Supporting Information

Salinity-Ultrasensitive Hydrogels for High-Performance Salinity Gradient Energy Conversion and Harvesting

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Characterization

FTIR analysis

Fourier transform infrared (FTIR) data were recorded with a Nicolet iS10 FTIR Spectrometer in KBr pellets with 32 scans. Prior to the measurements, the PNS hydrogel blocks were dried in a forced-air oven at 60 °C for 24 h to ensure a complete moisture removal. Also, the spectra were characterized with respect to the wavenumbers.

Swelling and deswelling measurements

To determine the time required for PNS hydrogel particles to reach their swelling and shrinking limits, PNS hydrogels with crosslinking densities of 0.3%, 0.4% and 0.6% were first swollen to equilibrium in deionized water. After equilibrium swelling, the hydrogels were passed through stainless-steel sieves with mesh sizes of 1 mm, 2 mm and 3 mm to obtain three particle size fractions. Each fraction was then immersed in 0.1 M NaCl solution; the stopwatch was started immediately upon immersion and the particles were observed in real time on the stage of a Nikon ECLIPSE Ti2-U microscope using a 4× objective. Observation was terminated when no obvious change in particle volume was detected; the recorded time was taken as the shrinkage time of that PNS hydrogel particle in 0.1 M NaCl. The particles were then carefully removed from the NaCl solution and the surface salt solution gently blotted with filter paper. The particles were immediately immersed in ultrapure water and a digital stopwatch started; they were observed again on the microscope stage until no further significant increase in volume was observed. The recorded time was taken as the swelling time in ultrapure

water. Each sample group was tested in triplicate (n = 3).

Ion accumulation detection via UV-Vis spectroscopy

To evaluate the ion accumulation degree in PNS hydrogels, PNS hydrogel samples equilibrated in pure water were cut into 1 cm^3 cubic pieces. Cycling tests were performed alternately in pure water and 0.1 M NaCl solution for 30 cycles. Before and after the cycling tests, all samples were fully swollen in pure water. Subsequently, the samples were immersed in pure water and 0.0141 M $AgNO_3$ solution for 20 s, respectively, followed by rinsing in pure water to remove surface-adsorbed $AgNO_3$. Finally, the treated samples were placed in quartz cuvettes and characterized using the UV-Vis spectrophotometer (Cary 60 UV-Vis).

Infrared spectra of different PNS hydrogels

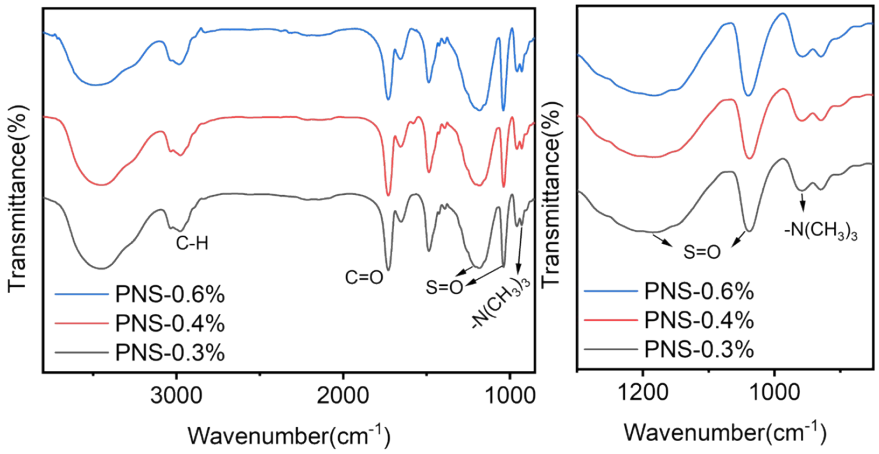

Figure S1. Fourier transform infrared (FTIR) spectra of PNS hydrogels with different crosslinking densities. The black curve represents PNS-0.3%, the red curve represents PNS-0.4%, and the blue curve represents PNS-0.6%. All three samples display identical characteristic peaks, indicating that their chemical composition remains unchanged irrespective of crosslinking density.

- **C-H stretching vibration**: Broad absorption peak at ~2850–2950 cm^{-1} (attributed to methylene ($-CH_2-$) and methyl ($-CH_3$) groups in the polymer backbones of DMAPS and NA);
- **C=O stretching vibration**: Sharp absorption peak at ~1730 cm^{-1} (derived from the ester carbonyl group ($-COO^-$) in the DMAPS monomer);
- **S=O stretching vibrations**: Two distinct absorption peaks at ~1200 cm^{-1} (asymmetric stretching) and ~1040 cm^{-1} (symmetric stretching), corresponding to the sulfonate group ($-SO_3^-$) in DMAPS;
- **C-N stretching vibration of $-N(CH_3)_3^+$**: Absorption peak at ~1480 cm^{-1} characteristic of the quaternary ammonium group in NA and DMAPS.

Cyclic piston height variation of PNS-0.4% hydrogels in different monovalent salt solutions

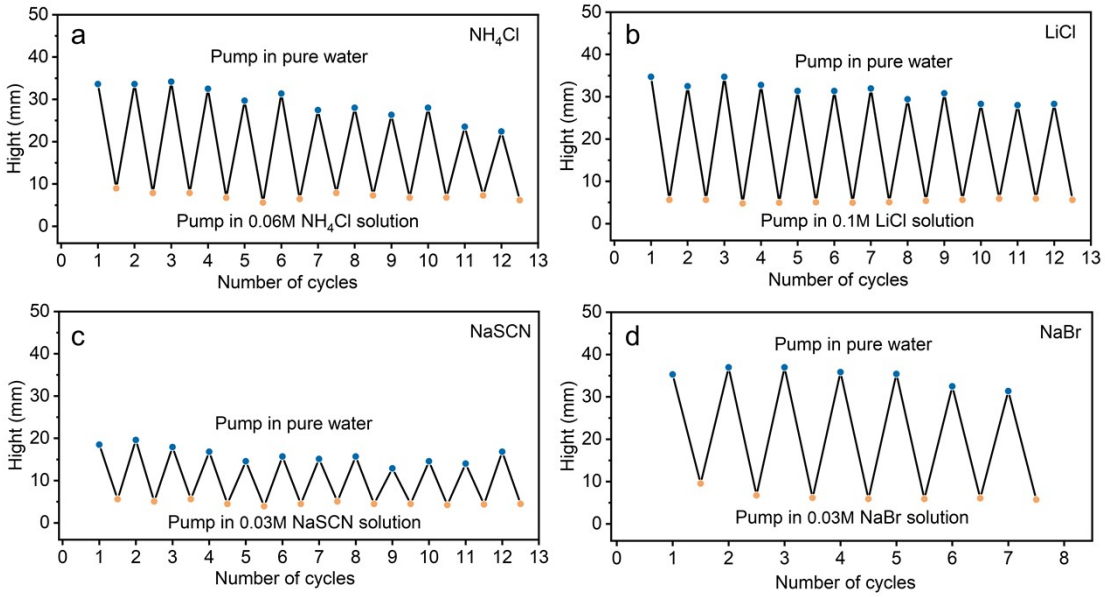

Figure S2. Cyclic piston height variation of PNS-0.4% hydrogel under alternating salt/pure water stimuli. (a) In 0.06 M NH_4Cl (12 cycles): The hydrogel swells to an initial height of ~35 mm upon exposure to pure water and shrinks to ~10 mm in 0.06 M NH_4Cl. A stable oscillatory pattern is maintained across all cycles, though the maximum swelling height decreases gradually to ~25 mm by cycle 12. (b) In 0.1 M LiCl (12 cycles): Similarly, pure water elicits swelling to ~35 mm, while 0.1 M LiCl reduces the height to ~5 mm. Consistent cyclic responses are observed throughout 12 cycles, with the swelling height retained at ~30 mm. (c) In 0.03 M NaSCN (12 cycles): Starting from ~20 mm in pure water, contraction occurs to ~5 mm in NaSCN solution. Reproducible mechanical actuation persists without significant degradation over 12 cycles. (d) In 0.03 M NaBr (7 cycles): Alternating between pure water (~35 mm) and NaBr solution (~10 mm) yields stable height modulation for 7 cycles, exhibiting negligible fatigue. When the salt solution was switched to single-salt environments—

namely 0.06 M NH_4Cl, 0.1 M LiCl, 0.03 M NaSCN, or 0.03 M NaBr—the hydrogel still maintained stable cycling performance (Fig. S2). In addition, replacing the NaCl solution with a mixed-salt solution (containing 0.025 M LiCl, 0.025 M NaCl, 0.025 M NaBr, and 0.025 M NaSCN) also resulted in maintained stable piston actuation over another 30 cycles. This confirms the great potential of smart-responsive ionic hydrogels as salinity-gradient energy-conversion materials even when complex ionic solutions are used.

Swelling ratio of PNS hydrogels versus crosslinking degree

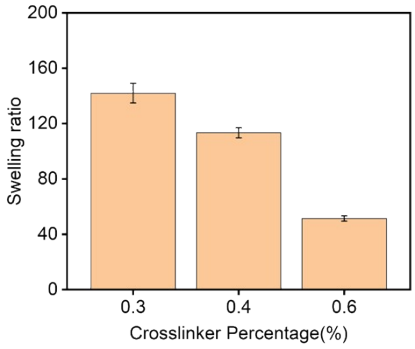

Figure S3. Swelling ratio (wet weight/dry weight) of PNS hydrogels with crosslinking densities (0.3%, 0.4%, and 0.6%). The swelling ratio decreases with increasing crosslinking density: ~145 for 0.3%, ~115 for 0.4%, and ~45 for 0.6%.

Average mechanical power output per cycle for PNS hydrogel (6 g) systems under varied operating conditions

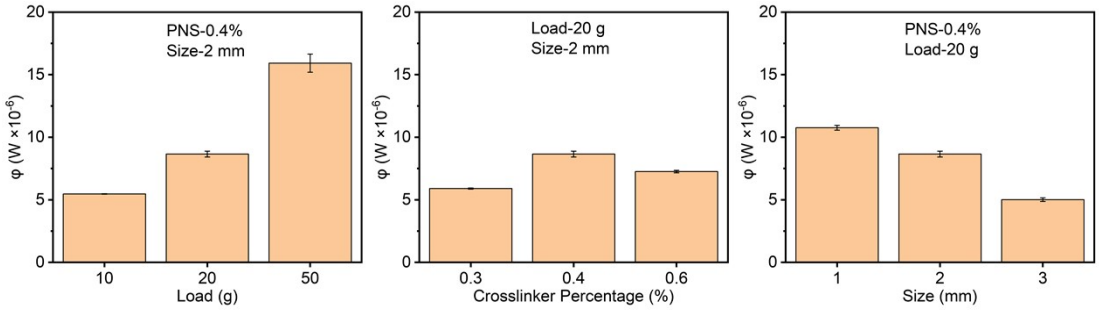

Figure S4. Average mechanical power output per cycle for PNS hydrogel systems under varied operating conditions (different load, crosslinking density, and particle size). (a) Effects of weight on piston on average power: Tested with 6g PNS-0.4% hydrogel (2 mm cubic particles), with the variable being the weight of weights on the piston (10, 20, 50 g). (b) Effects of crosslinking density on average power: Tested with 6g PNS hydrogels (2 mm particle size, fixed 20 g weight on piston), with crosslinking density as the variable (0.3%, 0.4%, 0.6%). (c) Effects of particle size on average power: Tested with 6g PNS-0.4% hydrogel (fixed 20 g weight on piston), with particle size as the variable (1, 2, 3 mm).

Energy harvested within one hour per 6 g PNS hydrogel

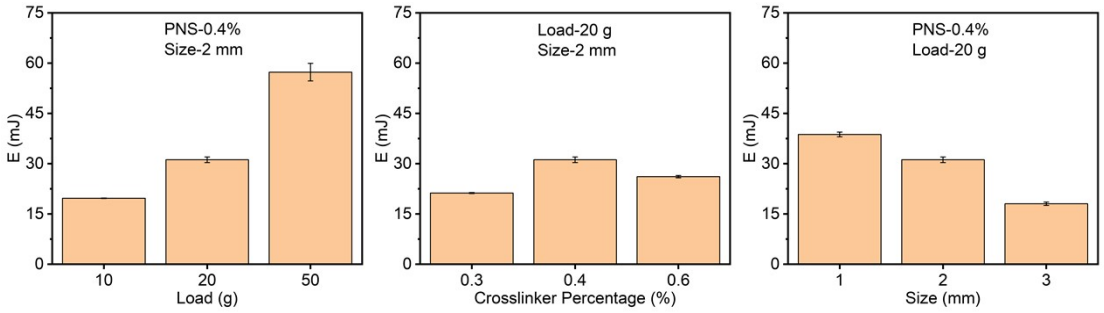

Figure S5. Energy captured per hour by PNS hydrogels during cyclic salinity-responsive processes. (a) Effects of weight on piston on hourly energy harvest: Tested with 6g PNS-0.4% hydrogel (2 mm cubic particles), with the variable being the weight of weights on the piston (10, 20, 50 g). (b) Effects of crosslinking density on hourly energy harvest: Tested with 6g PNS hydrogels (2 mm particle size, fixed 20 g weight on piston), with crosslinking density as the variable (0.3%, 0.4%, 0.6%). (c) Effects of particle size on hourly energy harvest: Tested with 6g PNS-0.4% hydrogel (fixed 20 g weight on piston), with particle size as the variable (1, 2, 3 mm).

Energy harvested within one hour per kilogram of PNS hydrogel

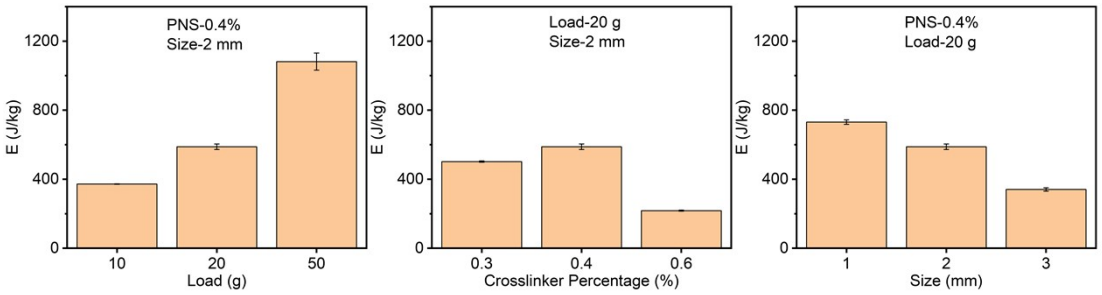

Figure S6. Energy captured per hour by PNS hydrogels during cyclic salinity-responsive processes. (a) Effects of weight on piston on hourly energy harvest: Tested with PNS-0.4% hydrogel (2 mm cubic particles, calculated per kilogram), with the variable being the weight of weights on the piston (10, 20, 50 g). (b) Effects of crosslinking density on hourly energy harvest: Tested with PNS hydrogels (2 mm particle size, fixed 20 g weight on piston, calculated per kilogram), with crosslinking density as the variable (0.3%, 0.4%, 0.6%). (c) Effects of particle size on hourly energy harvest: Tested with PNS-0.4% hydrogel (fixed 20 g weight on piston, calculated per kilogram), with particle size as the variable (1, 2, 3 mm).

Optical photographs of PNS Hydrogels during swelling-shrinking cycles

Figure S7. The photographs show the sequential states of the hydrogels during the cyclic swelling-shrinking process: the first state is the swelling state after equilibrating in static deionized water, the second is the shrinking state after equilibrating in static 0.1 M NaCl solution, and the third is the re-swelling state after re-equilibrating in static deionized water, with the tested variables including crosslinking densities (0.3%, 0.4%, 0.6%) and particle sizes (1 mm, 2 mm, 3 mm).

Time required for hydrogel particles to reach swelling/shrinking limit in static pure water and 0.1M NaCl solution

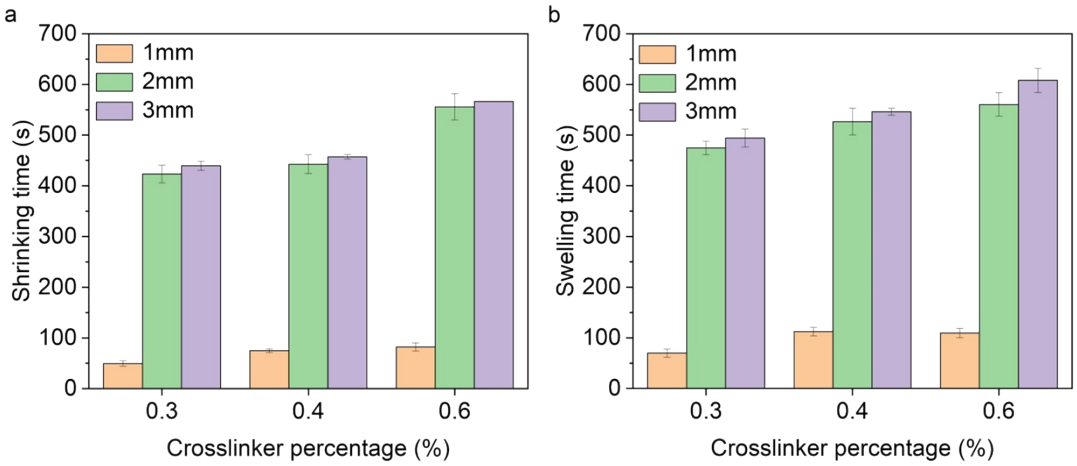

Figure S8. (a) Time for hydrogel particles to shrink to limit in static 0.1 M NaCl solution: The tested variables include crosslinking densities (0.3%, 0.4%, and 0.5%) and particle sizes (1 mm, 2 mm, 3 mm). (b) Time for hydrogel particles to swell to limit in static pure water: The tested variables include crosslinking densities (0.3%, 0.4%, and 0.5%) and particle sizes (1 mm, 2 mm, 3 mm).

Energy transformation performance of PNS hydrogels with different crosslinking degrees during one cycle of water and 0.46 M NaCl solution exchange

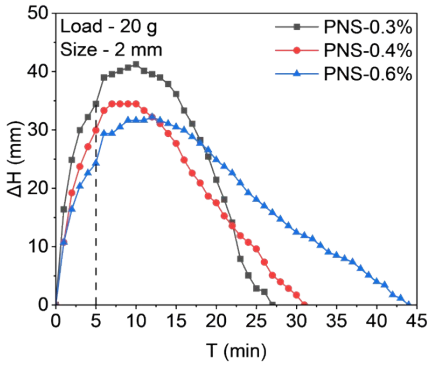

Figure S9. Energy transformation performance of 6 g of PNS-0.3%, PNS-0.4%, and PNS-0.6% particles (2 mm in size, pre-equilibrated in water) during one alternating cycle of 0.46 M NaCl and pure water under a load of 20 g.

The volume ratios ($V_0/V_{0.1M}$) of PNS hydrogels

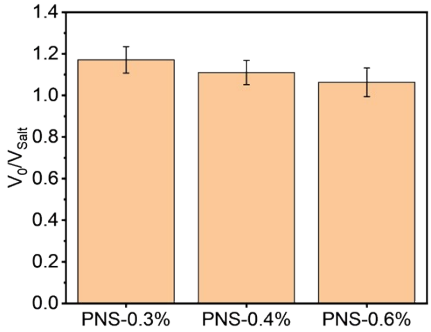

Figure S10. Statistical chart presenting the volume ratios ($V_0/V_{0.1M}$) of PNS hydrogels with different crosslinking degrees after 5 min immersion in a 0.1 M NaCl solution, respectively.

UV-Vis spectrum of PNS hydrogels before and after 30 cycling tests

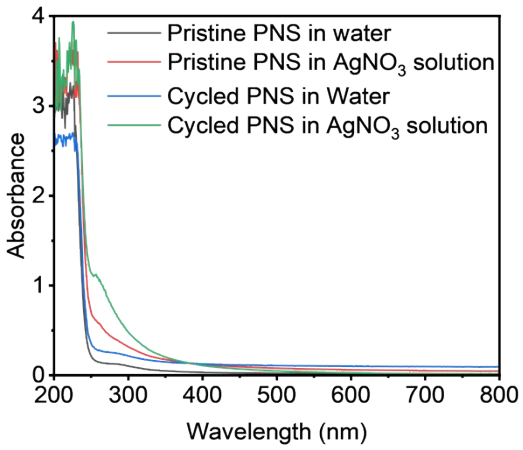

Figure S11. UV-Vis spectra of PNS hydrogels before and after cycling tests, following 20 s immersion in pure water and in 0.0141 M $AgNO_3$ solution, respectively.

Transmittance of PNS hydrogels before and after 30 cycling tests

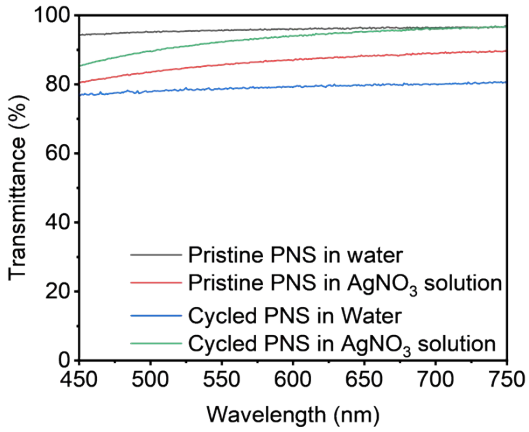

Figure S12. Transmittance of PNS hydrogels before and after cycling tests, following 20 s immersion in pure water and in 0.0141 M $AgNO_3$ solution, respectively. Using chloride ions as a monitoring indicator, the PNS hydrogel subjected to 30 cycles was treated with silver nitrate. The resulting transmittance in the visible light region showed no significant decrease compared to the as-prepared sample. This observation demonstrates that the accumulation of chloride ions within the PNS hydrogel matrix is negligible.

Table S1. Performance data of PNS hydrogels in the energy recovery experiments for various particle sizes, cross-linking degrees, and external loads.

Sample	Size (mm)	Crosslinker (g)	Load (g)	Φ ($W \times 10^{-6}$)	E, 1h (mJ)	E, 1h 1kg (J/Kg)	P, 1 kg (mW/kg)	η
0.04-10g	2	0.04	12.5	5.47096	19.695473	371.61271	103.2258	0.09%
0.04-20g	2	0.04	22.5	8.65837	31.170116	588.1154	163.3654	0.14%
0.04-50g	2	0.04	52.5	15.9207	57.314630	1081.4081	300.3911	0.26%
0.03-20g	2	0.03	22.5	5.90346	21.252440	502.06569	139.4627	0.10%
0.06-20g	2	0.06	22.5	7.26071	26.138555	217.82129	60.50591	0.12%
0.04-20g	1	0.04	22.5	10.7584	38.730158	730.75771	202.9883	0.18%
0.04-20g	3	0.04	22.5	5.01552	18.055885	340.67708	94.63252	0.08%

Table S2. Cycle times of reported hydrogels and PNS hydrogel for salinity gradient energy recovery.

Type of hydrogel	High concentration	Low concentration	Time for one cycle (min)	Reference
PNS hydrogel	0.1 M NaCl solution	Deionized water	11-18	This work
Poly(acrylic acid) hydrogel	0.6 M NaCl solution	0-0.012 M NaCl solution	25-70	Zhu et al. (2014)[1]
Poly(sulfobetaine) hydrogel	0.6 M NaCl solution	Deionized water	15-60	Zavahir et al. (2019)[2]
Poly(allylamine hydrochloride)-based	0.6 M NaCl solution	0-0.0086 M NaCl solution	60	Bui et al. (2018)[3]
poly (styrene sulfonate) hydrogel	0.6 M NaCl solution	0.01 M NaCl solution	20	Zhang et al. (2020)[4]
poly(acrylic acid-co-acrylamide) hydrogel	0.6 M NaCl solution	0-0.012 M NaCl solution	30	Hong et al. (2021)[5]

References

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