

Stimuli-Responsive Polymer Hydrogels as a New Class of Draw Agent for Forward Osmosis Desalination

Dan Li, Xinyi Zhang, Jianfeng Yao, George P. Simon, Huanting Wang*

Supplementary Information

Experimental Section

Synthesis and characterization of hydrogels: The polymer syntheses were performed via radical polymerization of different monomers and crosslinker -N,N'-methylenebisacrylamide (MBA) (Sigma-Aldrich, 99%) in aqueous solution using ammonium persulfate (Sigma-Aldrich, $\geq 98.0\%$) as an initiator. Briefly, a monomer, including acrylamide (AM, Sigma-Aldrich, 99%), sodium acrylate (SA, Sigma-Aldrich, 99%), N-isopropylacrylamide (NIPAM, Sigma-Aldrich, 96%), or their mixture was firstly completely dissolved in deionised water to form a 16.7 wt% monomer solution with a molar ratio of monomer, crosslinker and initiator of 100:1:0.5). The crosslinker and initiator were then dissolved in this solution, followed by deaeration via flowing nitrogen gas through the solution for 10 min. The resultant solution was kept in an oven set at 50 °C for polymerization. Polymer hydrogels synthesized from acrylamide, sodium acrylate, N-isopropylacrylamide, or sodium acrylate and N-isopropylacrylamide (molar ratio 1:1) mixture were denoted as PAM, PSA, PNIPAM and PSA-NIPAM, respectively.

The as-synthesized polymer hydrogels were taken from the bottles and cut into small pieces. The hydrogel pieces were then immersed in deionised water at 25 °C for 3 days, in which the water was exchanged every 4 h, to wash away unreacted monomers and crosslinker. The hydrogels were ground into small particles using a mortar and pestle, followed by drying at 50°C in a vacuum oven. The dried gel particles were sieved, and those in the size range of 50 μm to 150 μm used for characterizations and FO and dewatering tests.

The samples were characterized by scanning electron microscopy (SEM) and Fourier-transform infrared spectroscopy (FTIR). SEM images were recorded with a Model JSM-6300F microscope (JEOL) at an accelerating voltage of 5 kV. Fourier-transform infrared spectra (FT-IR) were recorded for the samples embedded in KBr pellets with a GX Spectrometer (Perkin–Elmer).

Testing of polymer hydrogels as draw agents in FO process: A commercial hydrophilic cellulose-based FO membrane (provided by Hydration Technologies Inc., Albany, OR) was used. Before each test, the FO membrane was immersed in a 2000 ppm NaCl solution overnight. 1 g of polymer hydrogel powders was placed on the one side of the membrane and the NaCl solution on the permeate side. As the water permeated through the membrane from the NaCl solution, driven by swelling of polymer hydrogel powders, the weight of hydrogel powders increased. Water flux was determined by measuring the weight change of the polymer hydrogel with time, and calculated by

$$\text{Water flux} = \frac{V}{A \times t}$$

where V is the volume of water permeating through the membrane (L), which is based on the mass increase of the swollen gel measured over a given period of time, t, (h); A is the effective area of FO membrane (m^2) used in the permeation cell.

Dewatering of deswollen polymer hydrogels: The swollen polymer hydrogel after the FO test was filled into a thermal mechanical dewatering cell. The apparatus for dewatering consists of a vertical cylinder with a movable piston through which a mechanical load is applied at the top of a confined bed of swollen gel particles. The inner diameter of the cell cylinder is 1.2 cm. The swollen polymer hydrogel was placed between the piston and a polysulfone UF membrane, which was supported by a porous stainless steel disc. A load of 3MPa was applied and kept constant for 2 min, resulting in shrinking of the gel particles. The water released from the polymer hydrogels was free to flow through the UF membrane and the porous stainless steel disc. The dewatering experiments were carried at 25 °C and 50 °C, respectively. The amount of water released was determined by taking the weight difference of the

polymer hydrogel before and after the dewatering test. Water recovery rate was derived from the weight of released water and the initial water content of the swollen polymer hydrogel.

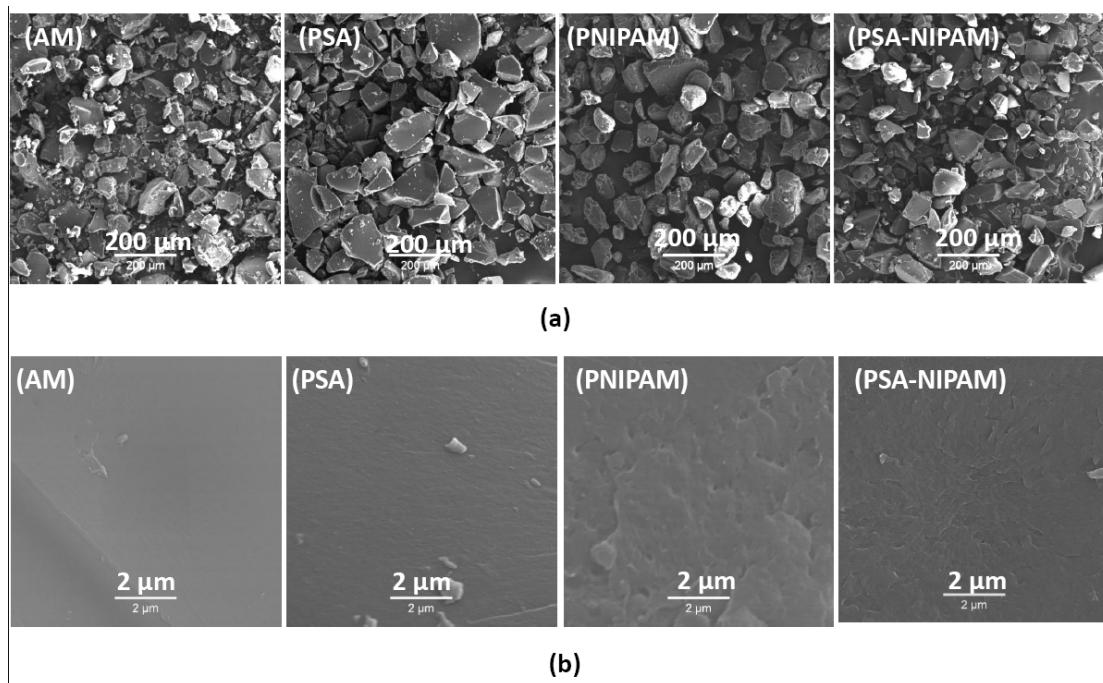
$$\text{Water recovery rate} = \frac{W_t}{W_o} \times 100\%$$

where W_t is the weight of water released in the dewatering test (g); W_o is the initial water weight of the swollen gel (g).

$$\text{Water flux} = \frac{Vt}{A \times t}$$

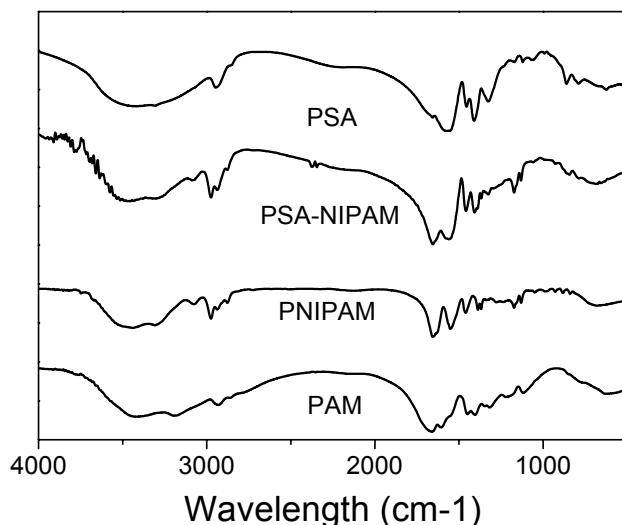
where V is the volume of water released in the dewatering test (L), which is calculated from the weight of water released in the dewatering test; A is the inner area of the cylindrical cell (m^2); t is the dewatering time (h).

S-Figure 1 shows the SEM images of different polymer hydrogels. All samples have sizes ranging from 50 μm to 150 μm , as well as some small, fine particles. SEM images reveal that PAM and PSA particles possess smooth surfaces, whereas PNIPAM and PSA-NIPAM have rough surfaces.

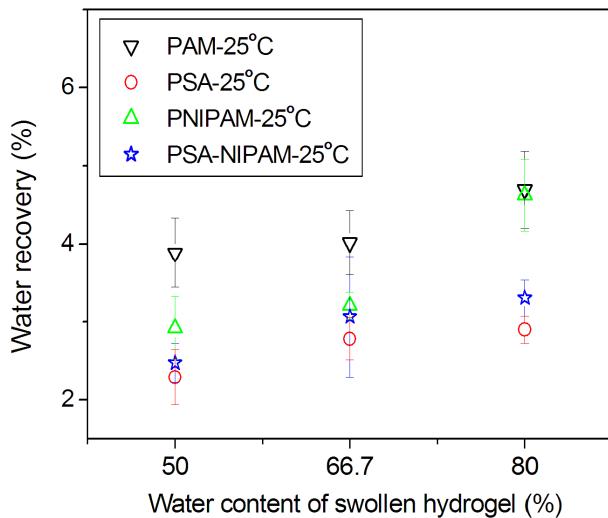


S-Figure 1. SEM images of polymer hydrogel particles: (a) at Low magnification and (b) at high magnification.

S-Figure 2 shows the FTIR spectra of four different polymer hydrogels, including PAM, PSA, PNIPAN and PSA-NIPAM. The FTIR spectrum of PAM shows a broad absorption band at 3430 cm^{-1} due to the N–H stretching of amide groups of acrylamide units. Two peaks at around 1663 and 1608 cm^{-1} arise from amide-I and amide-II of acrylamide units. C–N and C–H stretching bands appear at 1440 and 2922cm^{-1} , respectively, further confirming the presence of amide groups.¹ In spectrum of PSA, the absorbance at 2940 cm^{-1} is attributed to the –CH₂ stretching vibration, which is supported by the presence of –CH₂ bending vibration at 1455 cm^{-1} . Two strong absorption peaks are observed at around 1570 and 1410 cm^{-1} , which are assigned to the C=O stretching vibration of the ionic carboxyl group (–COO–).² In the FTIR spectrum of PNIPAM, the main peak assignments are as follows: 3292 cm^{-1} (secondary amide N–H stretching), 2970 cm^{-1} (-CH₃ asymmetric stretching), 1650 cm^{-1} (secondary amide C=O stretching, aka amide I bond), and 1550 cm^{-1} (secondary amide C=O stretching, aka amide II bond).³ Similar peaks in PSA or PNIPAM can be observed in the spectrum of PSA-NIPAM sample, confirming the presence of NIPAM and SA units in the hydrogel.



S-Figure 2. FTIR spectra of PAM, PSA, PNIPAM and PSA-NIPAM.



S-Figure 3. Water recovery for swollen hydrogels (PAM, PSA, PNIPAM and PSA-NIPAM) with different water loadings after 2 min dewatering process at ambient temperature.

References

- [1] Y. M. Mohan, J. P. Dickson, K. E. Geckeler, *Polym. Int.* **2007**, *56*, 175.
- [2] R. S. Tomar, I. Gupta, R. Singhal, A. K. Nagpal, *Polym. Plastics Tech. Eng.* **2007**, *46*, 481.
- [3] Y. Cui, C. Tao, Y. Tian, Q. He, J. Li, *Langmuir* **2006**, *22*, 8205.