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Thermoresponsive Polymers for Water Treatment and Collection

Xiaohui Xu,[⊥] Navid Bizmark,[⊥] Kofi S. S. Christie, Sujit S. Datta, Zhiyong Jason Ren, and Rodney D. Priestley*

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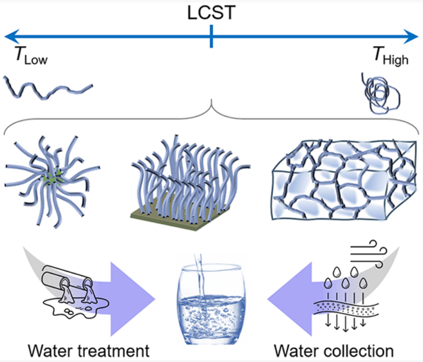
ABSTRACT: To overcome the current scarcity of fresh water sustainably, new technologies will be required that produce potable water from a range of sources, including seawater and moisture from the atmosphere. Moreover, we must recover and reuse water from wastewater streams to reduce our global water footprint. To date, there remain significant concerns about the environmental/ecological impact, high energy consumption, and extensive maintenance costs of current technologies that might prevent their transition to more sustainable routes of potable water generation. One class of material that can enable low-energy water production is thermoresponsive polymers. Due to their unique phase behavior, production flexibility, and biocompatibility, these materials may allow for sustainable routes to fresh water in current and new technologies. In this Perspective, we specifically summarize the design and application of poly(*N*-isopropylacrylamide)- (PNIPAm-) based thermoresponsive microgels and hydrogels. In particular, we show how these materials have been used for water purification, including wastewater treatment, seawater desalination, and moisture harvesting from the atmosphere. Finally, we discuss the opportunities and challenges of transforming current thermoresponsive materials into practical water-related technologies.



■ INTRODUCTION

Water is essential for every community and ecosystem on Earth. While fresh water only accounts for around 2.5% of Earth's water resources, its fraction has declined due to contamination and climate change.[1−3] According to a recent report by the World Health Organization (WHO), over 1.6 billion people lack access to safe water resources.[4] Meanwhile, half of the global population will live in a water-stressed environment by 2025.[2] Each year, unsafe drinking water causes the mortality of 361 000 children.[5] Moreover, water stress can hamper agricultural, manufacturing, and energy generation activities. The future demand for water will continue to grow with increasing population and economic development. Such massive stress on water resources, coupled with climate change-initiated temperature spikes, low precipitation, and flood events, threaten ecosystems and biodiversity and make planning urban spaces and infrastructures challenging. Consequently, water scarcity is an emerging challenge for socio-economic development in the 21st century.[6,7] To address the global water shortage, integrated water resource management must be implemented for sustainable development.[8] To this aim, technological advancements are required within a sustainable roadmap to supply freshwater at the local level.[9]

To date, three approaches show great potential to augment our clean water supply and directly alleviate the water shortage problem: (i) enabling water reuse from wastewater and other impaired water sources, (ii) extracting freshwater from seawater via desalination, and (iii) harvesting atmospheric moisture.[10,11] At the heart of these sustainable water supply technologies is innovation in materials with properties that can efficiently aid in water purification and harvesting. For instance, graphene-based membranes,[11−13] ion-exchange membranes,[14] functionalized wood,[15,16] and solar-powered gels[17,18] have been designed for seawater desalination and wastewater filtration. Moreover, emerging crystalline porous materials, i.e., metal−organic frameworks (MOFs), have been developed to harvest moisture from the air to address water scarcity in landlocked areas.[19,20] Despite significant progress in designing different advanced functional materials for water production from wastewater and other impaired water, seawater, and the atmosphere, most existing technologies still present challenges such as high energy consumption or low water production that significantly limit their efficiency in practical application.[21,22] From this perspective, it is critical to avoid the crippling resource trade-off between energy and water, i.e., the so-called energy−water nexus. Therefore, it is paramount to develop next-generation of water production systems that can generate

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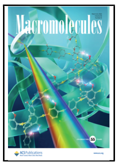

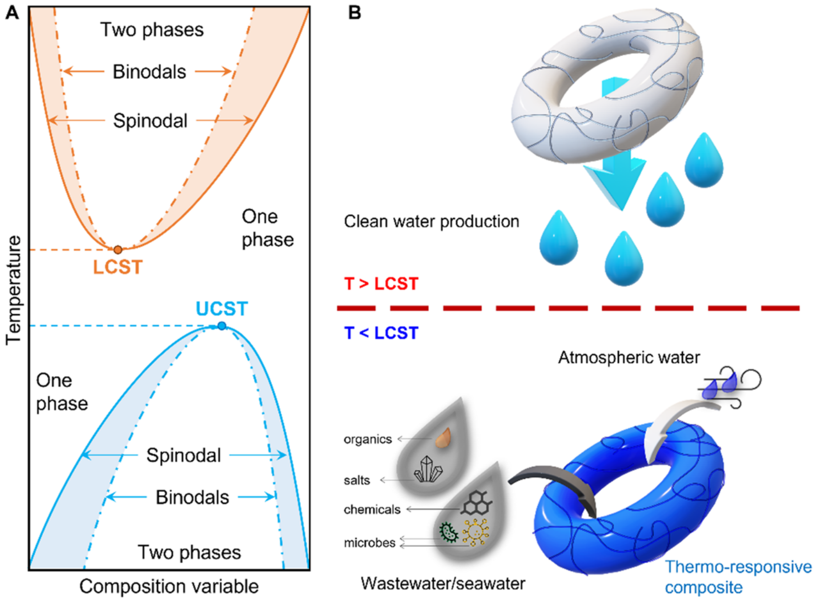

Figure 1. (A) Typical phase diagram for a thermoresponsive polymer with either a LCST or an UCST cloud point. The solid and dashed-dotted lines represent binodals and spinodals, respectively. (B) Schematic showing a section of membrane comprised of thermoresponsive composites used in water treatment and collection. The thermoresponsive property allows water absorption from wastewater, seawater, and the atmosphere at temperatures below the LCST. Above the LCST, the adsorbed water is released.

sufficient water sustainably. In this Perspective, we present the cases that thermoresponsive polymers have emerged as innovative materials that can meet these challenges by leveraging their adaptive properties.

Thermoresponsive polymers can exhibit one of the following critical temperatures at which phase separation occurs: lower critical solution temperature (LCST) or upper critical solution temperature (UCST) (Figure 1A).[23,24] All polymers theoretically exhibit a LCST or an UCST in a given solvent but often under extreme conditions at which solvent may not exist in the liquid state.[25] During the phase separation of thermoresponsive polymers, polymer-rich and solvent-rich phases are formed. The free energy of the demixed state is smaller than that for the mixed state (i.e., polymer solution). This free energy of mixing is a function of temperature and solution composition. Small fluctuations in composition lower the free energy between the two inflection points for the second derivative of the free energy, resulting in spontaneous phase separation, i.e., the spinodal curve (Figure 1A). Despite the larger free energy of the mixed state compared to the demixed state, when the mixture is locally stable to small composition fluctuations, a metastable region forms.[26]

Poly(*N*-isopropylacrylamide) (PNIPAm), the most studied LCST-type polymer, can undergo hydrophilic-to-hydrophobic switching at ~33 °C.[27,28] Below the LCST, the polymer is hydrophilic and can dissolve in water. Above the LCST, the polymer is hydrophobic and is insoluble in water, as revealed by the aqueous solution opacity.[29] PNIPAm-based materials have been used for generating clean water because of their superior ability to collect and rapidly release water under natural sunlight or moderate electrical heating.[30] This unique feature has inherent attributes toward developing sustainable techniques to treat wastewater streams or collect water from the atmosphere (Figure 1B). Inspired by these ideas, remarkable efforts have been made to design thermoresponsive materials in the form of brushes, microgels, and hydrogels.[31−33]

To achieve optimal water treatment/recovery performance, thermoresponsive polymers have been integrated with other water purification technologies. The early integration of thermoresponsive microgels with photocatalysis technology focused on the fast degradation of contaminants to directly purify water.[34,35] Over time, thermoresponsive hydrogels have been used for desalination when coupled with forward osmosis (FO) membranes.[36,37] Currently, their integration with hygroscopic materials has increased interest in harvesting moisture vapor from the air to provide clean water in arid and desert climates.[38,39] In the latter two systems, the primary challenge was to enhance the water release rate during the hydrophilic/hydrophobic switching using a low-energy consumption approach. To this aim, various photothermal agents have been incorporated into PNIPAm-based systems for solar-driven water purification/harvesting.[17,18,40,41] Thus, the rational design and implementation of thermoresponsive polymers provide a promising approach to fulfill the grand challenge of developing sustainable low-energy water generation technologies.

Although several reviews related to thermoresponsive polymers have been published,[42−44] there is no comprehensive report focusing on their applications' progress and future development trends for low-energy water purification/harvesting. Here, we discuss the design and application of thermoresponsive polymers in water treatment and collection settings. We start by discussing three widely used thermoresponsive forms of polymers: brushes, microgels, and hydrogels. Specifically, we will introduce the fundamental mechanism of thermosensitive behavior. Next, we discuss the synthesis pathways, architectures, and properties of thermoresponsive polymers. Subsequently, we focus on their use in water treatment settings by reviewing the ongoing studies of how thermoresponsive polymers are used to purify wastewater containing oils, dyes, and heavy metals via photocatalysis or physical adsorption processes. We discuss the integration of thermoresponsive hydrogels with conventional FO processes

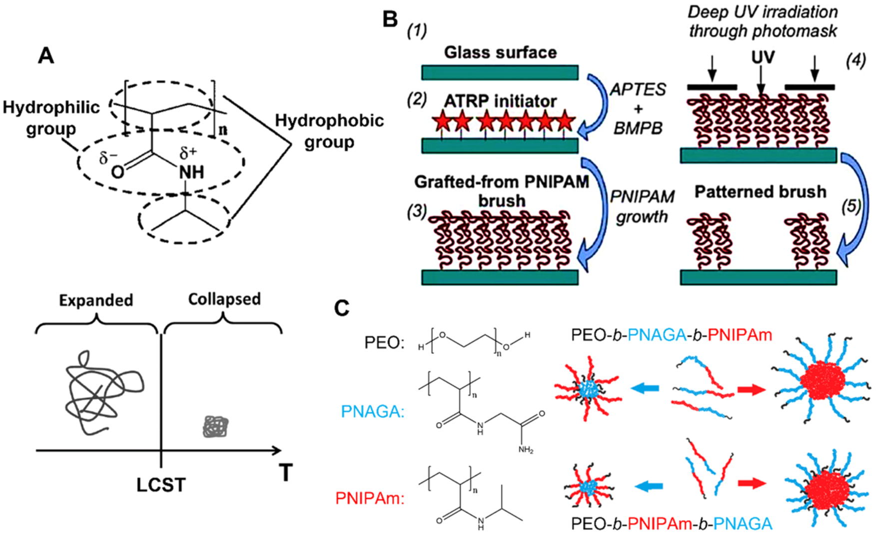

Figure 2. (A) Molecular structure of PNIPAm and its chain configuration below and above the LCST. (B) Grafting of an ATRP initiator onto a glass surface (2) is followed by NIPAM polymerization (3), yielding a polymer brush that is selectively removed by UV irradiation (4). (C) Schematics of the phase transitions and resulting structures for the triblock copolymers during cooling (leftwards blue arrows) or heating (rightwards red arrows). (A) Reprinted with permission from ref 42. Copyright 2017 MDPI. (B) Reprinted with permission from ref 31. Copyright 2012 PLOS ONE. (C) Reprinted with permission from ref 61. Copyright 2016 American Chemical Society.

for seawater desalination. We also review the current state-of-the-art PNIPAm-based technologies to harvest water from the atmosphere. Finally, we provide our perspective on where future research must be conducted to fill the gaps between lab-scale demonstrations and real-world implementation.

■ THERMORESPONSIVE POLYMERS

Research focused on smart materials with adaptive properties has grown over the past decade, inspired by the production of novel thermoresponsive polymers. This is primarily due to their excellent biocompatibility and ease of functionalization, combined with the convenience of controlling the external stimuli, i.e., temperature.[45−47] The thermoresponsive behavior of polymers reflects their interactions with the solvent, which are dictated by the polymer backbone and side group chemistry. A comprehensive library of thermoresponsive polymers has been previously reported.[48] In this section, we focus on the phase transition of thermoresponsive PNIPAm in the form of polymer brushes, microgels, and hydrogels. The section offers a brief overview of the fundamental mechanisms behind the phase transition of PNIPAm-based thermoresponsive materials.

In the case of PNIPAm (Figure 2A), the coexistence of hydrophilic amide moieties attached to hydrophobic isopropyl groups and the hydrophobic backbone makes the molecule thermoresponsive. Below the LCST, PNIPAm chains are in a hydrated state with an expanded structure due to hydrogen bonding of amide groups with water.[49] Above the LCST, the polymer−water hydrogen bonding is weakened. As a result, intramolecular hydrophobic interactions between the backbone and isopropyl groups become dominant, leading to a coil-to-globule conformation change (Figure 2A). Subsequently, intermolecular hydrophobic interactions cause the globules to aggregate, thus forming polymer-rich and water-rich microdomains, resulting in phase separation. This phase transition is reversible, and the value of the LCST can be modulated by a variety of techniques. Specifically, the LCST of PNIPAm decreases slightly (less than 1 °C) with increasing molecular weight, while its LCST is not affected when the molecular weight is higher than 50 kDa.[50] When copolymerized with various imidazolium-based ionic liquids, the LCST of PNIPAm/ionic liquid copolymers can be tuned between 25 and 90 °C.[49] Moreover, the addition of salts,[51−53] urea,[54] organic solvents,[55−58] and osmolytes[59] to the polymer solution was found to decrease the LCST of PNIPAm, but it increased by adding chaotropic anions (SCN^-) and surfactants.[60] These changes could be explained by the interference of additives with the hydrogen bonding between the amide groups of PNIPAm and the bound water molecules.

Polymer Brushes. As shown in Figure 2A, the reversible switching between the coil and collapsed states has inspired the functionalization of solid surfaces by thermoresponsive polymers. PNIPAm, in particular, was successfully grafted atop mica,[62] glass, and silicon[31] substrates via surface-initiated atom transfer radical polymerization (ATRP) (Figure 2B). Furthermore, ultraviolet radiation has been used to produce the desired grafting pattern.[31] PNIPAm functionality can be extended by introducing additional components such as catalysts during the material preparation. Alternatively, novel molecular architectures, including block copolymers and random copolymers, have been designed with desired functionalities and thermoresponsive properties.[61,63−66] For example, block copolymers such as polystyrene-*b*-poly(*n*-isopropylacrylamide)[67] and poly(*N*-isopropylacrylamide)-*b*-poly(vinylidene fluoride),[68] triblock copolymers including polystyrene-*b*-poly(*N*-isopropylacrylamide)-*b*-polystyrene,[69] and polylactide-*b*-poly(*N*-isopropylacrylamide)-*b*-poly(norbornenylethylstyrene-*stat*-styrene)[70] were produced. These block copolymers can form nanoporous water-filtration membranes via spin-coating, self-assembly, or nonsolvent induced phase separation. The membranes exhibited temperature switchable on/off permeability, with a higher permeability obtained at temperatures below the LCST of PNIPAm.[69] These temperature-responsive membranes allow new possibilities in the field of nanofiltration. In a more complex procedure, so-called schizophrenic polymers were

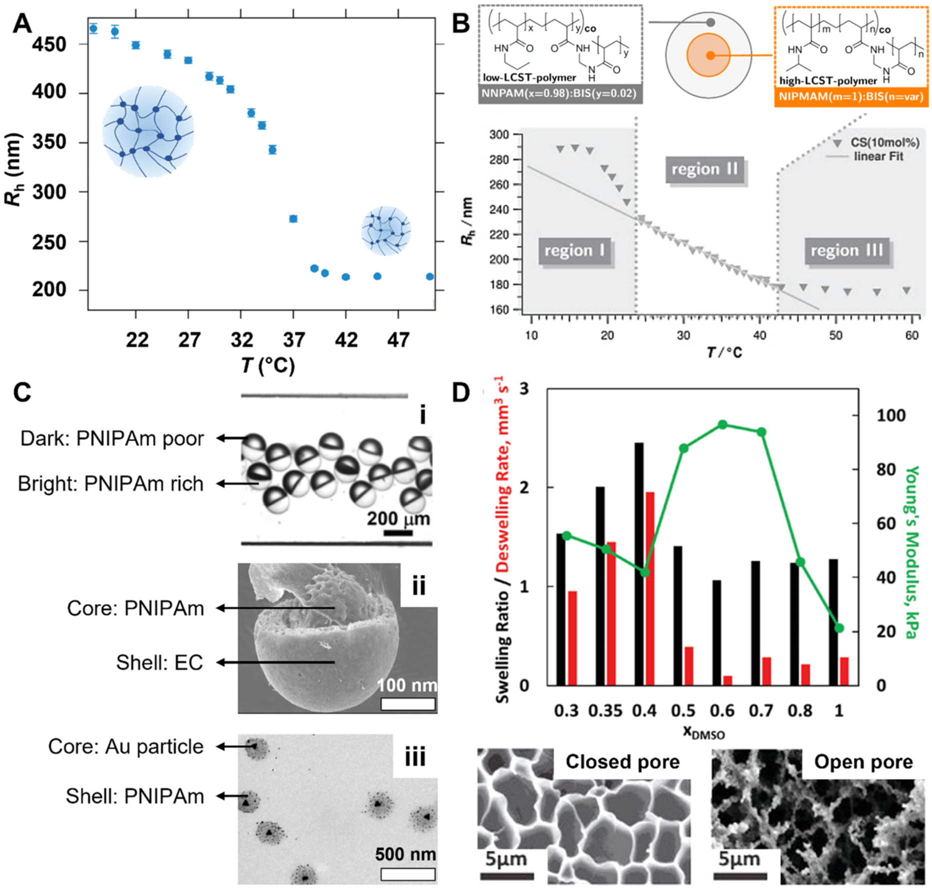

Figure 3. (A) Changes in the radius of a single thermoresponsive microgel at a fully swollen state at T < LCST and a fully collapsed state at T > LCST. (B) Schematic illustration of a core−shell microgel that undergoes three regions of different swelling behavior. (C.i) Optical micrograph of Janus microparticles composed of PNIPAm-poor and PNIPAm-rich domains, (C.ii) SEM image of a PNIPAm/ethyl cellulose core−shell microparticle, and (C.iii) TEM image of triangle gold nanoparticles encapsulated in PNIPAm microgels itself decorated with silver nanoparticles. (D) Compiled swelling ratios, deswelling rates, and Young's moduli of the rapid-responsive PNIPAM hydrogels and SEM images of the closed/open pore structures. (A) Reprinted with permission from ref 90. Copyright 2019 The Royal Society of Chemistry. (B) Reprinted with permission from 77. Copyright 2012 Elsevier. (C.i) Reprinted with permission from ref 85. Copyright 2016 JoVE. (C.ii) Reprinted with permission from ref 87. Copyright 2012 Elsevier, (C.iii) Reprinted with permission from ref 89. Copyright 2020 American Chemical Society. (D) Reprinted with permission from ref 91. Copyright 2021 Wiley-VCH.

designed that comprise polymeric blocks with LCST and UCST responses.[61,65] For example, block copolymers containing PNIPAm, poly(*N*-acryloylglycinamide) (PNAGA) with a UCST response, and nonthermoresponsive poly(ethylene oxide) (PEO) were synthesized with two different designs: PEO-*b*-PNAGA-*b*-PNIPAm and PEO-*b*-PNIPAm-*b*-PNAGA.[61] As shown in Figure 2C, during heating or cooling of aqueous solutions of these polymers, different particle morphologies were expected to form depending on the polymer's original architecture. In the case of PEO-*b*-PNAGA-*b*-PNIPAm, above the LCST of PNIPAm, a core−shell structure was formed where the core consisted of collapsed PNIPAm and the shell of PEO-*b*-PNAGA brushes. Below the UCST of PNAGA, a core−shell structure was also formed but with PNAGA in the core and PEO and PNIPAm in the shell layer. A similar trend was experienced for the block copolymer with a molecular architecture of PEO-*b*-PNIPAm-*b*-PNAGA. The only difference between these two architectures at the collapsed states was the location of PEO in the shell (Figure 2C).

While surface grafting of thermoresponsive polymers has been commonly used in biomedical and drug delivery settings, its application toward sustainable water purification has been limited. This limitation is mainly due to the difficulties in grafting polymer brushes atop solid substrates in a scalable manner.[71,72] Grafting of polymers with the desired pattern can be achieved by controlling the polymer synthesis process or using post-treatment physical methods such as plasma radiation, irradiation, or microwave energy.[72] These extra steps can delay the large-scale production of functional materials, making them less attractive for water treatment applications. Moreover, novel thermoresponsive polymer brushes with functionalities and features such as biocompatibility, long-term stability, and repellent/adsorption of specific ions remain to be developed to potentially expand their use in water processing applications.

Microgels and Hybrid Microgels. When thermoresponsive polymers become physically or chemically cross-linked in three dimensions, the resulting network undergoes a phase transition at the volume phase-transition temperature comparable to the LCST observed for single-chain polymers.[73,74] Emulsion polymerization, microfluidic techniques, coacervation and desolvation, and precipitation polymerization are all approaches that have been used to produce such polymeric networks.[75] In precipitation polymerization, the monomer and cross-linker are first dissolved in water at room temperature, then the solution is heated to a temperature above the LCST. At this elevated temperature, polymerization is initiated in the presence of an initiator, thus forming homogeneous nuclei. As polymerization continues, the nuclei grow through different mechanisms, including monomer condensation and nucleus flocculation, resulting in a cross-linked network of polymers known as microgels. For example, PNIPAm microgels have been typically synthesized by polymerizing NIPAm in the presence of ammonium or potassium persulfate and *N*,*N*′-methylenebis(acrylamide) (BIS) as the initiator and cross-linker, respectively.[73] The size of the microgels decreases (Figure 3A) and Young's modulus increases as temperature increases to and beyond the LCST.[76]

The phase transition behavior can be altered in thermoresponsive microgels by changing the structure of microgels. For example, a core–shell microgel comprising of *N*-isopropylmethacrylamide (NIPMAm) in the core with an LCST of ∼44 °C and *N*-*n*-propylacrylamide (NNPAm) in the shell with a much lower LCST (∼21 °C) underwent drastically different size transformations (Figure 3B) compared to that for a typical homopolymer microgel (Figure 3A).[77] For these core–shell microgels, particle size decreased as temperature increased in three different ways: a nonlinear decrease up to 25 °C due to the collapse of the shell, a linear reduction from 25 to 41 °C due to the mechanical compression of the core by the shell, and the active collapse of the core beyond 41 °C. Similar behavior has also been observed in other core–shell microgels, including aldehyde-functionalized PNIPAm,[78] PNIPMAm-PNIPAm,[79] PNNPAm-PNIPMAm,[80] PNIPAm-PNIPMAm,[81] and PNIPAm-poly(NIPAm-*co*-acrylic acid) (PNIPAm-*co*-PAA).[82] In addition to core–shell structures, microgels with more complex morphologies, including hollow[83] and Janus,[84] have been produced. For example, a microfluidic setup created Janus microgels comprised of PNIPAm but at two different contents (Figure 3C).[85] More advanced core–shell microgels with desired shapes have also been made with thermoresponsive and nonthermoresponsive compartments.[86,87] For example, PNIPAm/ethyl cellulose (EC) core–shell microgels (Figure 3C) were produced via a microfluidic setup to encapsulate vitamin B12 and improve its release at body temperature.[87] In a more complex design, gold nanotriangles and nano-octahedra were embedded in PNIPAm microgels. Subsequently, the resulting composite was decorated with silver nanoparticles (Figure 3C).[88,89] These microgels, with their unique structures, supported controlling the surface-enhanced Raman spectroscopy of a target molecule by changing the temperature.[89]

While the synthesis of novel thermoresponsive polymers requires a detailed sequential production procedure together with a series of stepwise optimizations during the polymerization process, the production of microgels with multiple polymeric or inorganic components—hybrid microgels—can be achieved more easily. Therefore, the fabrication of hybrid microgels has been an alternative pathway, if not a shortcut, to produce functional thermoresponsive materials. To use such microgels in water processing applications, unique features such as antifouling properties and selective permeability must be incorporated and optimized during the design and fabrication processes.

Hydrogels and Hybrid Hydrogels. PNIPAm-based thermoresponsive hydrogels, which exhibit a reversible volume change through swelling/shrinking near the LCST, have been considerably investigated.[44] The volume change leads to differences in network microstructure, transparency, permeability, and mechanical strength. When a PNIPAm hydrogel is heated above the LCST, a thick and dense polymeric layer forms around the hydrogel due to phase separation. The dense layer can prevent the contained water from diffusing out, leading to a relatively low deswelling rate and prolonging the hydrogel's shrinking process. A promising approach to improve the swelling/deswelling rate is to create heterogeneous porous structures via polymerization in mixed solvents,[92−95] adding pore-forming agents in the monomer solution[96,97] or introducing hydrophilic polymers into the conventional PNIPAm network.[98−100] For example, rapid-response PNIPAm hydrogels synthesized in dimethyl sulfoxide (DMSO)–water mixtures display a unique open porous network with continuous microchannels (Figure 3D), which enables a 2-fold enhancement in swelling ratio and 6-fold enhancement in deswelling rate compared to a hydrogel synthesized only in water.[91] These open porous PNIPAm hydrogels also exhibited increased Young's modulus (Figure 3D), but the mechanical properties of the swollen hydrogels remained unclear. Generally, increasing porosity and water content in hydrogels results in a compromise in mechanical properties. Hydrogel fragility makes their implementation in water treatment systems more challenging due to a shorter material lifetime. Therefore, efficient methods to overcome the weak mechanical properties of PNIPAm hydrogels are essential for their practical applications.

Monomer content, cross-link density, swelling ratio, and network structure can affect mechanical properties. Typically, a lower or higher cross-link density will generate a softer or more brittle hydrogel, respectively, at a fixed monomer concentration. Interestingly, a high monomer content with very low cross-link density can create a tough hydrogel due to the excess chain entanglement.[101] Increasing monomer concentration increases the production cost and limits the large-scale fabrication of PNIPAm hydrogels. Another strategy to obtain flexible and tough PNIPAm hydrogels is to incorporate nanofillers as macro-cross-linkers into the networks such as clay, silica, graphene oxide, microgels, and micelles.[102,103] Moreover, tuning the hydrogel structure from a single network to a double network and interpenetrating polymer networks seems promising to increase their strength and toughness.[104] Despite their good mechanical properties, the swelling ratios of these hydrogels are relatively low. Therefore, combining these methods with the techniques to make fast-responsive PNIPAm hydrogels will direct future research on smart hydrogels and trigger their application in water treatment fields. Another promising direction is the functionalization of hydrogels with additive components such as nanoparticles, catalysts, and polymer colloids to improve their water treatment performance. Current practices to develop innovative technologies in different water applications are discussed in the following section.

■ INTEGRATION OF THERMORESPONSIVE POLYMERS FOR WATER TREATMENT AND RECOVERY

Among the various thermoresponsive polymers, PNIPAm has been successfully utilized as polymer brushes, microgels, and bulk hydrogels for water treatment applications. Unlike specialty thermoresponsive polymers that have been optimized for a specific water treatment application, PNIPAm-based materials can be integrated within numerous existing water

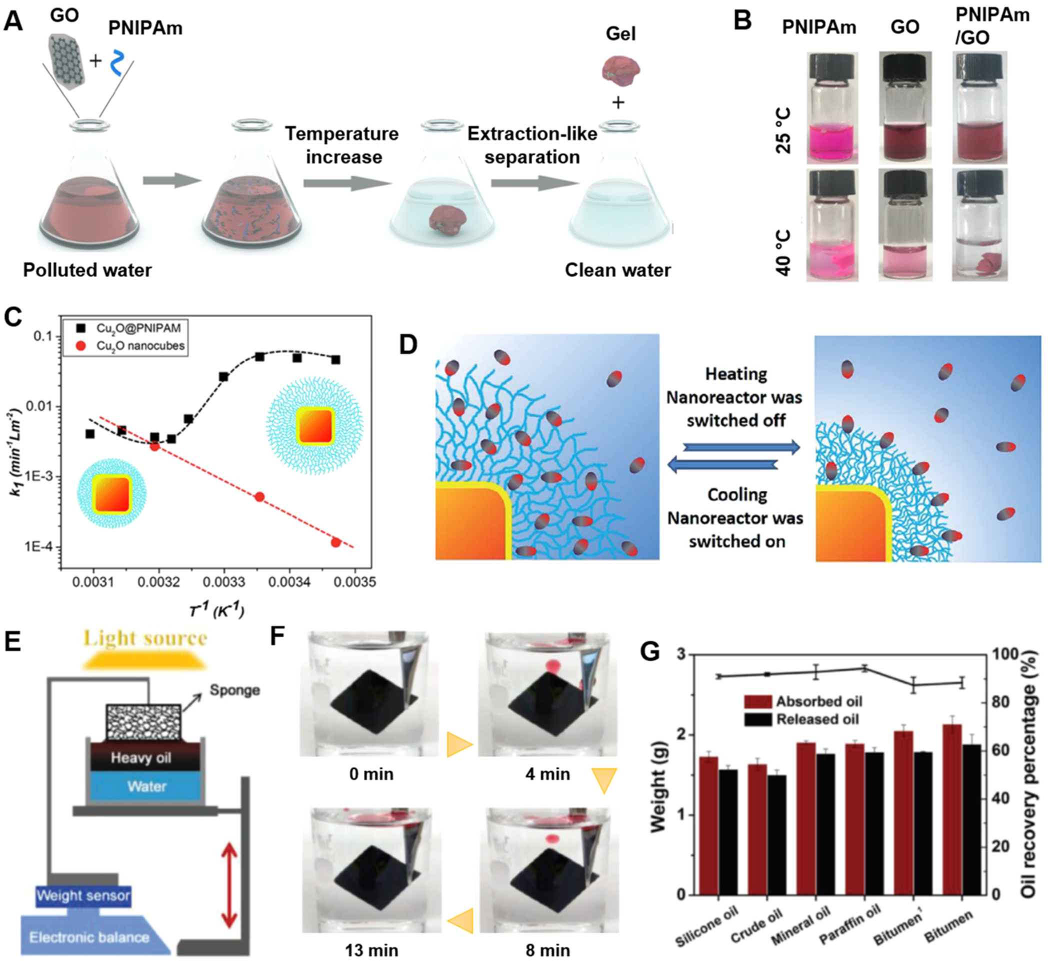

Figure 4. (A) GO/PNIPAm mixed system, which can realize temperature-responsive sol−gel transition and remove organic pollutants from water in an extraction-like process. (B) Photographs of 50 mg/L RhB solution containing the PNIPAm, GO, or the GO/PNIPAm at either 25 or 40 °C. (C) Kinetic analysis of methyl orange reduced by Cu_2O@PNIPAm microgels compared with pure Cu_2O nanocubes at different temperatures. (D) Illustration of the catalytic process in Cu_2O@PNIPAm microgels to degrade methyl orange. (E) Setup schematic used to measure the oil uptake by the PNIPAm/PPy/PDA functionalized melamine sponge exposed to sunlight. (F) Desorption of mineral oil (red drops) from the sponge in part E soaked in water at 22 °C. (G) Absorption and desorption of different oils for the sponge are shown in part E. The line in part G shows the oil recovery percentage. (A and B) Reprinted with permission from ref 118. Copyright 2021 Elsevier, (C and D) Reprinted with permission from ref 34. Copyright 2016 The Royal Society of Chemistry, (E−G) Reprinted with permission from ref 121. Copyright 2018 Wiley-VCH.

treatment and collection technologies. In the following section, we present the recent developments in this area.

Water and Wastewater Treatment. Wastewater discharge from municipal and industrial sources has released contaminants such as heavy metals, organic dyes, hydrocarbons, and pathogens to the aquatic environment. In particular, heavy metals including lead (Pb), arsenic (As), cadmium (Cd), chromium (Cr), and nickel (Ni) remain severe threats to public health and the environment. Adsorption has been regarded as one of the most powerful tools to remove heavy-metal ions from contaminated water.[105,106] However, the adsorption capacity typically decreases as more ions adsorb atop the adsorbent, which has prompted the need to improve adsorbent regeneration. In this context, thermoresponsive PNIPAm-based hydrogels and their derivative copolymers have demonstrated good potential to mitigate such challenges. In this approach, metal ions adsorb and release from the hydrogel below (hydrophilic) and above (hydrophobic) the LCST, respectively.[107] For example, thermoresponsive hydrogel adsorbents were fabricated for the selective removal of Pb^{2+} via UV-initiated polymerization of NIPAm and benzo-18-crown-6-acrylamide (BCAm) monomers, which have remarkable recognition ability toward Pb^{2+}.[108,109] When the ambient temperature was lower than the LCST of the hydrogel, it swelled to allow for the selective formation of Pb^{2+}/BCAm host−guest complexes. Then the adsorbents can be simply regenerated via desorbing at least 85% of Pb^{2+} by increasing the operating temperature above LCST. The driving force for desorption was the unfavorable affinity between Pb^{2+} and BCAm caused by the thermo-induced shrinkage of polymer network.

In a different approach, a metalloprotein-based hybrid hydrogel, prepared by immobilizing a reconstituted cadmium binding peptide (CadRP) into a PNIPAm gel network, was successfully used to adsorb a range of metal ions.[110] In particular, Cd^{2+} adsorption occurred at temperatures above the LCST, where the peptide was immobilized to preferentially capture Cd^{2+}. When the temperature was reduced below the LCST, the external driving force generated by the swelling process distorted the coordination structure and weakened the binding between Cd^{2+} and CadRP, resulting in an impressive Cd^{2+} release efficiency up to 99.5%. In contrast to traditional regeneration processes that occur under strongly acidic or basic conditions,[111] the regeneration of PNIPAm-based adsorbents is acid free and environmentally friendly. In order to improve the mechanical properties of PNIPAm hydrogels, nanomaterials such as clay and graphene oxide have been introduced into poly(NIPAm-*co*-maleic acid) and PNIPAm/alginate (Alg) cryogels, which provide a promising way for recycling rare earth elements such as La^{3+} from wastewater.[114,115] In addition, PNIPAm-based adsorbents have been developed to treat emerging per- and polyfluoroalkyl substances (PFASs) organic pollutants such as perfluorohexanoic acid[112] and perfluorooctanoic acid.[113] Adsorption of pollutants is primarily driven by the hydrophobic interaction between the fluoroalkyl chain of PFASs and isopropyl or methyl groups of PNIPAm at temperatures above the LCST. Below LCST, the adsorbed compounds can be released, driven by the formation of hydrogen bonding between the amide groups of PNIPAm and water. While more work needs to be done to improve their adsorption capacity, such LCST-driven reversible adsorption and desorption of PFASs make PNIPAm-based adsorbents attractive for the ease of water treatment at low cost.

Besides hydrogels, the phase transition of PNIPAm-based free polymers has inspired the development of sol−gel transition processes to remove pollutants from water. For instance, PNIPAm-*b*-PAA block copolymers were successfully utilized to capture Cu^{2+} via complexation of Cu^{2+} with the negatively charged AA units.[116] Above the LCST, the intramolecular hydrophobic interaction between PNIPAm-*b*-PAA/Cu^{2+} complexes led to the formation of larger aggregates, which could be easily separated from the aqueous medium by filtration.[117] A similar hybrid system was proposed to remove organic dyes from water by simply mixing graphene oxide (GO) and PNIPAm with dye solution (Figure 4, parts A and B).[118] In the mixture, dye molecules were first adsorbed by GO, which possesses an extremely high surface area and has been extensively explored for the adsorptive removal of pollutants from water.[119] Then, a dense hydrogel was formed above the LCST, encapsulating GO and the adsorbed dye within the hydrogel matrix. The encapsulated GO aggregates were then separated from water through a solid−liquid separation process. This novel approach can introduce a new, more effective coagulation technique for dye removal from wastewater. However, to establish a large-scale process and compete with alternative approaches,[120] a thorough economic assessment of capital and operating costs is still needed.

The reduction of organic dyes and nitroaromatic compounds by active nanocatalysts loaded into microgels is another widely investigated area for water remediation. Noble metal-based nanocatalysts are easy to aggregate and challenging to recover;[122−124] however, their integration within PNIPAm effectively mitigated such problems. A number of nanocatalysts, including Au, Pd, Ag, and Pt nanoparticles, have been stabilized within PNIPAm-based microgels and hydrogels to enhance catalytic activity and reusability.[35,88,125] Such hybrid microgels can effectively degrade different dyes and various hazardous nitroarenes, including *o*-nitroaniline, *p*-nitroaniline, 4-nitrophenol, and nitrobenzene in an aqueous environment.[126] These hybrid microgels shrank sharply upon increasing temperature to the LCST, which resulted in the suppression of organic dyes diffusion into the network and reduction in catalytic reaction rate. As a result, the catalytic activity of these hybrid microgel systems could be tuned by simply controlling temperature.

To replace the expensive noble metal nanoparticles, several semiconductors such as MoS_2,[127] TiO_2,[128] CdS,[129] and Cu_2O[34] were also incorporated into microgel systems to degrade 4-nitrophenol, pendimethalin, rhodamine B, and methyl orange. Specifically, Cu_2O/PNIPAm hybrid microgels were prepared with a Cu_2O nanocube as the core and a PNIPAm polymeric network as the shell to remove dyes from water.[34] Compared to bare Cu_2O nanocubes, a significant enhancement in the catalytic activity was observed for the Cu_2O/PNIPAm microgels (Figure 4C). This is because the PNIPAm shell layer prevented the oxidation of Cu_2O nanocubes in water and protected its nanostructure from pH and visible light effects. The reaction rate of the bare Cu_2O increased with increasing temperature. In contrast, the Cu_2O/PNIPAm exhibited a local maximum reaction rate at around 25 °C and a dramatic decrease when the temperature was increased near the LCST (Figure 4D).[34] This is because the dye molecules would be enriched at the collapsed hydrogel/solvent interface above the LCST, which would lead to a reduced dye concentration adjacent to the Cu_2O nanoparticles and thus, reduce the reaction rate. Although microgel-nanocatalyst systems exhibit excellent catalytic activity at low temperatures, their separation from reaction systems mainly relies on a high-speed centrifugation process. An efficient way to enhance the functions and practicality of these hybrid microgels is to immobilize them onto commercial polymeric membranes, which will make the catalytic degradation process more convenient. For instance, Pd and Fe−Pd bimetallic nanoparticles were immobilized within thermoresponsive PNIPAm-*co*-PAA- and poly(NIPAm-*co*-methyl methacrylate)-functionalized polyvinylidene difluoride (PVDF) to degrade 2-chlorobiphenyl and *o*-nitroaniline.[130,131] In one approach,[130] as the temperature was increased from 25 to 35 °C, the diffusion coefficient of 2-chlorobiphenyl increased from 6.6×10^{-11} to 8.7×10^{-11} m^2 s^{-1} and its mass adsorption increased from 40% to 70%, respectively. The promoted diffusion and adsorption in the membrane enhanced the overall catalytic degradation of 2-chlorobiphenyl.

The phase transition of thermoresponsive materials alters their water affinity—a feature at the core of smart membrane processes for efficient oil−water separation. Below the LCST, the membrane is hydrophilic, blocking oil but letting water pass through. On the contrary, above the LCST, the membranes are more hydrophobic, blocking water but passing oil through. This mechanism has been demonstrated in various polymeric membranes and sponges.[32,132−137] For example, a robust thermoresponsive polymer membrane was successfully fabricated by coating a thermoplastic polyurethane (TPU) microfiber with PNIPAm hydrogel.[138] The membrane exhibited switchable wettability between superhydrophilicity and superhydrophobicity as the temperature changed from 25 to 45 °C. Therefore, the membrane possessed excellent ability to separate oil-in-water and water-in-oil emulsions at 25 and 45 °C, respectively, with a high separation efficiency of ≥99.26%.[138] This switchable superhydrophilicity and superhydrophobicity property was also found in a PNIPAm and octadecyltrichlorosilane grafted melamine sponge.[134] When immersed in water containing dichloromethane (DCM) at 37 °C, the PNIPAm-coated melamine sponge quickly absorbed DCM until it became completely saturated. The sponge was soaked in a 20 °C water bath to recover DCM. At this

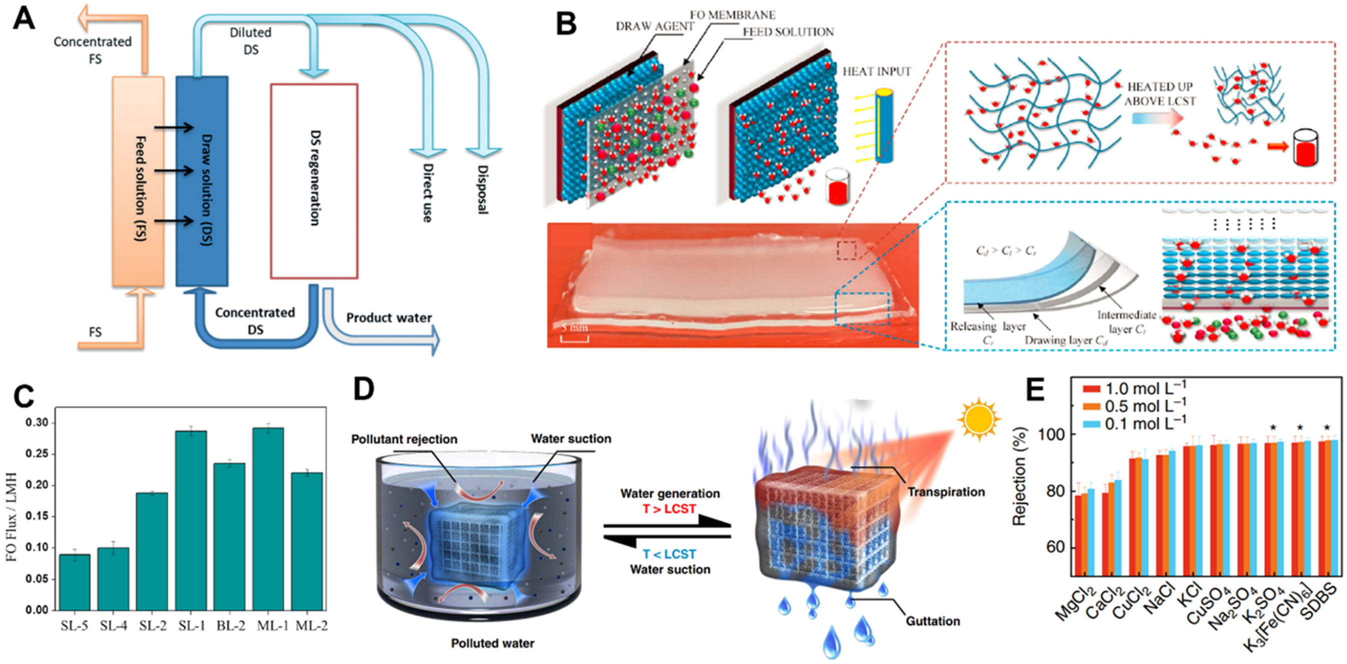

Figure 5. (A) Illustration of the typical forward osmosis process in which a semipermeable membrane is used to separate a feed solution (FS) from a draw agent (*aka* draw solution, DS) to enable the transport of solvent through the membrane driven by the osmotic pressure difference between the two solutions. The concentrated FS is either recycled to achieve further concentration by the DS or sent away for disposal. The osmotic pressure of the diluted DS is regenerated through a process that simultaneously produces clean water before the DS is used for further treatment. The depleted DS may also be used directly or disposed of if the energy requirement for regeneration exceeds its value. (B) FO process and dewatering process using multilayer hydrogel material as the drawing layer. (C) FO flux for different samples with a variation of concentration of SA and configuration—SL, single layer; BL, bilayer; and ML, multilayer. (D) Water purification procedure based on the PNPG-F purifier using solar energy. (E) Rejection of ions through PNPG-F under sunlight irradiation. (A) Reprinted with permission from ref 141. Copyright 2020 The Royal Society of Chemistry. (B and C) Reprinted with permission from ref 140. Copyright 2019 Elsevier. (D and E) Reprinted with permission from ref 18. Copyright 2019 Nature Publishing Group.

temperature, the sponge was hydrophilic, and thus, water imbibed into the sponge and pushed out DCM.[134] To take advantage of renewable energy sources, these thermoresponsive materials were functionalized by solar absorbers that convert sunlight to heat. For example, in addition to PNIPAm, melamine sponges were functionalized by polypyrrole (PPy) and polydopamine (PDA).[121] This sunlight-driven sponge absorbed organic components such as mineral oils and bitumen from the surface of water when exposed to sunlight (Figure 4E) and released the absorbed oil when exposed to cold water (Figure 4F). This cyclic process was not limited to a specific oil, and the oil recovery efficiency was as high as 87% (Figure 4G). However, only 61% of the adsorbed oil could be released from PNIPAm/PPy@MS after three cycles, and washing with hexane is necessary to recover its capacity. Therefore, it highlights the need for further optimization and improvement in the material's performance.

Seawater Desalination. Seawater is the most abundant water source on earth but cannot be easily treated for domestic water use due to its high salinity.[139] Forward osmosis (FO) can be a pretreatment for seawater desalination, credited to its reduced fouling propensity, ease of cleaning and operation, and low energy cost.[140] In the FO process, water molecules pass through a selectively permeable membrane driven by an osmotic pressure gradient imposed by a draw agent with a high osmotic pressure. In contrast, the solute molecules stay in the feedwater (Figure 5A). After separation of the draw agent from the permeated water, the draw agent can be regenerated using thermal or membrane separation, chemical precipitation, or response-stimulated separation by heat/magnetic field to produce freshwater.[141]

Compared with other membranes, FO membranes can achieve high transmembrane solvent flux, reject the dissolved solutes entirely in feed and draw agents, and maintain long-term mechanical robustness.[142] However, the functionality of the FO membranes is limited primarily by internal concentration polarization effects, which are exacerbated by diffusive resistance to the draw solute through the supporting layer of the membrane.[143−145] Despite recent progress, more effort has focused on developing beneficial draw agents.[146] Similar to membrane materials, the draw solute can significantly impact solvent transfer in FO. Ideally, draw agents should be inexpensive, stable, easily dissolvable, environmentally friendly, and of adequate molecular size to abstain from diffusing back through the membrane.[147,148] For example, organic components such as poly(aspartic acid sodium salt) and poly(sodium 4-styrenesulfonate), and inorganic salts (such as magnesium chloride, calcium chloride, and ferric and cobaltous hydroacid complexes) together with other emerging draw agents like magnetic nanoparticles have been developed recently.[149−151] Alternatively, polymeric materials, including thermoresponsive materials exhibiting LCST properties, have been demonstrated to be attractive drawing agents for FO.

Early investigations show that water flux suffers when pure PNIPAm hydrogels are used as draw agents.[152] Subsequently, ionic hydrogels comprised of poly(sodium acrylate-*co*-*N*-isopropylacrylamide) (PSA-*co*-PNIPAm)) were developed to increase the osmotic pressure and enhance water uptake flux.[152−154] Even though the ionic hydrogels exhibited high water uptake and 23% salinity reduction,[155] most water recovered at elevated temperatures was in the vapor state. This is because the ionic groups hindered the phase transition of PNIPAm above the LCST and thus compromised the water release.[36] To address this issue, a bilayer polymer hydrogel was designed in which the PSA-*co*-PNIPAm hydrogel served as a water-absorptive layer and the PNIPAm hydrogel as an upper dewatering layer.[37] Similarly, a multilayer hydrogel featured with a gradually decreasing PSA content away from the FO membrane was applied as an efficient draw agent (Figure 5, parts B and C).[140] In the multilayer hydrogel, the PSA-*co*-PNIPAm component with a high PSA content served as the drawing layer due to its high osmotic pressure. The pure PNIPAm hydrogel was the releasing layer to trigger water release with lower energy required than pressurized processes. Additionally, an intermediate PSA-*co*-PNIPAm hydrogel layer with a lower PSA content was introduced to reduce the mass transport resistance and promote water transport from the drawing layer to the PNIPAm layer. As a result, this multilayer hydrogel yielded a high FO flux of 0.292 L m^{-2} h^{-1} and a dewatering ratio of 72%, which was 39.5% higher than that for bilayer hydrogels.

Another way to preserve the high permeable flux and the excellent LCST of PNIPAm hydrogel-based draw agent is to prepare ionic thermoresponsive hydrogel with a semi-interpenetrating network (semi-IPN) structure. By polymerizing NIPAm monomers in the presence of linear poly(vinyl alcohol) (PVA) or PSA,[156] thermally sensitive semi-IPN hydrogels with LCSTs between 33 and 35 °C were fabricated, with a rapid release capacity of nearly 100% of the absorbed water when heated to 40 °C. An ionic polyglutamic acid (γ-PGA) and a pore-forming agent polyethylene glycol (PEG) were selected to copolymerize with NIPAm, forming semi-IPN PNIPAm/γ-PGA/PEG hydrogels.[97] The hydrogel exhibited a high-water adsorption capacity of 94.76 g g^{-1} due to the improved osmotic pressure and porous structure, and a dewatering ratio of 97.64% within 30 min at 35.2 °C.

Thermoresponsive microgels ranging from tens to hundreds of nanometers in diameter have also been applied as FO draw agents. Compared with bulk hydrogels, the microgels' smaller sizes and larger surface areas promoted better contact with the membranes, resulting in higher osmotic pressures and higher water flux performance. To date, a series of ionic thermoresponsive microgels have been reported by copolymerization of NIPAm with various anionic comonomers, including acrylic acid, itaconic acid, methacrylic acid, maleic acid, and 2-acrylamido-2-methyl-1-propanesulfonic acid[157,158] as well as cationic monomers such as 2-(diethylamino)ethyl methacrylate, 2-(dimethylamino)ethyl methacrylate and 4-vinylpyridine, and 1-vinylimidazole.[159] These microgels show promising water uptake fluxes between 1.5 to 5.5 L m^{-2} h^{-1} and water recovery of 30 to 50% with a thermal stimulus, thus ensuring their role as effective draw agents for FO. In particular, thermoresponsive magnetic microgels based on superparamagnetic nanoparticles coated with copolymers poly(sodium styrene-4-sulfonate)-*co*-poly(*N*-isopropylacrylamide),[160] poly(*N*-isopropylacrylamide-*co*-sodium 2-acrylamido-2-methylpropanesulfonate), and poly(*N*-isopropylacrylamide-*co*-acrylic acid)[161] have also been used as efficient draw agents to extract water from brackish water or seawater. Improvement in the recovery efficiency was observed using these microgels as water can be quickly recovered from the diluted draw agent using an external magnetic field and thermal stimulus.

In a recent solar-driven setting, a layer of PNIPAm-modified graphene was coated atop PNIPAm/melamine foam hybrid materials (PNPG-F) (Figure 5D) for water desalination and purification.[18] In this system, the graphene layer converted sunlight energy into heat, resulting in the phase transition of PNIPAm, consequently squeezing out the absorbed water. The hydrogel's absorbed water is clean because PNIPAm-modified graphene separates ions and molecules with a relatively high rejection rate (>99%). After desalination, the salinities of the brine samples (average salinity 3.0%) were significantly decreased to 0.7% or smaller, demonstrating the potential for saline water desalination (Figure 5E). Compared with conventional solar steam generation systems requiring high energy consumption for water evaporation and condensation, this system offers a higher water collection rate of 4.2 kg m^{-2} h^{-1} under natural sunlight owing to the thermoresponsive behavior. Such a high-efficiency sunlight-driven system could have great potential applications in diverse water treatments.

Moisture Harvesting. As a sustainable source of clean water, Earth's atmosphere preserves almost 13 billion tons of fresh water in the forms of vapor and aerosolized liquid water (fog)—equivalent to ∼10% of all fresh lake water or ∼50 000 km^3 of freshwater.[162] With such an abundance of fresh water, the atmosphere becomes a ubiquitous and sustainable source for the potable water supply. Consequently, moisture absorption has emerged as an attractive approach to mitigate the storage of worldwide water, especially in arid and landlocked regions.

The early investigation for harvesting water from humid air mainly focused on desiccants (e.g., metal−organic frameworks (MOFs) and hygroscopic salts), which rely on high energy to desorb/evaporate water and subsequent water condensation.[163−165] This feature significantly hindered their practical utilization as promising atmospheric water harvesters. In this context, thermoresponsive PNIPAm-based soft materials have emerged as highly efficient, simple, and inexpensive moisture collectors due to their ability to capture water from the air, condense the adsorbed moisture, and then release the liquid water above its LCST. This section presents the contributions of PNIPAm-based materials for the collection and purification of water captured from fog or humid atmospheres.

In designing PNIPAm-based soft materials for moisture harvesting, a particularly effective strategy was to coat PNIPAm atop a substrate surface to create a smart material that responded to temperature changes in the environment. For example, PNIPAm brushes were directly grafted onto a cotton fabric surface using surface-initiated ATRP.[166] The as-prepared PNIPAm-cotton fabric showed a water uptake of approximately 3.4 g/g when exposed to the humidity of ∼96% at 23 °C. When the temperature was increased, the swollen PNIPAm-cotton became increasingly opaque, and liquid water started to release due to the LCST transition of the PNIPAm. A similar platform of PNIPAm-coated cellulose acetate fibers were fabricated by the core−shell electrospinning technique with cellulose acetate as the core and PNIPAm as the shell with a moisture uptake capacity of ∼2.08 g g^{-1}.[167] Even though PNIPAm preserved effective thermosensitivity, the moisture adsorption capacity remained relatively low, raising the need to improve the performance of the gel systems for moisture harvesting and release.

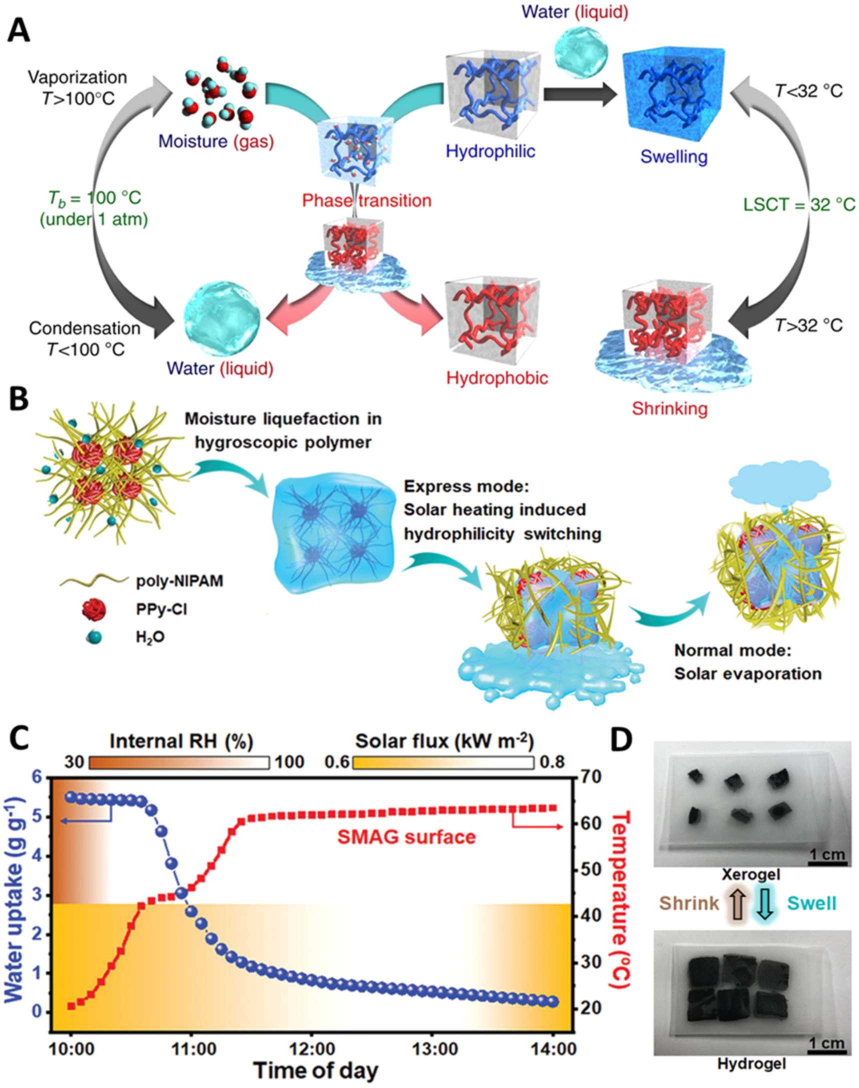

Figure 6. (A) Water-adsorption and oozing behavior of dried PNIPAm/Alg interpenetrating gel. (B) Super moisture-absorbent gel (SMAG) for water capture and release under solar irradiation. (C) Outdoor water releasing and the surficial temperature of SMAG under natural sunlight. (D) Volume change of SMAG. (A) Reprinted with permission from ref 169 Copyright 2018 Nature Publishing Group. (B–D) Reprinted with permission from ref 38. Copyright 2019 Nature Publishing Group.

One efficient way to enhance atmospheric water harvesting was to integrate hygroscopic materials such as mesoporous MOFs with a hydrophilic polymer and hygroscopic salts. In a recent study, PNIPAm was polymerized inside the nanocavities of MOFs. The composite material achieved a moisture adsorption of 4.4 g g^{-1} under a humidity of 96% at 25 °C.[39] In comparison with most MOFs with water releasing temperatures higher than 80 °C, the MOF/PNIPAm composites could release 98% of the adsorbed water at a relatively low temperature, i.e., 40 °C.

Compared to PNIPAm brush-modified materials which require synthetic procedures for surface modification, the direct use of PNIPAm-based hydrogels has become a more scalable strategy for capturing and quickly releasing moisture.[168] A hydrogel comprising PNIPAm and Alg with an IPN structure was developed for water harvesting (Figure 6A).[169] The introduction of hydrophilic Alg tripled the moisture adsorption capacity, compared to that for pure PNIPAm hydrogels, at a total amount of 0.6 g g^{-1} at 27 °C and a humidity of 80%. Recently, a super moisture-absorbent gel (SMAG) that integrated the hygroscopic chloride-doped polypyrrole (PPy-Cl) into a PNIPAm framework was demonstrated as an efficient moisture harvester functioning in a wide humidity range (Figure 6B–D).[38] The water sorption amount by SMAG was 0.7, 3.4, and 6.7 g g^{-1} at relative humidities of 30%, 60%, and 90%, respectively—a significant increase in the moisture capturing capability compared to PNIPAm and PNIPAm/Alg IPN systems. Interestingly, because of the excellent photothermal conversion property of PPy-Cl, the stored liquid water could be rapidly expelled, and some water could be collected via an evaporating-condensing process under natural sunlight irradiation. Recently, an attempt has been made to incorporate MOFs, $CaCl_2$, and photothermal Au nanoparticles into PNIPAm hydrogels.[40] The moisture adsorption capacity can reach up to 6 g g^{-1} at 90% relative humidity. These results demonstrate that thermoresponsive polymers combined with hygroscopic materials have immense potential in water collection using low energy.

Directly collecting aerosolized liquid water (fog) from the air is also one efficient approach to producing potable water. To this aim, a three-component network of agarose helices (Aga), PNIPAm, and Alg IPN hydrogels covered with a superhydrophobic copper mesh were developed as fog harvesting systems.[170] Compared to an Aga/PNIPAAm/Alg IPN hydrogel, a water harvesting enhancement of approximately 1.2 times was observed for the copper mesh covering the IPN hydrogel. This is due to the superhydrophobic copper mesh that increased the fog absorption rate and reduced the re-evaporation of the absorbed water. When heated to a temperature above the LCST (∼33 °C), the IPN hydrogel repelled and released water, indicating its strong potential in developing a sustainable approach to produce potable water in foggy areas. The moisture collection from the atmosphere has been vastly encouraged to produce potable water and address the global water shortage. However, atmospheric moisture and smog may contain harmful particulate matter and microorganisms, thus contaminating the collected water. To resolve this challenge, antimicrobial and antibiofouling matter such as metallic nanoparticles and enzymes could be incorporated into thermoresponsive hydrogels.

■ CHALLENGES AND OPPORTUNITIES

Due to their low energy consumption and high efficiency, thermoresponsive polymers are among the most promising soft materials for novel solutions in water decontamination, seawater desalination, and moisture harvesting. Their highly interconnected porous structure enables fast water uptake and transport. The collected water can be quickly released by regulating their temperature-induced polymer−water interactions. The switching between these two states can be actively modulated or passively controlled in novel water treatment and collection practices.

In water applications, thermoresponsive materials have been widely used as polymer brushes, microgels, and hydrogels. Despite the efficiency of these thermoresponsive materials, there are still challenges that need to be adequately addressed in the future. The most severe bottleneck lies in the manufacturing cost of the materials, especially the complicated routes to synthesize block polymers and microgels. Combining thermoresponsive cellulosic derivatives with PNIPAm could be promising to produce low-cost materials. Moreover, the need to impart heating and cooling devices as well as the required energy to trigger the phase transition is challenging. Although introducing photothermal agents into thermoresponsive hydrogels promises to reduce energy consumption, continuous operation remains a significant barrier to industrial use.[17,18] In addition, facile and efficient approaches to separate polymers/microgels from water after decontamination is helpful for their reusability. The thermoresponsive and mechanical properties should be improved for hydrogels to enhance water release rate and long-term durability without sacrificing the water uptake property. Possible solutions include synthesizing interpenetrating/double networks, incorporating nanofillers, or developing macro-cross-linkers.

Integrating thermoresponsive materials with existing membrane separation strategies provides a potentially efficient way to produce potable water from different water resources. Such integrations may increase capital costs by necessitating a more exotic selection of starting ingredients beyond typical commercial materials. However, they can save operational and maintenance costs by extending the lifetime of membranes and decreasing the amount of chemicals required for cleaning. Furthermore, such integrated systems can be deployed at small scales locally to remote or rural areas with flexibility in the production capacity. This strategy helps decentralize the current water supply systems, lowering the overall costs and opening the door to sustainably provide water for local needs.[171] Therefore, the large-scale implementation of thermoresponsive materials in water treatment should be carefully considered, including the target treatment capacity, production rate, material lifetime/costs, and investment support.[172,173] Specifically, for solar energy-driven water treatment, the location of the process, and therefore, the availability of sunlight will also need to be considered before installation.[164,174−176] Above all, a comprehensive economic analysis and energy-related factors for each proposed application should be undertaken to better understand the scale-up potential. One way to analyze this potential is to implement work breakdown structure (WBS) models developed by the United States Environmental Protection Agency (EPA) to estimate the costs associated with a given treatment technology. While the EPA's WBS models provide detailed analysis on multiple water treatment technologies, the inclusion of thermoresponsive polymer materials into this framework is needed to fully assess the feasibility of their industrial application.

We anticipate that the research efforts and prospects of thermoresponsive materials and systems will significantly contribute to alleviating the global crisis of water scarcity and inspire the better design of stimuli-responsive polymer-based materials. With an optimized design, the scope of application for hydrogels can be expanded beyond traditional pharmaceutical/biological disciplines into energy−water nexus management systems.

■ AUTHOR INFORMATION

Corresponding Author

Rodney D. Priestley − *Department of Chemical and Biological Engineering and Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey 08540, United States;* orcid.org/0000-0001-6765-2933; Email: rpriestl@princeton.edu

Authors

Xiaohui Xu − *Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08540, United States*

Navid Bizmark − *Department of Chemical and Biological Engineering and Princeton Institute for the Science and Technology of Materials, Princeton University, Princeton, New Jersey 08540, United States;* orcid.org/0000-0002-1582-9909

Kofi S. S. Christie − *Department of Civil and Environmental Engineering and Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey 08540, United States;* orcid.org/0000-0002-7039-7889

Sujit S. Datta − *Department of Chemical and Biological Engineering, Princeton University, Princeton, New Jersey 08540, United States;* orcid.org/0000-0003-2400-1561

Zhiyong Jason Ren − *Department of Civil and Environmental Engineering and Andlinger Center for Energy and the Environment, Princeton University, Princeton, New Jersey 08540, United States;* orcid.org/0000-0001-7606-0331

Complete contact information is available at:
https://pubs.acs.org/10.1021/acs.macromol.1c01502

Author Contributions

⊥The manuscript was written through contributions of all authors. All authors have approved the final version of the manuscript. X.X. and N.B. contributed equally.

Notes

The authors declare no competing financial interest.

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