻² h⁻¹ bar⁻¹ at 50 °C.

2.2 pH

The polyelectrolytes with weak acidic or weak basic groups are typically pH-responsive polymers. Depending on solution pHs, the weak acidic and basic groups undergo reversible protonation and deprotonation, leading to a reversible swollen and shrunken conformation transition due to on-and-off switch of electrostatic repulsion between these functional groups. The pH dependent conformation changes of the polymers have been widely used as functional gates in the intelligent gating membranes for controllable separation. Such gating membranes have been used towards adjustable water flux and molecular size selectivity for a variety of substances, including proteins,¹⁵¹ Fluorescein isothiocyanate-dextran (FITC-dextran),¹¹⁹ macromolecules,^{93, 152} vitamin B12,^{100, 153} riboflavin,¹¹⁶ Au nanoparticles,¹⁵⁴ *etc.*

The polymers with weak basic groups that have been applied to intelligent gating membranes include poly(4-vinylpyridine) (P4VP),^{74, 75} polystyrene-*b*-poly(4-vinylpyridine) (PS-*b*-P4VP),^{89, 151, 154-157} poly(methyl methacrylate-co-4-vinyl pyridine) (P(MMA-4VPy)),¹⁵⁸ poly(2-vinylpyridine) (P2VP),¹⁵⁹ PDMAEMA,^{109, 110, 160} poly(allylamine hydrochloride) (PAH).⁹³ Under suitable and generally acidic pHs, the weak basic groups of these polymers accept protons and become positively charged. The polymers thus exhibit a swollen conformation, leading to pore size reduction of the membranes. Under suitable and generally basic pHs, the same basic groups deprotonate and are charge neutral, and the polymers go back to their shrunken conformation state, leading to increased pore size of the membranes (Figure 1).

In 1984, Okahata *et al.* fabricated the first pH-responsive gating membrane and in this work P4VP was grafted onto a porous nylon membrane to act as NaCl permeation valve between pH 2 and 9.⁷⁵ In 1995, Childs *et al.* further grafted P4VP onto microporous PP and PE substrates for pH-responsive gating membranes, which moderately rejected NaCl (40-50%) at pH<3 and showed no salt rejection at neutral or basic conditions.⁷⁴ In 2006, Rubner *et al.* used layer-by-layer (LbL) method and assembled multilayers of PAH and poly(sodium 4-styrenesulfonate) (PSS) as intelligent gates in a nanoporous PC membrane. The method of LbL offered an advantageous capability of easy and precise control over the pore diameters of the modified porous membrane⁹³ and the functionalized membrane showed approximately 80% poly(ethylene oxide) (PEO) rejection at pH 2.5 and no rejection at all at pH 10.5. In 2007, Peinemann's group reported one step synthesis of asymmetric PS-*b*-P4VP isoporous membranes with nanometer-sized pores by non-solvent-induced phase separation⁷⁹ and thereafter successfully applied the membranes for controllable separation of protein and inorganic/organic molecules.^{151, 154-156, 161}

The typical weak acidic polymers that have been reported in the intelligent gating membranes include poly(acrylic acid) (PAA),^{87, 98, 108, 116, 152} poly(methacrylic acid) (PMAA),^{75, 100, 109, 162} poly(glutamic acid) (PGA),^{102, 163} Poly(L-glutamic acid) (PLGA),¹⁶⁴ polystyrene-block-poly(acrylic acid) (PS-*b*-PAA),¹¹⁹ poly(methyl methacrylate-co-acrylic acid) (P(MMA-AA)),¹⁵⁸ among others. The weak acidic polymers have a pH responsive behavior opposite to the weak basic polymers.

The first weak acidic polymeric (i.e., PMAA) gating membrane was reported in 1984 by Okahata *et al.*⁷⁵ Between 1996 and 1999, Lee *et al.* fabricated PAA-grafted polymeric membranes by plasma¹⁰⁸ and UV-irradiated¹¹⁶ graft-polymerization method, respectively, all showing a decreased riboflavin permeability in pH 4-5 compared to lower pH values. Since 1992, Ito *et al.* had demonstrated several methods in making weak basic polymer-based intelligent gating membranes.^{102, 152, 162, 163, 165, 166} One example is PAA modified PC membrane reported in 2001,¹⁵² which showed significant water flux decrease and PEG (Mw~8000) selectivity increase with pH increasing from 2 to 7.

In 2006, Qu *et al.* designed a pH-responsive intelligent controlled-release system which contained PMAA-g-PVDF as pH responsive valve and a crosslinked PDMAEMA hydrogels as substance pump,¹⁰⁹ which has potentials to be used as chemical carriers and environmental sensors as well as to environmental separation.

In 2011, Lewis et al. applied a pH responsive intelligent gating membrane in an multilayered and all-in-one Fenton-reaction-active filtration system for advanced oxidation (Figure 3).⁸⁷ The top layer of the membrane contained glucose oxidase (GOx) for *in situ* H₂O₂ generation by reacting

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with deliberately added glucose in the raw water, which allowed for the flexibility of on-demand initiation of the Fenton reaction. The bottom porous PVDF layer was functionalized with a pH-responsive PAA network and iron species was immobilized in the PAA layer as catalysis for Fenton reaction. The H_2O_2 generated in the top layer decomposed and generated free radical oxidants under the help of iron species to oxidize the organic containments in the feed water and the degradation generated alkali ions as byproducts. The alkali ions in turn increased the pH and stimulated the expansion of PAA, leading to a decrease in water flux and thus a longer residence time for pollutant degradation. On the other hand, in case with the feed water being free of organic contaminants, the water passed through the membrane with a large flux. Therefore, this all-in-one reactive filtration system possesses a responsive and self-initiated intelligent behaviors.

Figure 3 Schematic of all-in-one Fenton reactive membrane-based filtration system for water purification. (A) The stacked membrane system consists of two membranes with different functionality. (B) Pore of top membrane containing electrostatically immobilized GOx for the catalytic production of H_2O_2 from glucose. (C) Pore of bottom membrane consisting of pH-responsive PAA gel with immobilized iron species in shrinking state. (D) The PAA gel inside the pores of bottom membrane switch to swelling state due to the increased pH, which is caused by the byproducts of toxic organics degradation reaction.⁸⁷ Reprinted with permission from ref. 87. Copyright National Academy of Sciences, USA 2011.

2.3 Light

Azobenzene and spiropyran derivatives are among the most investigated light responsive polymers in intelligent gating membranes. The pore size of azobenzene-based intelligent membranes increases upon UV irradiation and decreases under visible light irradiation.^{76, 117, 123} On the other hand, spiropyran groups undergo a transition from non-polarity to polarity upon UV exposure, leading to a reduced pore size of intelligent membrane. The polar state returns to the non-polar and hydrophobic state *via* either a thermal or visible light treatment.¹²⁰

In 1983, Anzai *et al.* pioneered azobenzene-functionalized PVC membrane for the photo controlled K^+ ion permeation.¹¹⁷ In 2003, Liu *et al.* introduced azobenzene-containing moieties into an ordered and rigid silica framework to enable photo control over its pore size.¹²³ In 2014, Shi *et al.* designed a photo-responsive system based on the host–guest complex between azobenzene and β -cyclodextrin, which showed highly controllable pure water flux and PEG selectivity under irradiation of 450 nm and 365 nm.⁷⁶

In 2015, Fujiwara *et al.* reported a special responsive gating membrane for water desalination by grafting azobenzene on a AAO membrane and using UV and visible light as a gate switch.⁵⁶ The membrane blocked the water passage in darkness, but allowed water vapor passing through when simultaneously exposed under UV and visible light. The simultaneous irradiation of UV and visible lights onto the azobenzene induced its consecutive motion between the trans and cis Isomers, which promoted the water vapor permeation. Since only water permeated through the membrane, the membrane was utilized for water treatment to remove dye and protein, and also for seawater desalination (Figure 4). In 2017, Fujiwara *et al.* further improved the membrane by using a visible-light responsive dye, disperse red 1 (DR1), to replace azobenzene, which permitted solely visible light responsiveness.⁵⁷ By simultaneously grafting DR1 and blue 14 (DB14) on a PTFE membrane, the membrane was responsive to a wider range of light spectrum.⁵⁸ The flux of the double-dye-modified PTFE membrane was higher than the single-dye-modified PTFE membrane.

In the middle 1920s, Fisher and Hirshbergin observed the photochromic characteristics and reversible reaction of spiropyrans for the first time and thus set in motion the research on spiropyrans.¹⁶⁷ In 1994, Ito *et al.* pioneered a spiropyran-containing methacrylate and acrylamide functionalized PTFE membrane, whose pore size and permeability for H₂O/CH₃OH were tuned by UV and visible light irradiation.¹⁰³ Four year later in 1998, the same group fabricated spiropyran-containing PMMA grafted glass filter for controllable permeation of toluene liquid. The copolymer chains in toluene shrank under UV irradiation but swelled under visible irradiation. Thus, grafted filter showed increased flux by UV irradiation and decreased flux under visible irradiation.¹⁶⁸ Very recently, Padeste *et al.* demonstrated a two-step approach to prepare PMAA-spiropyran grafted PP membrane and the water flux of the membrane increased by 40% after UV irradiation for 30 s and visible light exposure for 30 min.¹⁶⁹

Figure 4 A seawater desalination system using azobenzene modified AAO membrane and solar light energy.⁵⁶ Reprinted with permission from ref. 56. Copyright American Chemical Society 2015.

In conclusion, valuable efforts have been made in making intelligent gating membranes responsive to a variety of external triggers. The responsive pore size modulation has been the

major focus in the past while trigger-initiated responsiveness of other membrane performance parameters are emerging.

Some of the concerns regarding the state-of-the-art of the intelligent membranes are summarized as follows. (1) All of the intelligent membranes in literature were proved their utilities at bench scales with simplified testing conditions to provide proofs of concepts. So far efforts in scaling up these membranes and challenging them with more realistic testing conditions are rare. (2) The size modulation of these intelligent membranes is far from being precise. This is so also partially due to the fact the current fabrication methods for filtration membranes largely lack molecular-level design,¹⁷⁰ which limits the value of the intelligent gating in the overall improvement of membrane performances, especially selectivity. The precise pore size modulation of the intelligent membranes at nanometer or even sub-nanometer range would be a significant target in the future development. (3) The responsiveness of the intelligent membranes is typically induced by changes in the bulk water chemistry, such as pH, temperature, which involves high chemical and/or energy consumption.¹⁷¹ (4) The previous research on the intelligent membranes was dominantly focused on the chemistry and conformation changes of the responsive materials and little attention was paid to the detailed mechanisms for mass transfer and separation within the intelligent gating membranes.⁵⁵

While important efforts have been made to utilize responsive chemistry to improve performance parameters of membranes other than pore size, their importance should be further strengthened. Intelligent membranes have potential to make some difference in the following areas. (1) Membrane fouling is always a major challenge in all kinds of membrane based separation and it worsens along with increasing water flux. The self-initiated conformations or chemistry changes in response to changing environmental conditions by stimuli-responsive materials can be a good platform to design membranes with improved anti-fouling and fouling-resistance performance. (2) Stimuli-responsive materials have been combined with and helped produce a number of filtration membranes with self-healing performance and more efforts should be invested in this interesting topic. (3) Light, especially UV light, as a remote and clean trigger, has been used to induce performance adjustment of the intelligent membranes. However, direct utilization of solar light to induce the same performance has been rare. Solar light is the most renewable energy source and thus the integration of photothermal component into conventional and intelligent membranes would result in more energy efficient membrane separation with better performance. (4) Synergistically multifunctional and all-in-one membranes in the format of point-of-use devices can be a niche area for intelligent membrane to thrive.

3. Switchable wettability materials for controllable oil/water separation

Oily wastewater is commonly produced in every major step of the lifetime of petroleum: exploration, transportation, storage, refining, application, and disposal. Moreover, accidental oil release and spill into unintended environment, including sea, soil, groundwater, river, lake, *etc.* often occur, leading to environmental pollutions. The oily wastewater and oil spill, once produced, demand timely actions to separate oil out of generally bulk water since dissolution of oil in water as well as spreading of oil slick is a strong function of time under these scenarios. Thus, petroleum industry, environmental protection agencies, and even nongovernmental organizations (NGOs) have been investing heavily on technologies that can efficiently and effectively separate oil/water mixture.⁶¹

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Depending on the amount of the oil spilled or present and the timing of response, the traditional oil contamination treatment technologies include: direct burning, physical collection by skimmer and pumping, physical confinement by floating boom, air flotation, gravity separation (*e.g.*, centrifugation), microorganism-based oil digestion, and so on.¹⁷²⁻¹⁷⁹ Each technology has its own niche application scenario, out of which it becomes ineffective. Moreover, with the increasingly stringent environmental regulations, the development of more efficient and cost-effective oil/water separation approaches is imperative to improve the quality of the oil spill cleanup and of treated oily wastewater effluent. The last decade has experienced remarkable progresses in fundamental understanding to special- and super-wettability, which has contributed significantly to oil/water separation.^{61, 62, 180-182}

The surface wettability states of materials are defined based on their actual contact angles (CAs) that are physically measured, not calculated. Basically, hydrophilic/oleophilic surfaces are the surfaces with water/oil actual contact angle < 90°, while hydrophobic/oleophobic ones are with actual water/oil contact angle > 90°. ¹⁸³ Superhydrophobic or superhydrophilic states of materials are the states with water contact angles >150° or ~0°, ¹⁸⁴⁻¹⁸⁶ with sliding angels (SAs) and liquid spreading time being taken into consideration in making categorization in some cases. Many review articles are available on the basic concepts of the surface wettability,^{62, 180, 187} which thus will not be repeated in this review. However, it is noteworthy that recently, in addition to air, new bulk phases (*e.g.*, water and oil) have been supplemented in contact angle measurement, leading to relatively new wettability states, such as underwater (super)oleophilicity, underwater (super)oleophobicity.^{180, 181, 188-190}

The materials with superwetting states can selectively attract or repel oil or water, which are beneficial to highly efficient and selective oil/water separation. It is worth pointing out that the wettability-based oil/water separation has its own limitations and is not meant to compete with, but complementary to, most of the conventional processes. The conventional processes generally work satisfactorily as the first-step treatment of high oil content mixtures while the wettability-based separation can be a beneficial follow-up step after many conventional processes when the composition of the treated mixtures is simpler and more amicable.

Typically, the wettability-based oil/water separation systems work in two major ways: filtration-based separation by using modified mesh, textile, membrane, *etc.* and adsorption-based oil capture by using modified foam, sponge, *etc.* ^{61, 62, 181, 189} Jiang and coworkers pioneered the use of superoleophilic membranes for oil/water separation by filtration in 2004,¹⁹¹ in which the membrane permeated oil and repelled water, now known as oil-removing mode. However, the membranes' oleophilicity led to their inevitable fouling and blockage by heavy oil. In 2011, Jiang *et al.* further developed a superhydrophilic and underwater superoleophobic hydrogel coated mesh,¹⁹² which, when wetted, percolated only water and repelled oil, namely water-removing mode. The water removing membranes overcome the oil fouling problem in the oil-removing mode and can achieve natural gravity-driven oil/water separation given the fact that water is generally heavier than oil.¹⁹³⁻¹⁹⁹

In the past few years, considerable progresses have been made in making materials with switchable wettability, especially switchable superwettability, toward oil/water separation.^{61, 62, 180} Compared with conventional materials with nonresponsive and prefixed wettability, these materials switch their wettability between two opposite sides in response to external triggers, and thus can be considered having intelligence (Figure 5). These intelligent oil/water separation materials can operate in either oil-removing mode or water-removing mode, suitable for oil

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removal from wastewater with oil density either higher or lower than water. Therefore, they possess superiority in developing versatile separation processes, easy recycling and regeneration, and enhanced anti-fouling performance, all of which would potentially lead to reduced operation cost toward oil contamination treatment.²⁰⁰

Figure 5 Scheme of intelligent materials with stimuli-responsive and switchable wettability for controllable oil-water separation.

To confer a surface with switchable wettability, for instance, underwater superoleophobicity and superoleophilicity, the surface chemistry should combine hydrophilic and oleophilic plus hydrophobic characteristics, with either one dominantly exposed over the other in response to environmental stimuli. Generally speaking, the chemical components for building responsiveness into surface wettability transitions are largely organic materials and more specifically polymeric materials due to their reversible conformation changes and polarity transition in response to environmental stimuli.¹⁸⁷ Generally, the conformation transitions of polymeric chains induce the reorientation of polar functional groups, change surface free energy, and thus modulate adhesive forces between the surface and liquid phases (oil or water) in question.

Nevertheless, there are some inorganic materials, especially semiconductor metal oxides such as ZnO,²⁰¹ TiO₂,²⁰²⁻²⁰⁴ SnO₂,²⁰⁵ Ga₂O₃,²⁰⁶ WO₃,^{207, 208} and V₂O₅²⁰⁹ that have been applied in photo-responsive wettability transitions. These photocatalytic materials can generate electron-hole pairs under irradiation of light with suitable wavelength and the holes can react with lattice oxygen, leading to creation of defective oxygen vacancies that presumably absorb water molecules at interfaces. The absorbed water molecules in turn would dissociate to generate two hydroxyl groups each, which present hydrophilicity to the surface. While sitting under dark condition for a certain period of time, the hydroxyl groups are removed by oxygen in the ambient environment, reverting back to the hydrophobic state.²¹⁰⁻²¹³

This chapter reviews the recent development of using polymeric and photocatalytic inorganic materials for stimuli-responsive and switchable wettability towards controllable and on-demand oil/water separation. Among the diverse wettability switching triggers, temperature, pH and light have received the most attentions in oil/water separation while other unconventional conditions, such as solvent, ion, gas, electric field, are emerging.

3.1 Temperature

Thermoresponsive polymers, especially PNIPAM which has been extensively discussed in section 2.1, have been applied to switchable and controllable oil/water separation.²¹⁴⁻²²¹ In 2013, the temperature controlled wettability transition was first applied to oil/water separation by Jiang *et al.* who employed PMMA-*b*-PNIPAM copolymer coated steel mesh as separation membrane.²¹⁶ This material reversibly switched its wettability in response to temperature change. Below the LCST, the modified mesh membrane was hydrophilic and thus was water-removing

mode, while, above the LCST, it switched to oil-removing mode because of its hydrophobicity. In 2016, Wang *et al.* deposited PNIPAM hydrogel into elastic polyurethane (PU) microfiber web structure and obtained a highly flexible, mechanically tough, and thermoresponsive oil/water separation membrane with a 1 wt % oil-in-water emulsion (at 25 °C) and 1 wt % water-in-oil emulsion (at 45 °C) separation efficiency of >99%.²²¹ In 2015 and 2016, electrospinning methods were reported by Xin *et al.*²¹⁷ and Luo *et al.*²¹⁴ to make PNIPAM based nanofibrous membranes for thermal responsive and switchable oil/water separation.

In 2015, Jin *et al.* reported a light-induced *in situ* local heat generation strategy for PNIPAM by combining gold nanorods with PNIPAM-based copolymer.²¹⁹ Photothermal conversion by the gold nanorods generated heat locally right at the interface and was the key to the material design. As a result, the membrane worked as a light-controlled chemical valve to tune water permeation flux for highly controllable separation of oil-in-water emulsions with high separation efficiency (>99%).

In addition to filtration based oil/water separation, in 2017, Wang *et al.* grafted octadecyltrichlorosilane (OTS) and PNIPAM onto the surface of melamine sponge skeletons and prepared a thermoresponsive sponge with reversible superwettability (Figure 6a,b).²²⁰ The sponge, when placed on an oil-spilled water zone, absorbed oil at water temperature at 37 °C and released the absorbed oil at 20 °C (Figure 6c).

Figure 6 (a) The water contact angle of a OTS/PNIPAM modified sponge switched between 0° and 150° at temperatures of 25 and 40 °C and (b) the switch between superhydrophilicity and superhydrophobicity was reversible for more than 20 cycles. (c) Fast oil (dichloromethane dyed with Sudan I) absorption at 37 °C (upper) and slow oil desorption at 20 °C (bottom) of the OTS/PNIPAM modified sponge.²²⁰ Reprinted with permission from ref. 220. Copyright American Chemical Society 2017.

3.2 pH

Overall, polyelectrolytes with weak acidic or weak basic groups are the most commonly used pH-responsive polymers for switchable wettability surfaces. At different pHs, these polymers change their charge property and conformation and thus switch their wettability based on the deprotonation or protonation states. In literature, PMAA,²²² P4VP,²²³ poly(2-vinylpyridine)-*b*-polydimethylsiloxane (P2VP-*b*-PDMS),^{224, 225} 11-mercaptopundecanoic acid (SH(CH₂)₁₀COOH),²²⁶⁻²³⁰ 2-pyridinecarboxylic acid,²³¹ poly(methyl methacrylate)-block-poly(4-vinylpyridine) (PMMA-*b*-P4VP),²³² poly(vinylidene fluoride)-graft-poly(acrylic acid) (PVDF-*g*-PAA),²³³ and PDMAEMA^{234, 235} have been employed in pH responsive and switchable wettability for oil-water separation.

In 2012, Wang *et al.*, for the first time, revealed a surface with switchable underwater super-oil wettability for highly controllable oil/water separation. The surface was fabricated by grafting the rationally selected copolymer comprising pH-responsive block, P2VP, and oleophilic/hydrophobic PDMS block, onto many commonly available substrates.²²⁴ P2VP block altered its conformation and surface wettability in response to pH changes (from 6.5 to 2), while oleophilic PDMS block on the surface provided controllable and switchable access by oil (Figure 7a). The surface modification strategy and oil/water separation selectivity and efficacy were successfully demonstrated *via* filtration based oil/water separation systems (Figure 7b) and sponge-based oil capture. This surface is the first of its kind that can switch its superoleophilicity and underwater superoleophobicity only under room temperature and without any organic solvent involved. In 2016, the same chemical approach was applied to producing electrospun PDMS-*b*-P4VP fibers for pH responsive oil/water separation.²²⁵ Similarly, mixture of alkyl thiols and SH(CH₂)₁₀COOH were also employed as the surface modifier to porous substrates.^{226, 228, 229, 236} In addition to modifying functional polymers onto existing materials, in 2015, Li *et al.* electrospun PMMA-*b*-P4VP fibrous membranes and applied them to pH-controllable oil/water separation.²³² In 2017, Cheng *et al.* reported a tree-like nanofibrous membrane of PVDF-*g*-PAA for pH-responsive oil/water purification.²³³

Figure 7 (a) Schematic diagrams for the controllable oil wettability of the P2VP-*b*-PDMS grafted surface in response to pH 6.5 and 2. (b) Dry P2VP-*b*-PDMS modified textile selectively permeated oil (left) whereas, once the membrane was wetted with acidic water (pH=2.0), it selectively permeated water only (right).²²⁴ Reprinted with permission from ref. 224. Copyright Nature Publishing Group 2012.

3.3 Light

Photo-responsive wettability transition has its advantage of being contactless and remote. In 2012, Jiang *et al.* demonstrated photo-triggered switchable oil/water separation on aligned ZnO nanorod array-coated mesh (Figure 8a), which switched to superhydrophilicity and underwater superoleophobicity under UV irradiation and returned to superhydrophobicity after being stored in darkness for 7 days (Figure 8b,c).²³⁷ Later, ZnO-based photo-responsive oil/water separation devices were facily fabricated by spraying method to modify ZnO nanoparticles/PU mixtures on stainless steel mesh²³⁸ and by one-step thermal evaporation method to synthesize aligned ZnO array onto stainless steel mesh.²³⁹ In both cases the materials were able to switch between oil-removing and water-removing modes in response to light illumination. TiO₂ has a similar light-responsive behavior to ZnO, and by integrating TiO₂ into membrane materials, photo-triggered switchable oil/water separation were also widely reported.²⁴⁰⁻²⁴³

Figure 8 (a) SEM images of the aligned ZnO nanorod array-coated stainless steel mesh films. (b) Photographs of a water droplet on the coated mesh film with hydrophobic surface after dark storage (left), with hydrophilic surface under UV irradiation (middle) in air, and water passing through the hydrophilic mesh film (right). (c) Photographs of an oil droplet (1,2-dichloroethane) on the pristine ZnO coated mesh film with oleophilic surface in air (left) and it turned into underwater oleophobic surface after UV irradiation (middle, and right).²³⁷ Reprinted with permission from ref. 237. Copyright Royal Society of Chemistry 2012.

3.4 Gas, solvent, ion, and electric field

In 2015, Lin *et al.* fabricated superamphiphobic coating by dip-coating of a mixture of silica nanoparticles and heptadecafluorononanoic acid (HFA)-modified TiO₂.²⁴⁴ The superamphiphobic coating modified membrane repelled both hexadecane and water, but it

permeated only water upon exposure to ammonia gas, which was ascribed to the formation of ammonium carboxylate ions through breakage of titanium carboxylate coordination bonding. Che *et al.* fabricated nanofibrous membrane of polymethylmethacrylate-*co*-poly(N,N-diethylaminoethyl methacrylate) (PMMA-*co*-PDEAEMA), which delivered CO₂ gas controlled oil/water separation because CO₂ in water reduced the pH value of aqueous media, leading to the protonation of PDEAEMA.²⁴⁵

In 2014, Feng *et al.* prepared solvent responsive oil/water separation copper mesh membrane.²⁴⁶ In this case, tetrahydrofuran (THF) and stearic acid were the solvent species to induce superwettability switch due to the formation of self-assembled monolayer of stearic acid molecules with low surface energy and the removal of the stearic acid by immersing in THF solvent. Later, the same group reported mercury ion responsive PAA hydrogel coated oil/water separation mesh. The mesh switched its wettability in response to an increase of Hg²⁺ concentration due to the chelation between mercury ion and PAA and the cleavage of the interaction between carboxylic acid groups and water molecules (Figure 9a-c).²⁴⁷

An electric field between a liquid and an underlying conducting solid can induce rearrangement of charges and dipoles, leading to reduction in interfacial energy and wettability transition from hydrophobicity to hydrophilicity, which is known as electrowetting.²⁴⁸⁻²⁵² In 2012, Kwon *et al.* extended the electrowetting concept into switchable oil/water separation and fabricated a fluorodecyl polyhedral oligomeric silsesquioxane (POSS)/PDMS coated nylon membrane. The coated mesh, under a voltage, turned into hydrophilic state from its original hydrophobicity, leading to water permeation and hexadecane repellence (Figure 9d-i).²⁵³ In 2016, Jiang *et al.* coated root-like polyaniline nanofibers on stainless steel mesh and the modified mesh became gradually hydrophilic and underwater superoleophobic under an increasing voltage, which performed a water-moving type of oil/water separation under proper voltages.²⁵⁴

Figure 9 Oil/water separation behavior of PAA hydrogel coated meshes in different condition: (a) the pristine mesh with superhydrophilic and underwater oleophobic property; (b) the mesh soaked in 1 mg/mL Hg²⁺ solution for 5 min turned into hydrophobic and under water oleophobic; (c) the mesh became hydrophobic and under water oleophilic after soaking in a saturated Hg²⁺ solution for 5 min. Red solution was petroleum ether and colorless solution was water.²⁴⁷ Reprinted with permission from ref. 247. Copyright American Chemical Society 2014. (d, e) The macroscopic contact angle for hexadecane on the surface of fluorodecyl POSS/PDMS coated nylon membrane

remained unchangeable with or without charge. (f, g) the macroscopic contact angle for water decreased from 115° to 56° as the potential of the membrane increased to 1.5 kV. (h) An apparatus with a liquid column of oil (dyed red) and water (dyed blue) above the membrane before applying an electric field. The inset shows a schematic of the membrane module. (i) Water permeated through while hexadecane was retained above the membrane when a voltage of 2.0 kV applied.²⁵³ Reprinted with permission from ref. 253. Copyright WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2012.

In conclusion, switchable wettability materials offer certain promise in controllable oil/water separation without external energy input. However, one has to be cautious in predicting their applicability to real-world oil contamination problems, as, under the state-of-the-art, almost all of these materials were tested at bench scales with surrogate model water and oils having much simpler compositions and smaller viscosity.

Thus, more research efforts need to be directed toward using these materials for real-world applications, such as separation of crude oil with high viscosity, emulsion separation, oil/water mixture with high salinity, industrial oily wastewaters, *etc.* In doing so, the efficacy, stability, longevity and fouling propensity of the switchable materials toward practical applications need to be systematically investigated.

In practical oil/water separation, the adsorption of dissolved species, including dissolved oil ingredient species, surfactant monomers, dissolved natural organic matter, salt species, onto the separating materials can be a concern for long-term separation, but unfortunately has not been looked at thoroughly with switchable wettability materials.

Noteworthy are recent developments in applying external energy to oil/water separation to improve separation performance. Yu *et al.* designed and prepared a joule-heated sponge for fast clean-up of viscous crude oil spill, requiring electricity to generate heat.²⁵⁵ The heat being generated by other energy sources, especially solar light, would have a place to provide assistance to wettability-based separation of oil/water mixtures deemed difficult otherwise, such as crude oil spill cleanup.

It is still a big challenge how to effectively separate surfactant-stabilized oil-in-water or water-in-oil emulsions, to which both the conventional wettability and switchable wettability materials seems to offer no solution. The adsorption of surfactants onto the material surfaces would degrade surface wettability and make many wettability-based designs not working properly, causing a rapid decline of separation efficiency. In this regards, breakage of emulsion and subsequent phase separation by wettability-based separation looks a reasonable approach. Thus, effective breakage of emulsion by using sustainable energy source deserves considerable research attention.

4. Self-healing materials for environmental applications

In practice, surface molecules can be gradually decomposed or removed by mechanical damage or upon exposure to light irradiation and highly oxidative chemicals in water and air, leading to the loss of their intended functions.^{256, 257} It is thus undisputed that self-healing materials would offer enormous possibilities, in particular for applications where long-term reliability in poorly accessible areas is important.

Biological organisms demonstrate their amazing self-healing capability of restoring health and soundness of a system, such as, regeneration of tissue structures and fractured bones. This has been a great inspiration for scientists and engineers to make artificial materials that can heal

themselves when damaged.⁶⁴ In the past decade, the concept of self-healing has slowly but steadily been appreciated by and applied to environmental fields. Some exploratory works on endowing conventional environmental processes with self-healing materials have been conducted, including but not limited to, water filtration,⁸³⁻⁸⁵ oil/water separation,²⁵⁸ pollutant absorption²⁵⁹ and antifouling surface.^{257, 260-262}

Depending on the source of self-healing agents, the self-healing materials are categorized into two types: extrinsic and intrinsic self-healing materials. (1) Extrinsic self-healing materials have their healing agent embedded across the entire host matrix materials in the form of micro/nano capsules or vascular networks.^{64, 263} When a damage occurs, the capsules or vascular networks break to release the healing agent to initiate healing process. (2) In contrast, intrinsic self-healing materials do not need additional healing agent and the molecules that constitute the matrix can act as the healing agent by themselves.^{64, 264} As a consequence, intrinsic self-healing materials can achieve multiple healing cycles, are more versatile, and therefore are more widely adopted in in environmental applications than the extrinsic self-healing materials.

The damages of materials generally include physical crack and surface function loss, and the later one may be owing to the removal of surface functional components or due to surface contamination. Accordingly, the following discussions are organized into three parts (1) self-healing of physical cracks, (2) self-restoring of surface chemical components, and (3) self-cleaning of contaminated surfaces. The following section presents and discusses examples of self-healing materials what have been preliminarily applied into environmental field in the above categories.

4.1 Self-healing of physical cracks

The application of self-healing of physical cracks to environmental processes is relatively new. In 2012, Tyagi *et al.* reported a porous membrane formed by micelles of triblock copolymer poly(styrene-*co*-acrylonitrile)-*b*-poly(ethylene oxide)-*b*-poly(styrene-*co*-acrylonitrile) (PSAN-*b*-PEO-*b*-PSAN) and its application to water filtration. The membrane material was not crosslinked and therefore could self-heal its macroscopic structural defects under an applied pressure of 0.8 bar under which the micelles rearranged and the new block copolymer bridges were formed on the damage site.⁸³

In 2013, Lu *et al.* fabricated a self-healing and pollutant-adsorbing hydrogel by using polydopamine-modified clay as the main building block and Fe³⁺ ions as the physical cross-linkers.²⁵⁹ This hydrogel could be self-healed via reformation of damaged catechol-Fe³⁺ complexes. Moreover, working as an adsorbent, it effectively removed Rhodamine 6G (Rh6G) from water owing to the hydrogen bonding and π - π stacking interactions between the aromatic moieties of polydopamine and Rh6G.

In 2016, Kim *et al.* fabricated a self-healing filtration membrane by embedding into PES membrane the extrinsic microcapsules that had PU shell and isophorone diisocyanate core.⁸⁴ Once damaged, the healing agent of isocyanate from the broken microcapsules was released and diffused towards the crack sites, followed by reaction with the surrounding water to form polyurea plug to cover the damage sites (Figure 10a). Once healed, the water flux and particle rejection performances of the membrane were recovered to 103% and 90% of the original ones, respectively.

Nevertheless, the microcapsule-type extrinsic self-healing agent results in a limited number of healing cycles at a given region. Kim *et al.* further developed a water filtration PES membrane with membrane pores filled with poly(2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS) hydrogel.⁸⁵ The self-healing capability of the membrane was majorly attributed to swelling effect of the pore-filling hydrogel at the damage site and the strong hydrogen bonding and molecular interdiffusion of the hydrogel polymer chains (Figure 10b). As a consequence, the particle rejection by the membrane was up to 99% once self-healed compared with as low as 30% upon damage. In 2017, the same group further developed an improved *in situ* healing method by using branched polyethylenimine-functionalized silica microparticles.⁸⁶ The *in situ* healing recovered the membrane's particle rejection to 99.1% of the original one before damage without any flux decline.

Sun *et al.* fabricated self-healing and anti-fouling films via LbL of PEGylated branched poly(ethylenimine) (bPEI) and hyaluronic acid (HA). The structural damage and antifouling function of the films could be healed rapidly due to the high mobility of polyelectrolytes and their reversible electrostatic and hydrogen bonding interactions.²⁶⁵

Figure 10 (a) Schematic illustration of the self-healing process of microcapsule-embedded membranes.⁸⁴ Reprinted with permission from ref. 84. Copyright American Chemical Society 2016. (b) Schematic illustration of self-healing pore-filled membranes with the pore-filling hydrogel anchored on PES membrane that acted as the active layer by allowing water to pass through and repelling unwanted particles (red spheres).⁸⁵ Reprinted with permission from ref. 85. Copyright American Chemical Society 2017.

4.2 Self-restoring of surface functional components

The surface function, especially surface wettability, is usually achieved by depositing an ultrathin functional layer (e.g., a single molecular layer) on a substrate material, which makes the surface function being easily degraded even without any appreciable structural cracks.

Particularly, the self-healing of surface wettability (e.g., hydrophobicity, hydrophilicity) is largely based on surface-free-energy-driven migration of hydrophobic or hydrophilic polymer

chains. In practice, surface hydrophobic molecules can be gradually decomposed or removed by mechanical damage or upon exposure to light irradiation and highly oxidative chemicals in water and air. With the hydrophobic molecules gone from the surface, the surface energy would rise in air, which draws up the low-surface-energy molecules underneath/near the damaged sites onto the outer surface to restore the original hydrophobicity.²⁵⁶ Alternatively, this process can also be explained by the fact that the air is a very hydrophobic medium and the low-surface-energy molecules like to make contact with the air according to the principle of like dissolves like. Similarly, in underwater condition, hydrophilic molecules have a tendency to migrate to the interface to replenish the lost molecules there and thus self-restore surface underwater hydrophilicity.²⁵⁷

As a proof to this surface wettability self-healing concept, in 2010, Sun *et al.* reported a self-healing superhydrophobic coating, which was fabricated by chemical vapor deposition (CVD) of fluoroalkylsilane on the LbL assembled polyelectrolyte film.²⁵⁶ The surface superhydrophobicity, once lost, could be self-restored at room temperature by means of self-migration of fluoroalkyl chains to the outer surface from the underneath polyelectrolyte film to minimize the interfacial free energy. Even since, the self-healing superhydrophobic coatings and textiles have been widely prepared from a variety of fluorine-containing polymers.²⁶⁶⁻²⁷⁵

In 2015, Wang *et al.* further applied this superhydrophobicity self-healing mechanism to a photothermal conversion membrane, which was the first report on using polymer as photothermal material, for the purpose of solar-driven water evaporation and seawater desalination (Figure 11a). The membrane was fabricated by fluoroalkylsilane modification of polypyrrole (PPy) coated stainless steel mesh.²⁷⁶ It was revealed in this study that the migration of fluoroalkyl chains to the outer surface of the coating could be accelerated by solar light irradiation and multiple cycles of self-healing were achieved (Figure 11b).

In 2016, Fang *et al.* demonstrated a self-healing electrospun N-perfluorooctyl-substituted PU fibrous membrane for oil/water separation.²⁵⁸ The oil-water separation efficiency was maintained at above 98% after 20 cycles of wettability loss-and-restoration cycles since the fluorine-containing PU could self-migrate to the outer surface of the fibers to restore the superhydrophobicity of the membrane. In the same year, Liu *et al.* fabricated an anti-smudge coating of perfluorooctanoate (PFO) modified LbL assembled poly(diallyldimethylammonium) (PDDA) and PSS film²⁶¹ and the film showed sliding angel <12° for a variety of oils and easily self-restored its oil repellency upon lost.

In 2013, Minko and his coworkers grafted PEO on P2VP polymer 3D network.²⁵⁷ When the surface was damaged underwater, the grafted PEO polymers spontaneously migrated to the surface. As a result, the anti-fouling performance of the material showed a 4-fold increase as compared to the traditional anti-fouling materials. Based on the same concept, in 2015, Wu *et al.* fabricated a similar material by grafting self-assembled hydrophilic copolymeric chains on the hierarchical microgel spheres. The prepared material achieved the capability of self-restoring its original underwater superoleophobicity and antifouling properties (Figure 11c).²⁶⁰

Figure 11 (a) Schematic configuration of the point-of-use device for direct and all-in-one solar distillation. (b) Reversible water contact angle changes on the plasma-treated and light-irradiated PPy-coated mesh. The insets in (b) were the shapes of the water droplets on the surfaces after plasma-treatment and light-irradiation.²⁷⁶ Reprinted with permission from ref. 276. Copyright WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim 2015. (c) Schematic illustration for the structure and self-healing process of underwater superoleophobic and antibiofouling coating.²⁶⁰ Reprinted with permission from ref. 260. Copyright American Chemical Society 2015.

4.3 Self-cleaning of contaminated surfaces

The surfaces of environmental materials during their applications inevitably suffer from contaminant, such as attachment and absorption of dirt, bacteria, oil, and protein, resulting in weakened and impaired surface structures and performances.²⁷⁷ Therefore, materials with self-cleaning surfaces are highly desirable in many environmental processes and are necessary before ideally anti-fouling surfaces, if any, can be developed. The majority of self-cleaning surfaces can be placed into three categories: superhydrophilicity, superhydrophobicity, and photocatalysis.

In case of superhydrophilic surfaces, the surfaces have water contact angle as small as 0°, and allow for water to spread out to form a thin water film between fouling debris and the underneath surface, which leads to separation of the debris from the surface.²⁷⁸⁻²⁸¹ As for superhydrophobic surfaces, they have very high water contact angles and small water sliding angles in air and thus rely on rolling droplets to get rid of surface contaminants.^{65, 281, 282} On a photocatalytic self-cleaning surface, contaminant is washed away due to the synergistic effect of photocatalysis and photo-induced superhydrophilicity.^{210, 283}

Superhydrophobicity based surface self-cleaning is well developed. So far, a multitude of self-cleaning materials with superhydrophobicity and low-adhesion characteristics have been reported,^{65, 210, 281} some of which have been applied in anti-fogging,^{284, 285} anti-icing,²⁸⁶ corrosion resistance,²⁸⁷⁻²⁸⁹ solar water evaporation,²⁹⁰ light energy harvesting by solar cell,^{291, 292} water drop energy harvesting,^{292, 293} etc.

On the other hand, hydrophilic polymers, especially PEO,²⁷⁸ zwitterionic polyelectrolytes,^{279, 280} and copolymers with hydrophilic domains²⁹⁴ have been widely employed to make self-cleaning and antifouling coatings.²⁹⁵ For example, Liu *et al.* grafted poly(2-methacryloyloxyethyl phosphorylcholine) (PMPC), a typical zwitterionic polyelectrolyte, onto steel meshes and the modified meshes repelled oil due to their high water affinity.²⁸⁰ Jin *et al.* reported polyacrylate-grafted poly(vinylidene fluoride) (PAAS-g-PVDF) hydrogel coated membrane which repelled viscous oils.²⁹⁶

In 2017, A Janus membrane was designed by integrating an omniphobic substrate and a hydrophilic and underwater superoleophobic surface layer.²⁹⁷ As-prepared composite membrane overcame the existing limits in conventional MD membranes: amphiphilic surfactants-induced wetting and fouling by hydrophobic contaminants, and thus enabled an effective desalination of hypersaline wastewater with complex compositions driven by low-grade-thermal energy.

The first photocatalytic self-cleaning surface was fabricated in 1995 when Paz *et al.* fabricated a transparent TiO₂ film coating on glass.²⁹⁸ The photocatalytic self-cleaning concept later extended its impact on oil/water separation and wastewater treatment.^{241, 299-301} For example, in 2013, Zhang *et al.* fabricated oil/water separation materials with underwater superoleophobicity through LbL assembly of sodium silicate and TiO₂ nanoparticles on a stainless steel mesh (Figure 12a).³⁰² Under UV irradiation, the mesh effectively removed and decomposed fouling oil contaminants, leading to a facile recovery of its wettability and oil/water separation ability (Figure 12b). In 2017, Xu *et al.* modified polydopamine-polyethyleneimine (PDA-PEI) nanofiltration membrane with β -FeOOH nanorods. The modified membrane exhibited efficient photocatalytic activity for degrading organic contaminant through the photo-Fenton reaction in the presence of hydrogen peroxide and under visible light, thus showing self-cleaning property.³⁰¹

Figure 12 (a) Preparation of a self-cleaning underwater superoleophobic mesh for oil/water separation by LbL assembly of sodium silicate and TiO₂ on a steel mesh. (b) The water contact angle of the coated mesh could be repeatedly recovered by UV illumination (▲) after it was contaminated by oleic acid (●).³⁰² Reprinted with permission from ref. 302. Copyright Nature Publishing Group 2013.

Overall, self-healing materials, once made, would minimize external intervention, including monitoring, maintenance and repairing, during their lifetime of operation, and therefore

potentially elongate their lifetime. The field is still at its birth stage and the applications of the self-healing materials have only been to membrane filtration, oil-water separation and anti-fouling surface. Thus its application perspectives ought to be expanded to other environmental processes to further explore their potentials.

At the state-of-the-art, the following points are noteworthy. (1) Although some promising advances have been made, there is still a long way to go to implement self-healing environmental materials in real-world conditions. Moreover, the methods of integrating self-healing agents into base materials are typically nontrivial, expensive and time-consuming. The environmental safety and toxicity of many self-healing agents/materials used in the environmental processes have not been assessed. The future self-healing materials that are suitable to practical applications should offer fast healing, environmental compatibility and cost-effectiveness. (2) Polymeric self-healing agents are commonly used due to their inherent flexibility and softness, which, to some extent, discourages their applications to rigid materials and the design of high-strength self-healing materials would break this bottleneck.^{64, 303} (3) Computer modelling can provide deeper and more thorough insight into the behavior of autonomous polymers and thereby aid the formulation of effective guidelines for optimizing both the synthesis of these polymers and the design of the system.³⁰⁴ (4) Design of self-cleaning materials with the capabilities of self-healing of physical cracks and/or self-restoration of chemical components would be another key future research since the self-cleaning components on the surface are always fragile and easily damaged when operating in extreme environments.^{261, 305}

The future development direction for the self-healing materials is to further emulate nature. Bio-inspired self-healing materials have recently developed as a major branch of intelligent materials in the future, designed to recover mostly mechanical damage or/and surface functions at ambient conditions without using external stimuli or energy input.^{63, 64}

5. Emerging nanofibrous air filters for PM2.5 removal

Atmospheric fine PM possesses varying and complex chemical compositions due to its diverse sources from suspended dust, high-temperature metallurgical processes, atmospheric reactions, and various incomplete combustion activities, such as vehicular emission, coal combustion and diverse industrial combustion.³⁰⁶⁻³⁰⁸ PM is commonly classified into PM2.5 and PM10 with aerodynamic diameter below 2.5 and 10 μm ,^{309, 310} respectively. In comparison, PM2.5, due to its ability to penetrate into deep lung and blood vessel,^{309, 310} induces more serious human health concerns than PM10 and has become a notorious air pollutant across the globe nowadays.

During hazy days, ventilation system and central air conditioning are most effective to filter out PM and produce fresh air. However, this technology is only available in modern commercial buildings,^{311, 312} and it entails high-energy consumption to power bulk pumping systems and is not applicable to personal protection in outdoors environment. Therefore, air filter with natural ventilation is regarded as a more ideal green method to obtain fresh air because no additional energy input required and suits both outdoors and indoors application scenarios.³¹³ Moreover, the increasingly enhanced public health awareness worldwide incentivizes development of more effective and mass-affordable personal protection equipment for PM2.5 removal at personal and household levels.

The conventional air filters for removing PM particles are porous membranes fabricated by creating pores on solid substrate and microfibrinous membranes consisting of stacked fibers with

diameter within micrometer range.³¹³⁻³¹⁶ However, both approaches either are unsatisfactory for PM_{2.5} removal or lead to unbearable air pressure drop across the membranes.

Compared with the conventional microfibrinous air filters, the nanofibrous membrane air filters with fiber diameters in the range of 10 to 1000 nm offer a multitude of attractive features, such as high specific surface area, high porosity, interconnected porous structure, low resistance to airflow, more active sites, easy functionalization ability, and good mechanical strength, and all of these features are beneficial for PM_{2.5} removal (Figure 13).³¹⁷⁻³²¹

Figure 13 Schematic of nanofibrous membrane air filter with high transparency and low resistance to airflow that captures PM particles by strong surface adhesion.

Owing to the existence of various ions and water vapor in atmospheric environment, the PM particles are inclined to be highly polar in air.³²² With this understanding, nanofibrous membranes with high polarity have been made to aim at high adhesion interactions between PM particles and the nanofibers. It was also revealed, as the PM particles capturing continues, the incoming particles would directly attach onto and merge together with the preexisting PM along the fibers, leading to stable sphere-shaped aggregates around the nanofibers.³¹³ This phenomenon is to the benefit of PM removal since it allows PM particles to enlarge their contact areas with nanofibers and thus to bind tightly onto the nanofibers.

Guided by the above interaction principles, nanofibrous air filters have been made for PM_{2.5} removal from suitable polymers and composite materials, including, polyacrylonitrile (PAN),^{313, 323-325} polyvinylpyrrolidone (PVP),^{313, 326} PS,³¹³ polyvinyl alcohol (PVA),^{313, 327} PI,³²⁸ PU,^{329, 330} poly(lactic acid) (PLA),³³¹ poly(*m*-phenylene isophthalamide),³³² PC,^{333, 334} silk,³³⁵ nylon-6,³³⁶ PMMA,³²⁶ protein,^{337, 338} PVDF doped with negative ions powder,³²¹ PVDF/PTFE,³³⁹ PVC/PU,³⁴⁰ PAN/Fluorinated PU,³⁴¹ PAN/silica,³⁴² nylon-6/PAN,³⁴³ PVA/PAN,³⁴⁴ PAN/ionic liquid,³⁴⁵ polysulfone/titania (TiO₂),³⁴⁶ PAN/Polysulfone,³⁴⁷ PLA/TiO₂,³⁴⁸ PAN/MOF.³²²

This rest of this chapter reviews major milestones in this budding field of nanofibrous air filters for PM_{2.5} removal.

In 2015, Cui *et al.* pioneered the design of nanofibrous air filter by utilizing electrospun polymeric nanofibrous membranes including PAN, PVP, PS, PVA and PP for indoor air protection. Among them, the PAN nanofibers showed the greatest efficiency of PM_{2.5} removal (>95%) and 90% transparency (Figure 14a-c).³¹³ The PM_{2.5} capture was ascribed to the dipole-

dipole and dipole-induced interactions in this work. In 2016, the same group further developed transparent and high-temperature stable PI nanofibrous air filter which showed great mechanical properties, thermal stability and high and consistent PM_{2.5} removal performance at the temperatures ranging from 25-370 °C for 120 h.³²⁸

In 2017, for the first time, thermal management was introduced into nanofibrous air filter face mask by Cui *et al.* for personal cooling/warming purposes.³⁴⁹ In this design, the nano PE was chosen as a supporting substrate due to its transparency to the mid-infrared (IR) radiation and electrospun nylon nanofibers were modified on the PE substrate. As prepared PE/nylon composite membrane mask showed excellent heat dissipation and high IR transparency (92.1%), generating radiative cooling effect. Separately, if the nano PE substrate was coated by a thin layer of Ag before the nylon fiber deposition, it gave rise to a high IR reflectance (87.0%) for personal warming purpose. These two type of face masks are desirable under hot and cold weather, respectively.

For the purpose of large scale and commercial production, Cui *et al.* proposed and tested a roll-to-roll transfer fabrication method of nanofibrous air filter (Figure 14d).³³⁶ Later, a roll-to-roll blow-spinning technique was developed by Cui and Wu *et al.* (Figure 14e) and applied to the mass production of transparent air filters. Such transparent nanofibrous air filter films could be coated rapidly on regular window screens and easily removed by gentle wiping.³²⁶

Figure 14 (a) PM_{2.5} removal efficiency of PAN, PVP, PS and PVA nanofibrous air filters at different transmittances. (b,c) SEM images of the PAN transparent air filter after 100 h PM capture test. Scale bars, 50 and 10 mm, respectively.³¹³ Reprinted with permission from ref. 313. Copyright Nature Publishing Group 2015. (d) Photograph of a roll-to-roll process for the transferring of electrospun nanofiber film onto a plastic mesh in a continuous fabrication process for PM_{2.5} filter.³³⁶ Reprinted with permission from ref. 336. Copyright American Chemical Society 2016. (e) Schematic illustration of the blow-spinning method of the window screen coating for indoor protection (upper) and successful wiping of nanofibers coating from the window screen by tissue paper (bottom).³²⁶ Reprinted with permission from ref. 326. Copyright American Chemical Society 2017.

To endow the nanofibrous air filters with more intelligence, Wang *et al.* demonstrated a concept of self-powered air filter for capturing PM from automobile exhaust using triboelectrification effect. In 2015, they fabricated a triboelectric nanogenerator (TENG) to form a space electric field, which facilitated PM_{2.5} removal (>95.5%).³⁵⁰ In 2017, they developed a TENG-assisted positively charged PI electrospun nanofibrous air filter to enhance the removal of especially superfine PM with diameter smaller than 100 nm.³⁵¹ In the same year, Ko *et al.* fabricated a percolation network of Ag nanowire on nylon mesh as a transparent, reusable, and active PM_{2.5} air filter. By applying a low voltage on Ag nanowire network, the membrane exhibited a high PM_{2.5} removal efficiency (>99.99%) due to voltage-induced strong electrostatic force.³⁵²

In reality, the pollution of PM particles is always concomitant with gaseous chemicals, such as formaldehyde (HCHO), carbon monoxide (CO), sulfur dioxide (SO₂), nitrogen dioxide (NO₂), benzene, dioxin, ozone, and in some cases with biological agents, for example, bacteria and viruses.^{308, 353} Metal-organic frameworks (MOFs) have offered some help in this regard.³⁵⁴ In 2016, Wang *et al.* prepared MOF based nanofibrous air filter for the simultaneous removal of PM and toxic gases.³²² In this work, MOFs (ZIF-8, UiO-66-NH₂, MOF-199, Mg-MOF-74) were embedded within polymers to prepare nanofibrous air filters, and among all, UiO-66-NH₂/PAN and MOF-199/PAN hybrid nanofibrous air filters showed the best SO₂ adsorption and PM removal performance (Figure 15). Furthermore, Wang *et al.* used a roll-to-roll hot-pressing method and fabricated MOF-based air filters.³⁵⁵ In this method, the MOF nanocrystals were generated onto the flexible substrates *via* continuously roll-to-roll pressing. The MOF-based nanofibrous air filters showed long-term (i.e., 30 consecutive days) and consistently high PM removal (> 90%) under a wide temperature range (80 to 300 °C). Besides MOF, in 2016, Zhong *et al.* employed soy³³⁷ and gelatin protein³³⁸ and fabricated nanofibrous air filter for PM and toxic gas removal.

Figure 15 (a) PM removal efficiency of PAN filter, Al₂O₃/PAN filter and PAN/MOF filters tested on hazy days in Beijing ($T = 23.4^{\circ}\text{C}$, $\text{RH} = 58.6\%$, $\text{PM}_{2.5} = 350 \mu\text{g}/\text{m}^3$, $\text{PM}_{10} = 720 \mu\text{g}/\text{m}^3$). (b) The dynamic adsorption capacities of SO₂ on PAN filter and PAN filters with different MOF materials at 25 °C with a 100 ppm of SO₂/N₂ flow at the rate of 50 mL/min.³²² Reprinted with permission from ref. 322. Copyright American Chemical Society 2016.

Research efforts were also made to endow antibacterial functions to nanofibrous air filters by Ag,³³⁵ ZnO³⁵⁶ and TiO₂³⁴⁸ nanoparticles. The reactive hydroxyl radicals generated by ZnO and TiO₂ under UV irradiation are highly oxidative³⁵⁷⁻³⁶⁰ and have been employed to inhibit bacterial growth along with PM removal. In 2015 Wang *et al.* synthesized ZnO/PTFE and in 2016 Zhao *et al.* fabricated PLA/TiO₂ nanofibrous air filters and both filters exhibited both high PM removal and high antibacterial performances.^{348, 356}

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In conclusion, nanofibrous air filters have evolved rapidly in the past few years and have shown great PM2.5 removal performance along with other desirable features. However, there are challenges lying ahead as summarized below.

In the current designs, the majority of the nanofibers were deposited on nonwoven substrates to construct composite filter media and the active nanofibrous layers could not stand alone due to their low mechanical strength.⁶⁷ Thus, increasing mechanical strength of the nanofibrous layers deserves more attention. Continuous and inexpensive production procedure of nanofibrous air filters must be developed to further reduce their production cost and affordability.

Many of the current nanofibrous filter designs have multiple functions, but they are put together plainly without synergy. Thus one of the future directions of nanofibrous air filters is to have more intelligence with multi-functions being smartly integrated in one device with feedback communication cycle to maximize its performance.

The self-cleaning and/or anti-fouling capability would improve the filters' longevity and the better thermal management can further increase their comfort during their use.³⁴⁹ The incorporation of energy harvesting and generating materials (e.g., piezoelectric or triboelectric materials) would make possible some unprecedented applications, such as air filter with self-powered environmental sensors, air filters with their own lighting systems.

Last but not the least, the interaction mechanisms between PM particles and nanofibers have been paid little attention in the past and are largely unclear, so more fundamental and detailed experimental investigations are warranted. With a clearer understanding to the interaction mechanisms, more effective air filter can thus be rationally designed and fabricated in the future.

6. Concluding remarks

Ensuring reliable access to clean air, clean and affordable water is one of the greatest global challenges of this century. Overcoming this challenge requires new resource management approaches and technological reform. Nanotechnology holds significant promise for enabling water treatment, wastewater reuse and air pollution treatment.

This article reviews the impressive progresses made in the area of intelligent environmental nanomaterials in the past two decades. The intelligent nanomaterials, in response to external triggers, autonomously adjust their behaviors so to achieve their best performances and they have unproved potential of changing the landscape of the future environmental engineering.

However, there are significant barriers standing between the status quo and the full-scale and practical applications of the intelligent nanomaterials. First, the external triggers applied in most of the previously exploratory works were not natural changes of environmental conditions, but the parameters controlled and operated by human. Therefore, in a strict sense, the intelligence of the previous nanomaterials hasn't been truthfully challenged. Research addressing this is in great need. Secondly, the performances of these materials in treating real natural and wastewater need to be tested and validated. Thirdly, the long-term efficacy of these materials as well as their environmental implications are largely unknown. Fourthly, the feasibility of the scale-up of these approaches for commercial purposes and the economics of the processes involved for large-scale applications have not been investigated. Issues such as scaling up fabrication methods, large-scale applications, overall cost effectiveness must be addressed.

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The intelligent nanomaterials are expected to make contributions to the following areas in a foreseeable future. (1) Point-of-use (POU) treatment. Intelligent nanomaterials are yet universally applicable, but they have a great hope of supplementing and more importantly complementing the conventionally centralized basic treatments by providing POU water and air treatment. Nano-enabled POU water purification systems should be capable of exploiting alternative and challenging water sources especially for drinking, keeping energy consumption to a bare minimum.¹⁴ This should especially benefit natural disaster-impacted areas and the developing countries, which are more prone to degradation of water quality. The intelligent nanomaterials-enabled POU treatment can lead to personal water supply devices that utilize any impaired source water.

(2) Fit-for-purpose treatment. As the requirement of differential water quality or fit-for-purpose treatment is heightened nowadays due to energy cost consideration, the intelligent nanomaterials are poised to make significant contributions to distributed differential treatment paradigm. Given their nature, intelligent nanomaterials are easily subject to tailored designs to fit a specific purpose, which gives rise to numerous variants of them. Thus, the large variety of intelligent nanomaterials makes it possible to have modular units for differential and fit-for-purpose treatment goals, which allow easy control of functionality and capacity by plugging in or pulling out modules.¹⁴ The fit-for-purpose treatment pushes the water and even air treatment to be more sustainable and resilient.

(3) Issues of emerging contaminants. Current centralized treatment and distribution systems allow little flexibility in response to changing demand for water quality and are reaching their limits in meeting increasingly stringent water and air quality standards. They usually fall short of coping with emerging contaminants such as pharmaceuticals and personal care products (PPCPs), pesticides, and viruses. The rationally designed intelligent nanomaterials have a potential to provide makeshift and fast responses in the form of POU treatment to fill the gaps. Furthermore, future intelligent nanomaterial enabled systems might function on-demand by detecting contaminants in real time and triggering corresponding treatment when needed.^{361, 362}

Looking at the far future, the key factor of intelligent materials is to have the materials autonomously to perceive their own surroundings and activate fast and precise reactions to realize their designed goals. The materials, assisted with other means, might even assess ongoing situations and forecast what to come so to maximize their chance of success in the future.

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