Bifunctional Polymer Hydrogel Layers As Forward Osmosis Draw Agents for Continuous Production of Fresh Water Using Solar Energy

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S Supporting Information

ABSTRACT: The feasibility of bilayer polymer hydrogels as draw agent in forward osmosis process has been investigated. The dual-functionality hydrogels consist of a water-absorptive layer (particles of a copolymer of sodium acrylate and *N*-isopropylacrylamide) to provide osmotic pressure, and a dewatering layer (particles of *N*-isopropylacrylamide) to allow the ready release of the water absorbed during the FO drawing process at lower critical solution temperature (32 °C). The use of solar concentrated energy as the source of heat resulted in a significant increase in the dewatering rate as the temperature of dewatering layer increased to its LSCT more rapidly. Dewatering flux rose from 10 to 25 LMH when the solar concentrator increased the input energy from 0.5 to 2 kW/m². Thermodynamic analysis was also performed to find out the minimum energy requirement of such a bilayer hydrogel-driven FO process. This study represents a significant step forward toward the commercial implementation of hydrogel-driven FO system for continuous production of fresh water from saline water or wastewaters.
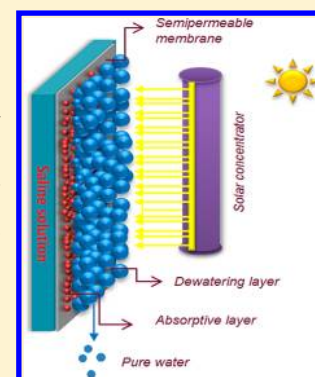
INTRODUCTION

The population suffering from water scarcity is increasing due to increasing domestic and industrial usage and climate change. Water shortage has a direct impact on poverty and food security, which needs to be addressed internationally. Applications of membrane-based processes such as nano-filtration (NF),[1] reverse osmosis (RO),[2] membrane distillation (MD),[3] and forward osmosis[4] for water desalination and water recycling have started to provide some solutions to solving the scarcity of fresh water. Recently, desalination by forward osmosis (FO) process has particularly attracted attention because of its potential to produce fresh water at a much lower energy cost when compared with RO, NF, and MD. The FO process involves two stages of water permeation and separation; typically, osmotic pressure gradient provided by a draw agent with a high osmotic pressure drives water from saline water to draw (solution) agent with a low osmotic pressure.[4] In the second stage, the draw agent needs to be separated from the permeated water and recovered. Currently, the full recovery of draw agents at a modest energy cost is one of the main obstacles for commercial implementation of FO processes.[5] In addition to the problem of low-cost energy regeneration of any newly researched draw agent, there are a few criteria relating to the resultant water which must be taken into account. These criteria include nontoxicity, particularly for potable water production, near neutral pH and compatibility with the membrane surface.[4] One of the commonly reported draw agents which can produce adequate water flux is thermolytic ammonium salts such as ammonium bicarbonate.[6] However, their practical application, particularly in the production of potable water, has been limited due to issues such as the need for regeneration via thermal decomposition of

the ammonium salt at about 60 °C, high reverse salt diffusion, early decomposition of ammonium salt at the ambient temperate of above 30 °C, and difficulty in complete removal of such a draw agent.[5,7,8] Very recently we have demonstrated that the thermoresponsive polymer hydrogels can be used as draw agent to generate osmotic pressure difference in the FO process.[9] Thermoresponsive polymer hydrogels such as poly-(N-isopropylacrylamide) (PNIPAM) can absorb water and create high swelling pressures across the FO membrane to draw water from high salinity seawater through the membrane. The hydrogels undergo a reversible volume change or solution−gel phase transition under temperature-stimuli to deswell and release the absorbed water. Further modification of hydrogels by introducing highly hydrophilic ionic groups (e.g., copoly-merization of NIPAM with sodium acrylate, PSA-PNIPAM)[9] and/or the incorporation of light absorbing moieties such as carbon particles[10] or graphene sheets[11] can significantly improve the efficiency of the draw agent. Although such efforts effectively improve the water flux and the permeation performance, the hydrogels need to be collected from the FO cell to recover and separate them from the absorbed water at higher temperature than the lower critical solution temperature of NIPAM hydrogel, all occurring in a batch fashion. In addition, most of water recovered is in the vapor, rather than liquid, phase. Another advantage of this new FO process is that there is no reverse diffusion of draw solute, as the covalently incorporated ionic groups are balanced by mobile counterions

trapped inside the hydrogel network. The issue of reverse diffusion of draw solute is one of the main challenges in the design of other draw agents.[12]

Herein we demonstrate that when bifunctional thermoresponsive hydrogels layers are used as draw agents in a FO process, there is no need for removal of the draw agent from the membrane module, making it possible to continuously produce liquid fresh water. As schematically illustrated in Figure 1, the synthesized hydrogels are placed on the FO membrane in
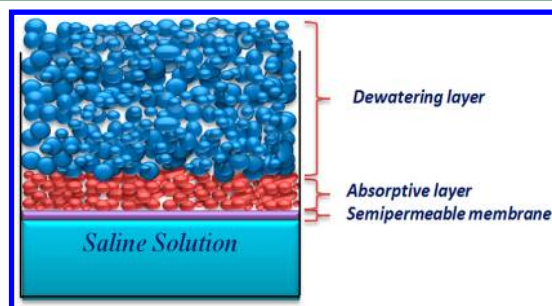

Figure 1. FO process with bilayer thermoresponsive hydrogels as a draw agent.

a bilayer arrangement of absorptive and dewatering layers. The first adsorptive layer of ionic hydrogel provides the high osmotic pressure to withdraw water from the feed. The second dewater layer of more themosensitive hydrogel adsorbs the water from the adsorptive layer. Once the water content of the dewatering layer reaches a certain level, the water can be recovered by increasing the temperature to the lower critical solution temperature of the dewatering hydrogel layer to induce a volume phase transition using renewable solar energy or reclaimed heat. In this work, in addition to the proof of this concept of using bilayer polymer hydrogels as draw agent, the energy requirement of such a process was discussed to provide guidelines for future optimization and scale-up.

■ EXPERIMENTAL SECTION

The N-isopropylacrylamide (NIPAM, 96%) and sodium acrylate (SA, 99%) monomers, N,N′-methylenebisacrylamide (MBA, 99%) cross-linker, ammonium persulfate (APS, ≥98.0%) initiator, were all purchased from Sigma-Aldrich.

Cellulose triacetate forward osmosis (FO) cartridge membranes with an embedded polyester screen mesh were kindly provided by Hydration Technologies Inc. (Albany, OR).

Free-radical polymerization of monomers (NIPAM and SA) was used to synthesize the thermo-responsive hydrogels. For synthesis of absorptive hydrogels, first, an equimolar ratio (1:1) of SA and NIPAM monomers were dissolved in deionized water at room temperature in a capped bottle to form 16.7 wt.% solution (2 g of NIPAM was used). After the complete dissolution of monomers, the 0.057 g of N,N′-methylenebisacrylamide cross-linker was added to the monomer solution. The polymerization was initiated by adding 0.04 g of ammonium persulfate into the solution at 70 °C. The molar ratio of monomers, cross-linker and initiator was set to 50:1:0.5. For the preparation of dewatering hydrogels, a similar procedure was followed to synthesize dewatering hydrogels except that the monomer solution was made of nonionic monomers of NIPAM. To ensure complete polymerization, the hydrogels were then kept at 70 °C overnight. The products were immersed into daily fresh deionized water at room temperature for a few days before drying at 80 °C in a convection oven to remove any possible un-cross-linked oligomers or unreacted reactants. Finally, a SPEX 6870 Freezer/Mill (SPEX SamplePrep.) was used to grind the hydrogels into small particles (2−25 μm) cryogenically. Gravimetric method was used to study forward osmosis performance at a feed salinity of 2000 ppm NaCl, swelling behavior and dewatering of hydrogels by calculating the swelling ratio "Q", permeation and dewatering flux (LMH) in a homemade FO cell. The released water was determined by measuring the weight of the FO cell before and after dewatering. For the concentrated solar dewatering a Fresnel lens was placed between sunlight simulator and FO cell. For more details on Q, flux and dewatering procedures and calculations, see Supporting Information (SI).

■ RESULTS AND DISCUSSION

In Situ FO and Water Recovery. In the bilayer arrangement, it is critical that the dewatering layer maintains its shape and absorption capacity during different cycles of FO permeation and dewatering. Therefore, a FO cell with a thin layer of NIPAM-SA hydrogels (0.2 g on 1.77 cm² membrane)
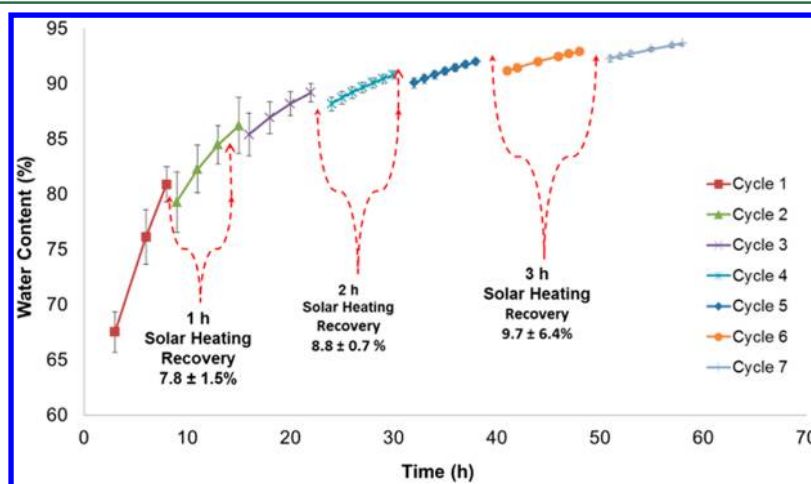

Figure 2. The water content of NIPAM-SA hydrogels during sequential cycles of water permeation and solar water recovery at an irradiation intensity of 0.5 kW m^{-2}. The simulated sunlight was switched off after 1, 2, and 3 h solar heating to allow for water withdrawal from the feed.
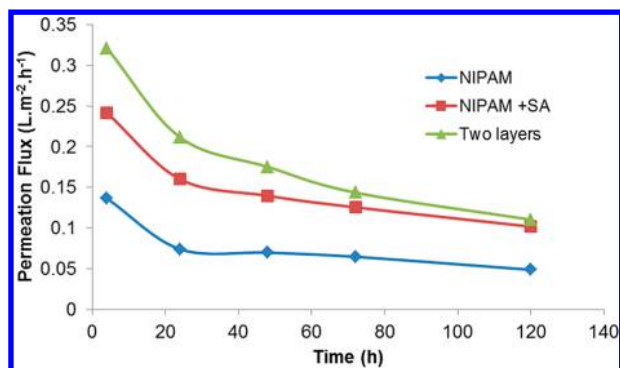
Figure 3. Water permeation fluxes produced by hydrogel draw agents in FO processes at room temperature. The amounts of hydrogel particles: 0.1 g of NIPAM, 0.02 g of PNIPAM+SA. The membrane area was 1.77 cm^2 and the feed solution was 2000 ppm sodium chloride solution.

was used and subjected to different cycles of FO permeation and solar dewatering. When the swollen hydrogel is exposed to a solar heating source, hydrogel temperature increases.

Figure 2 shows the water content of the thin layer of NIPAM-SA hydrogels during in situ FO water permeation and recovery process at a solar energy of 0.5 kW m^{-2}. Increasing the solar exposure time leads to an increase in the water recovery from 7.8 for 1 h exposure to 8.8 and 9.7%, for 2 and 3 h exposure, respectively. In general, the water content increases as a function of permeation time during the seven cycles. This is because the amount of water permeated in the first cycles is greater than the amount of water recovered in shorter solar dewatering times; but when the solar exposure time increases the amount of the water permeated through the membrane becomes close to the amount of the water recovered from the hydrogel in each cycle. The effect of the solar intensity on the water recovery enhancement was also investigated. As shown in SI Figure S2, the water recovery increased with increasing the solar intensity. The results also show that the dewatering hydrogel layer maintains its performance during seven cycles of FO water permeation and solar dewatering. These results show that in situ FO water permeation and solar dewatering can be achieved without a need to remove the hydrogel from the membrane cell for dewatering, indicating that it is feasible to
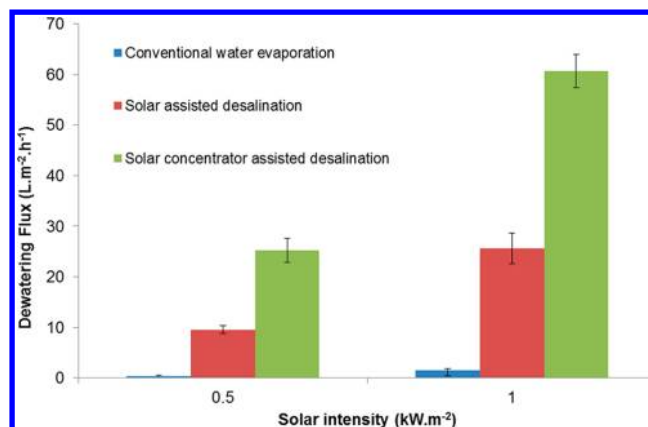

Figure 5. Comparison between water production via conventional solar evaporation and solar assisted FO process using bilayer hydrogels after 10 min (Fresnel lens increases the solar intensity by 4 fold).
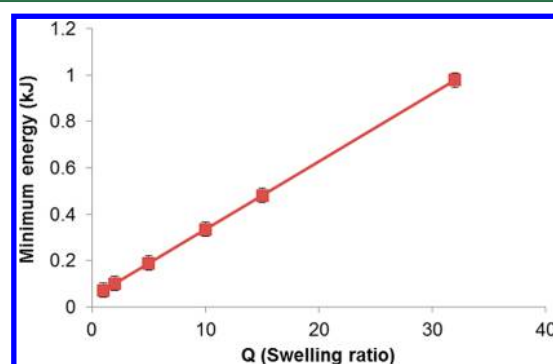

Figure 6. Minimum energy required for dewatering of swollen hydrogel (m_h = 1 g, 25 °C).

design a hydrogel-driven FO process for continuous production of fresh water using solar energy.

In order to use solar energy more efficiently, a flat sheet Fresnel lens was used to concentrate simulated sunlight and the hydrogel bilayer was placed on the membrane surface. As mentioned before, the first layer was made from a very thin layer of copolymer of PNIPMA-PSA as the absorption layer while the second layer is made from PNIPAM to function
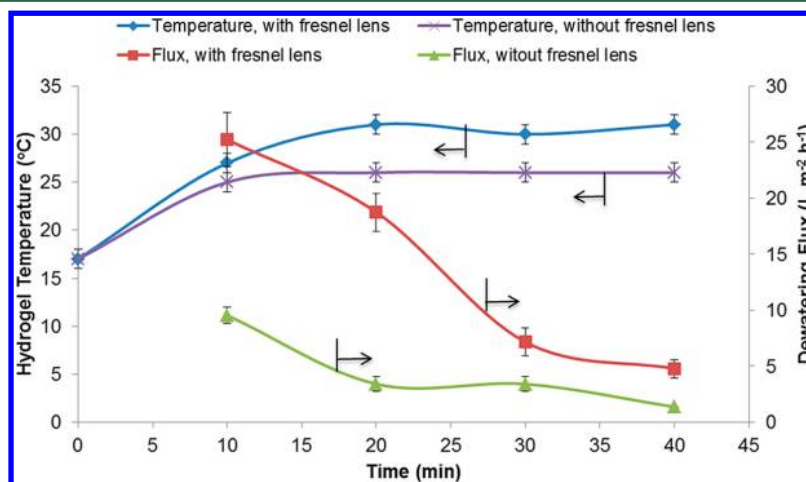

Figure 4. Dewatering flux of thermoresponsive hydrogel as draw agent in the bilayer arrangement (solar intensity = 0.5 kW/m^2 (W_{input} = 2 kw/m^2), Q = 15, 0.2 g dewatering layer, 0.01g absorptive layer).
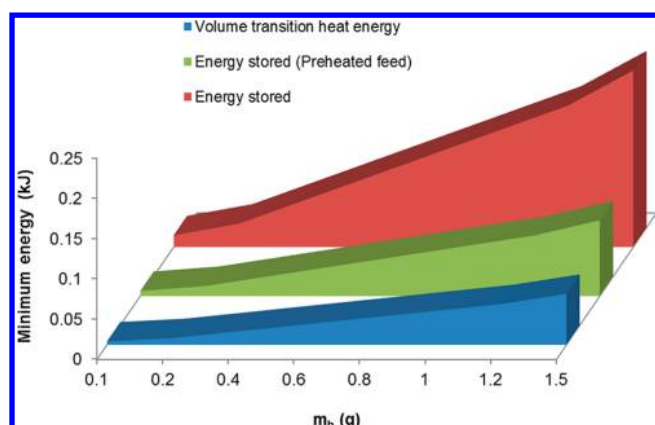
Figure 7. Effect of increasing the dewatering hydrogel layer mass on the volume transition heat (at LCST, 32 °C) and stored energy ($Q = 5$, at room temperature 25 °C) with/without preheating feed solution by reusing the consumed energy.

mainly as the water releasing layer. Figure 3 shows the permeation fluxes produced by NIPAM layer, PNIPAM+SA layer and combined PNIPAM+SA and NIPAM bilayer. As can be seen, the flux of the combination layer is not the superposition of the first and second layer. In the multilayer arrangements there are three driving forces which drive water across the membrane and hydrogel layers. Those driving forces are (i) osmotic pressure difference from saline water (feed) to the first ionic hydrogel layer, (ii) water absorption from the first layer to the second nonionic hydrogel layer by hydrophilic segments of PNIPAM and (iii) an osmotic driving force from the second nonionic layer to the first ionic layer. The last driving force acts against the first two driving forces, and thus reduces the permeation flux.

Figure 4 shows the effect of using concentration solar energy for dewatering (see SI for experimental details). Form the figure, after 10 min of solar irradiation the dewatering flux reached 25 LMH when Fresnel lens was used whereas without the lens it was around 10 LMH. As time passes, the dewatering fluxes reduced due to the significant reduction in the hydrogel water content. From this figure, during solar-concentrated illumination, the hydrogel bulk temperature reaches around 31−34 °C which is the lower critical solution temperature (LCST) of N-isopropylacrylamide, at which point hydrogel collapses and releases the absorbed water.[13,14] When solar intensity increased to 1 kW·m², the solar concentrator assisted dewatering flux jumped to about 60 LMH after 10 min irradiation and dropped to less than 10 LMH after 20 min (see SI Figure S4). This means a significant, rapid release of absorbed water in a short period of time, which helps the deswollen hydrogel return to its original role quickly as draw agent to continue FO process.

For comparison, water production via conventional solar evaporation was conducted under the similar conditions for dewatering of swollen hydrogel with Fresnel lens. To achieve
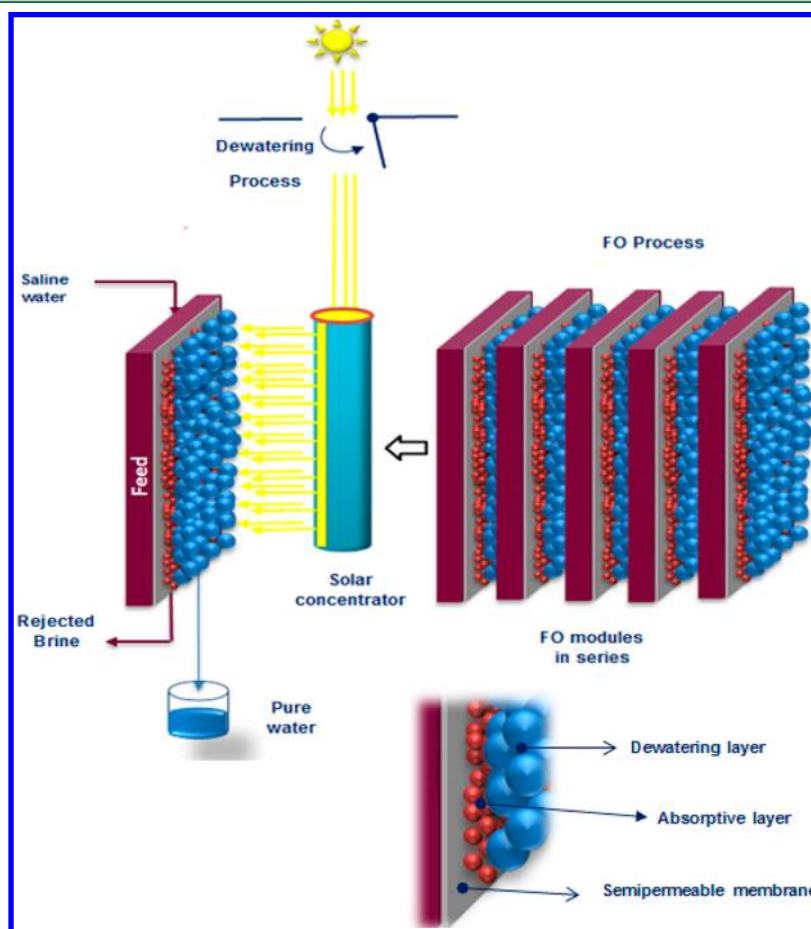

Figure 8. Schematic of continuous semibatch process of the production of pure water from saline water using bilayer thermoresponsive hydrogels as draw agent.

this, 3 mL of saline solution (2000 ppm) was placed under the Fresnel lens and evaporation was recorded by measuring the water mass changes as a function of time. As shown in Figure 5, dewatering fluxes via the FO process using hydrogels as draw agents are significantly higher than that of solar evaporation, regardless of using the solar concentrator. In addition, the recovered water from the swollen hydrogels is in liquid form, whereas the evaporated water from the solar evaporation process needs to be condensed.

Energy Requirement. It is important to determine the energy requirement in hydrogel-driven FO process to compare with other well-established desalination techniques such as Reverse Osmosis (RO). In a reversible process, the separation energy is equal to the free energy of mixing (ΔG_{mix}) but in opposite sign.[15,16] The results in SI Figure 5S were calculated based on the minimum separation energy for desalination (see SI for more details). As can be seen, the minimum energy increases as salinity and recovery increase. From this figure, the minimum energy for the separation of standard seawater (35 g/L) with 50% recovery at which most of RO plants operate is around 1.09 kWh/m^3 (3.93 kJ/kg). However, current well-designed and optimized RO plants consume energy as low as 2.2 kWh/m^3 (7.92 kJ/kg), which is almost 2 times greater than the minimum theoretical value.[17] Other desalination techniques consume even more energy than RO plants. In our case, thermo-shrinking NIPAM hydrogel is used as the second layer to release the absorbed water by heating above LCST. In such thermoresponsive hydrogel-assisted FO desalination, the swollen hydrogel collapses and releases its absorbed water in an endothermic process. Therefore, understanding the molecular structure of monomer units in the hydrogel and the mechanism by which the hydrogel endothermically collapses provides a guideline for comparison. Furthermore, such data is critical for hydrogel-driven FO implementation on an industrial scale, where the energy demand is high, and renewable or reclaimed energy resources are not sufficient for such industrial scale water production.

In PNIPAM aqueous system, water molecules reorient around nonpolar regions of PNIPAM to form "water cages" or "water clathrates", while they hydrogen bound around the polar segments of PNIPAM (the amid group) to form bond water.[18,19] Above the LCST, NIPAM hydrogels experience a reversible lower critical solution temperature phase transition from a swollen to nonswollen state, as PNIPAM chains receive sufficient energy to rearrange the bound water into free water and to cause the association of the hydrophobic segments in the PNIPAM chains, thus releasing the absorbed water.[20] In the three process model,[18,20] volume phase transition occurs in three stages: absorbing heat (ΔH_c) for apolar dehydration due to restructuring of water cages to bulk water, absorbing energy (ΔH_{hg}) for polar dehydration because of the rearrangement of water molecules around the amide group to bulk water, and releasing heat (ΔH_{res}) as a result of intermolecular interaction between the PNIPAM residues. Therefore, the transition heat ($\Delta H_{transition}$) of collapse of NIPAM hydrogel is

$$\Delta H_{transition} = \Delta H_c + \Delta H_{hg} - \Delta H_{res} \tag{1}$$

In the literature, 7.9 kJ/mol is reported as the value of ΔH_c while a range of 17−22.6 kJ/mol is reported for ΔH_{hg}.[18,20,21] The exothermic heat of ΔH_{res} is reported at least −22.6 kJ/mol by Cho et al.[18] Therefore, from eq 1 the minimum transition heat of collapse will be 2.3−7.3 kJ/mol. Considering the molecular weight of NIPAM (113.6 g/mol) used in this study,

the transition heat ($\Delta H_{transition}$) of collapse of NIPAM hydrogel will be 20.25−64.26 kJ/kg$_{(PNIPAM)}$ or on average 42.25 kJ/kg$_{(PNIPAM)}$. It should be noted that the chemical modification of NIPAM hydrogels such as the addition of ionic groups into polymer network may increase the LCST.[13,22] For example, the addition of SA into NIPAM at a high concentration (e.g., the ratio of NIPAM to SA < 4.5) increases the LCST up to 80 °C.[9] Although the addition of ionic groups increases the swelling pressure and thus the FO water permeation, the compromise is a significant increase in $\Delta H_{transition}$, which must be taken into account for future optimization and process design.

Practically, the minimum energy of dewatering of swollen NIPAM hydrogel in a FO process is higher than $\Delta H_{transition}$ because a part of input energy (q) is being stored by free water trapped in the hydrogel network to cause an increase in the bulk temperature until it reach LCST (see Figure 4). The amount of this energy is directly proportional to the swelling ratio; the higher the swelling ratio is, the higher the q value will be. Such internal energy changes or stored energy can be calculated as follows

$$q = m \cdot c \cdot \Delta T = Q m_h \cdot c \cdot \Delta T \tag{2}$$

where m is the mass of free water in the network, c is specific heat of water (4.18 J/g °C), ΔT is temperature change from room temperature to LCST, m_h is the mass of dry hydrogel and Q is the swelling ratio. Hence, the minimum energy required for dewatering of swollen hydrogel is calculated based on eqs 1 and 2:

$$w = q + m_h. \, \Delta H_{transition} \tag{3}$$

Equation 3 is used to generate Figure 6 and 7 which shows the minimum energy required for dewatering of dewatering layer. As can be seen in Figure 6, increasing the swelling ratio proportionally increases the required energy. When swelling ratio is 5 and m_h is 1 g the minimum amount of energy is around 0.19 kJ which corresponds to 32 kJ/kg (10.55 kWh/m^3) assuming 100% recovery during hydrogel collapse. This value is higher than the energy demand of conventional membrane pressure based desalination plants. This is because the free water requires a significant amount of energy to rise its temperature to LCST. As can be seen in Figure 7, the contribution of this energy (q) in the minimum energy (w) significantly increases as the mass of the dewatering hydrogel layer increases. However, this obstacle can be overcome by reusing energy consumption, as the released water temperature is in LCST of hydrogel and its internal energy can be reused in the next stage. As shown in Figure 7, a significant reduction in the stored energy can be achieved by only increasing the feed temperature 4 °C using the energy of released water. Therefore, the stored energy (q) can be recovered to high extend, and thus it is possible to rewrite eq 3 as below

$$w \approx m_h. \, \Delta H_{transition} \tag{4}$$

In this case, the minimum required energy for the recovery of 1 g (m_h) swollen hydrogel with the swelling ratio of 5 will be in the range of 4−12.8 kJ/kg (1.12−3.57 kWh/m^3), which shows a great potential of using thermoresponsive hydrogel as draw agent in FO desalination process.

Semibatch Hydrogel-Driven FO Process. Figure 8 shows the conceptual design of semibatch hydrogel-driven FO process using solar energy for the continuous production of pure water. A hydrogel-driven FO process is a time dependent process such that dewatering and water release can be performed when the

dewatering layer water content reaches a desired level. In order to continuously produce pure water, cascades of FO modules should be set in series in a way that volume phase transition is induced only to those in which the dewatering layer has the desired hydrogel water level. In a semibatch hydrogel-driven FO process, FO water permeation begins in all modules, and bilayer hydrogels swell and withdraw water through the membranes. When the hydrogels in the first module have reached the desired swelling ratios, water collection begins by opening the sunlight aperture to induce heating for deswelling at LCST (32 °C). Once dewatering in this module is finished, its aperture being closed to let the FO process restarts. At this time the aperture of next module will be opened to initiate the dewatering process. This process is repeated to ensure continuous production of fresh water from the overall modules.

The number of modules and water production rate depend on the swelling ratio of hydrogels. Higher swelling ratio results in higher FO water flux and dewatering flux. Our previous study shows that the swelling ratio and water flux can be significantly increased by tailoring the hydrogel structure such as adding graphene nanosheets.[11] In the swelling process of a dry hydrogel particle, its swelling ratio increases sharply at the beginning of the FO process because of high initial osmotic (swelling) pressure.[23,23] However, its water absorption rate reduces significantly as the driving force decreases. Therefore, the optimum swelling ratio should be chosen based on the number of modules and the water production rate. In order to improve process efficiency, the internal energy of released water can be transferred to the feed solution through a heat exchanger. Although the schematics in Figure 8 is based on the solar energy, the heat induced can be readily achieved by blowing hot gas generated from any other renewable or reclaimed energy source such as abundant industrial waste heat. This will make it feasible to adopt the design of spiral wound membrane and hollow fiber membrane modules in the construction of the membrane-hydrogel FO modules. Therefore, the concept of using semibatch hydrogel-driven FO process for the production of pure water has great potential to be used commercially after further process optimization and molecular structure alteration of the hydrogel layers.

ASSOCIATED CONTENT

Ⓢ Supporting Information

Additional information as noted in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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