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Tough, anti-freezing and conductive ionic hydrogels

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Abstract

With rapid advances in soft electronic devices, the demand for soft conductive materials, including hydrogels, with superior mechanical properties, high conductivity and functionality under extreme environmental conditions are increasing at an unprecedented rate. Although hydrogels have favorable properties such as softness and broad tunability ranges, they freeze at subzero temperatures, leading to materials failure and device malfunctions, and the introduction of antifreezing agents into hydrogels often severely compromises their conductive or mechanical properties. The tradeoff between simultaneously endowing antifreezing hydrogels with excellent mechanical properties and high conductivity severely limits their practical applicability over a broad range of conditions. Herein, we discovered that potassium acetate (KAc) induces a salting-out effect on polyvinyl alcohol (PVA), promoting aggregation of the polymer chains and significantly improving the mechanical properties of the hydrogels. Moreover, concentrated KAc exhibits excellent anti-freezing capacity and high conductivity. The hydrogels produced by soaking frozen PVA in KAc solutions show superior mechanical properties, with a tensile strength of 8.2 MPa, conductivity of 8.0 S/m and outstanding freeze tolerance to a temperature of -60°C . This strategy also works for other polymers, such as poly(acrylamide) and poly(2-hydroxyethyl acrylate). Additionally, the as-prepared hydrogels possess excellent anti-dehydration capacity, which is another important feature that is desirable for further enhancing the applicability and durability of hydrogel-based devices.

Introduction

Wearable electronics are capturing an increasing amount interest due to their broad applications in daily activities, sports, medical treatments and entertainment^{1,2}. Numerous efforts have been made toward the innovation of relevant devices, such as soft aqueous batteries^{3,4}, supercapacitors^{5,6}, wearable sensors^{7,8}, soft robots^{9,10}, ionic skins^{11,12}, and ionic touch panels^{13,14}. The emergence of wearable devices is also increasing the demand for soft conductive materials that exhibit excellent mechanical performance and high conductivity,

which are crucial for the overall performance of the devices. Over the past few years, considerable efforts have been made to improve the conductivity and mechanical properties of soft conductive materials, including their stretchability and toughness; for example, a class of liquid-free, solid-state conductors has been systematically studied¹⁵. Among the studied soft conductive materials, conductive ionic hydrogels consisting of crosslinked networks of hydrophilic polymer chains with high loadings of water and incorporated ions have captured a tremendous amount of attention for their solid-like mechanical performances and liquid-like transport properties, and they have been widely applied for various soft devices^{16–19}. However, conductive ionic hydrogels freeze in subzero-temperature environments, leading to a significant loss in their conductivity and stretchability, which severely limits

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their applications over a broad range of conditions, especially at low temperatures²⁰.

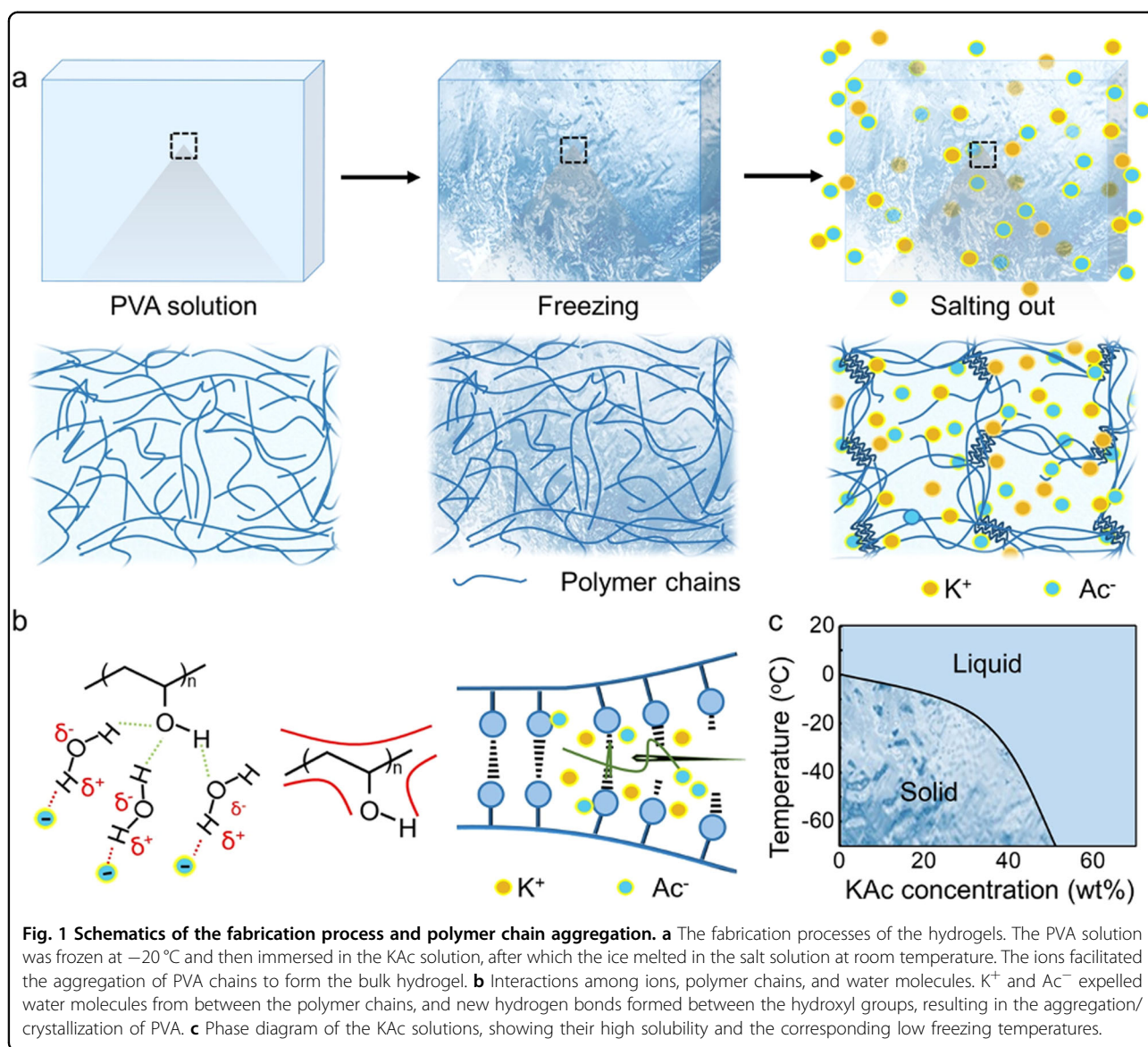
To tackle this critical freezing issue, organic solvents in combination with high salt contents have been widely introduced into these materials to depress their freezing temperatures^{20–29}. However, these proposed strategies have shown multiple drawbacks. For example, excellent anti-freezing capacities can be induced by the introduction of organic solvents such as glycerol, propylene or ethylene glycol, but salts can precipitate with decreasing temperatures due to their relatively low solubility in the organic solvents³⁰. Organic solvents are also known to suppress the dissociation of salts³⁰. These two factors, i.e., low salt solubility and the suppression of salt dissociation in water-organic mixtures, reduce the conductivity of conductive ionic hydrogels. Additionally, organic solvents are known to be environmentally hazardous and raise health and safety issues.^{31–33} However, high salt contents can lead to higher conductivity values and satisfactory anti-freezing performances. A polyacrylamide–alginate double-network hydrogel containing CaCl_2 has been indicated to possess high conductivity and excellent freeze tolerance³⁴. Both its conductivity and antifreezing capacity were dependent on the concentration of CaCl_2 . However, as the content of CaCl_2 increased, the mechanical properties were significantly compromised due to a salting-in effect. Salting-in refers to the phenomenon by which increasing salt solution concentrations increase the solubility of a solute (polymer chains, in this case). In contrast, a salting-out effect promotes the aggregation of solutes, decreasing solubility. Such effects of salts on solutes are known as the Hofmeister effect or the ion-specific effect^{35–37}. Recently, the Hofmeister effect has been utilized to broadly tune the mechanical properties of hydrogels³⁸. Salting-out salts, such as Na_2SO_4 and Na_2CO_3 , promote the aggregation of polyvinyl alcohol (PVA), leading to tough hydrogels; salting-in salts, such as NaNO_3 and NaI , soften hydrogels. In principle, the antifreezing performance and strengthening or softening effects of salt solutions depends on the salt concentrations and solubility. Salting-out salts, such as Na_2SO_4 and Na_2CO_3 , have limited solubility, while salting-in salts, such as NaNO_3 , NaI and CaCl_2 , have much higher solubilities in water. Since salting-in salts typically compromise gel mechanical properties, it is highly desirable to identify optimal salting-out salts with high solubilities for fabricating highly conductive, anti-freezing gels that remain mechanically robust at low temperatures.

In this study, we discovered that potassium acetate (KAc) simultaneously provides high solubility and induces a salting-out effect on polyvinyl alcohol (PVA). The freezing temperature of a KAc solution can be as low as -70°C when the concentration is 50 wt%. We utilized a freeze-soak method, i.e., soaking frozen polymer solutions in KAc solutions, to fabricate tough, anti-icing and conductive ionic hydrogels. We systematically studied the

effect of salt concentrations and the effect of PVA molecular weights on the mechanical properties of the hydrogels. Hydrogels soaked in a 50 wt% KAc solution exhibited the most favorable mechanical properties, with an ultimate stress of 8.2 MPa and toughness of 25.8 MJ/m³, surpassing most reported results for anti-freezing gels. At 50 wt% KAc, the hydrogels also exhibited the best antifreezing performance, remaining unfrozen at temperatures below -60°C . They also showed a high conductivity of 8.0 S/m at room temperature and 1.2 S/m at -60°C . To explore the universality of this strategy, we treated poly(acrylamide) and poly(2-hydroxyethyl acrylate) hydrogels in the same manner and observed an increase in toughness of up to two orders of magnitude. Additionally, all hydrogels containing KAc showed outstanding anti-dehydration capacities, which further augmented their practical applicability, especially under low humidity conditions. With these merits, this simple and scalable strategy for fabricating conductive, antifreezing hydrogels could substantially broaden the applications for hydrogels in diverse applications, such as soft aqueous batteries, wearable sensors, and soft robots.

Results and discussion

We first studied the salting-out effect induced by KAc on PVA by introducing 10 wt% PVA solutions into a salt solution of 50 wt% KAc. The PVA salted out in the KAc solution, yielding clumps of white, opaque structures (Fig. S1). In contrast, PVA dispersed in a CaCl_2 solution, remaining in the form of a transparent solution. Next, we utilized a freeze-soak method to fabricate hydrogels. Specifically, PVA solutions were poured into molds, frozen at -20°C , and then immersed in a KAc solution, after which the ice melted in the salt solution at room temperature (Fig. 1a). Freezing fixes PVA into a specific shape macroscopically and prepacks the polymer chains microscopically to facilitate the aggregation of PVA chains to form a bulk hydrogel during the subsequent salting-out process³⁹. The effects of different ions on the gelation of PVA have been studied in previous works³⁸. Anions such as SO_4^{2-} , CO_3^{2-} and Ac^- and cations such as K^+ and Na^+ have shown salting-out effects. Generally, during the salting-out process, two possible interactions are possible among the ions, the polymer chains, and the hydration water molecules of the polymer⁴⁰, as illustrated in Fig. 1b. In the first scenario, the salting-out ions can polarize the hydration water molecules, which destabilizes the hydrogen bonds between the polymer and its hydration water molecules³⁹. In the second scenario, the ions can interfere with the hydrophobic hydration of the macromolecules by increasing the surface tension of the cavity surrounding the polymer backbone³⁹. During the melting process of frozen samples in salt solutions, both scenarios probably take place, ultimately resulting in the



expulsion of water molecules from between the polymer chains and giving rise to new hydrogen bonds between the hydroxyl groups, resulting in aggregation/crystallization of the polymer chains^{37,38} (Fig. 1a, b). KAc has high solubility, and a phase diagram shows its outstanding antifreezing capacity under concentrated solution conditions (Fig. 1c). We performed a simple experiment to demonstrate the extremely low freezing temperature of the concentrated KAc solution. As shown in Fig. S2, the 50 wt% KAc solution remained transparent after being stored at $-60^{\circ}C$ for 1 h. The salting-out effect is concentration dependent, with higher concentrations resulting in stronger salting-out effects, improving the strength of the hydrogel. Hence, a tough, antifreezing and conductive ionic hydrogel was by soaking PVA in a concentrated KAc solution.

Hydrogels were fabricated following the design principle presented above, and they were systematically tested for their mechanical properties. First, the effect of KAc concentration on hydrogel mechanical properties was studied (Fig. 2a). Hydrogel samples were prepared by immersing frozen 10 wt% PVA (molecular weight, $M_w = 89$ kDa) solutions in KAc solutions of different concentrations for 96 h. The control hydrogel samples were semitransparent and too weak to characterize when they were not soaked in salt solutions. In contrast, the hydrogels soaked in KAc solutions became opaque and toughened significantly. When the concentration of KAc increased from 10 wt% to 50 wt%, the tensile strength and toughness increased from 0.1 MPa to 4.0 MPa (Fig. 2b) and from 0.1 MJ/m³ to 7.8 MJ/m³ (Fig. S3), respectively. Next, we changed the molecular weight of PVA to observe

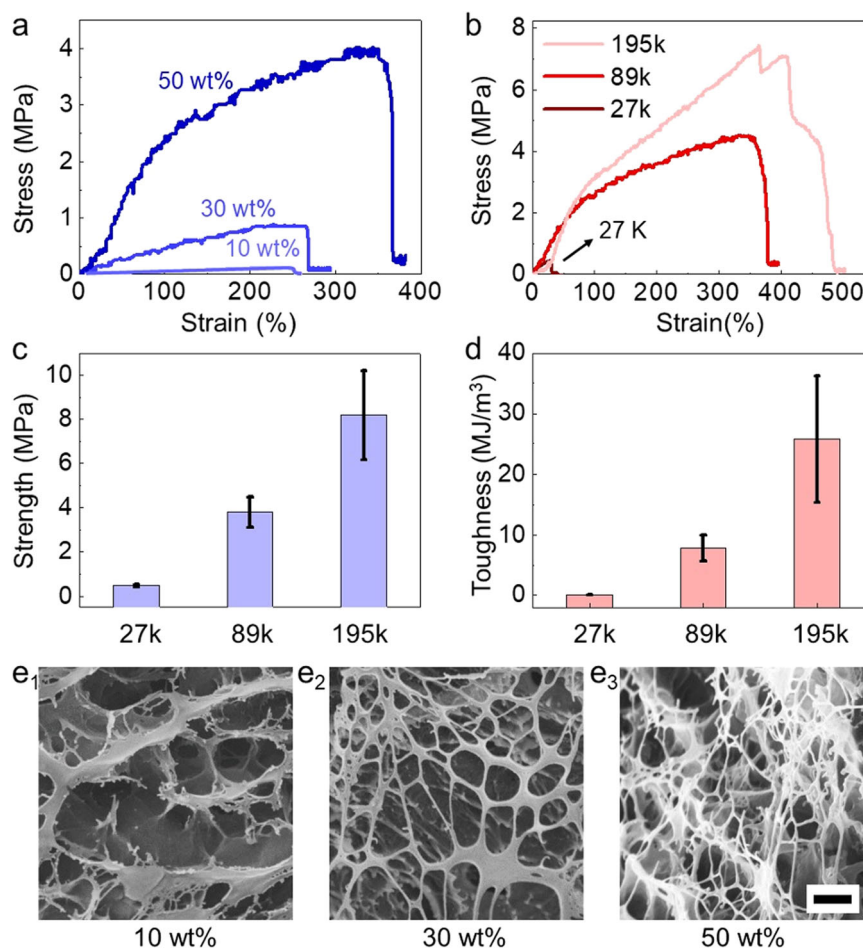
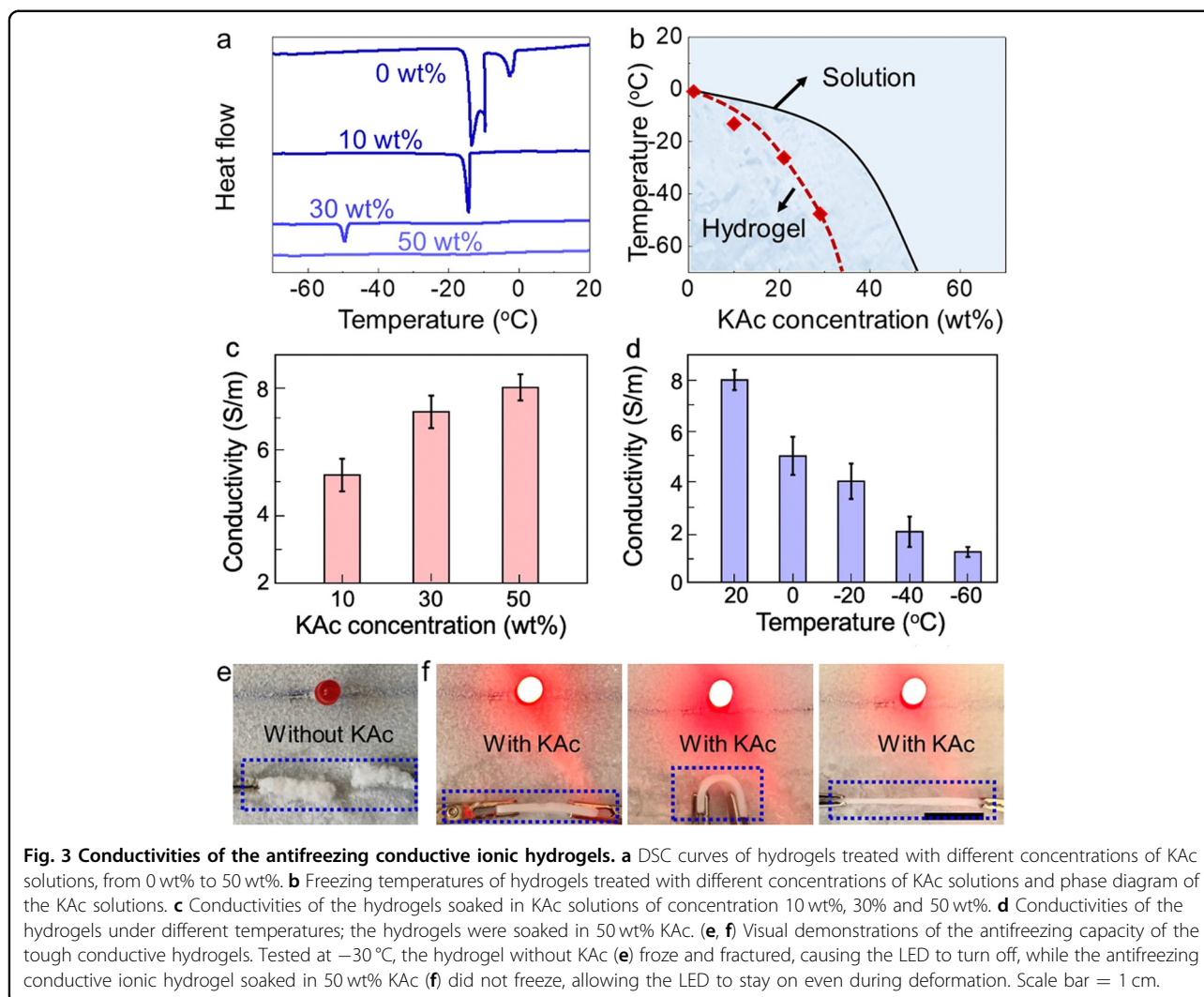


Fig. 2 Mechanical properties of PVA hydrogels. **a** Representative stress–strain curves of the PVA hydrogels soaked in different concentrations of KAc solutions. The PVA concentration was 10 wt%, and the molecular weight of PVA was 89 kDa. **b** Typical stress–strain curves of the PVA hydrogels of different molecular weights soaked in a 50 wt% KAc solution. The concentration of the PVA solutions was 10 wt%. **c, d** Tensile strength and toughness of PVA hydrogels made of different molecular weights. **e** SEM images of PVA hydrogels soaked in KAc solutions of concentration 10 wt%, 30 wt% and 50 wt%. Scale bars = 500 nm.

how the mechanical properties of the salt solution-treated hydrogels were impacted. As the molecular weight of PVA was increased from 27 kDa to 195 kDa, the hydrogel mechanical performance greatly improved (Fig. 2b); tensile strength and toughness increased from 0.5 MPa to 8.2 MPa (Fig. 2c) and from 0.1 MJ/m³ to 25.8 MJ/m³, respectively (Fig. 2d). The toughness of the hydrogels made of 195 kDa PVA was 2 orders of magnitude greater than that of the 27 kDa PVA hydrogel. To showcase the excellent strength of the 195 kDa PVA hydrogel, we demonstrated how a small strip of the toughened hydrogel (8 cm*5 mm*2 mm) could be used to easily lift 4 gallons of water (Fig. S4). According to the Lake–Thomas theory ($\Gamma \propto \sqrt{n}$), the energy (Γ) required to fracture a polymer chain scales proportionally with the polymer chain length (n refers to the number of repeating units)^{41,42}. The salting-out effect appears to be

concentration dependent; a higher concentration leads to a stronger salting-out effect and a greater aggregation of polymer chains. As shown in Fig. 2e, the pore size of the hydrogels decreased, and the fiber structures became denser as the KAc concentration was increased from 10 wt% to 50 wt%.

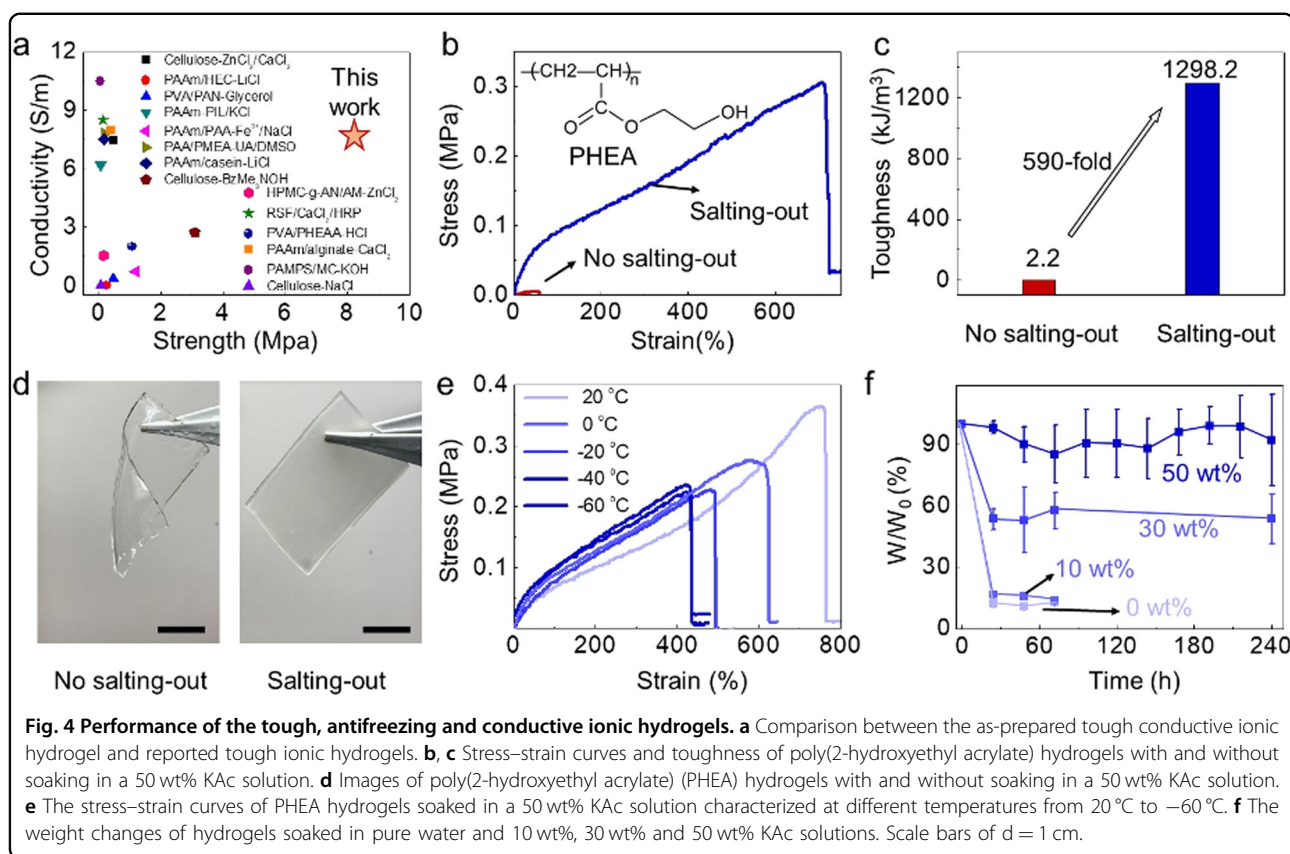
The freezing temperatures of the hydrogels soaked in KAc solutions at varying concentrations were measured with a differential scanning calorimeter (DSC) (Fig. 3a). As the salt concentration was increased from 0 wt% to 50 wt%, the freezing temperatures of the hydrogels dropped from 0 °C to below –70 °C. Compared with the theoretical phase diagram of KAc solutions, the freezing temperatures of salt-treated hydrogels were even lower than the freezing temperature of KAc solutions at corresponding concentrations. This was most likely due to a synergetic effect between the confinement of the polymer



matrix and the colligative properties of KAc⁴³. The conductivities of the PVA hydrogels soaked in KAc solutions were measured with an electrochemical workstation. The conductivity of the PVA hydrogel increased from 5.2 to 8.0 S/m as the KAc concentration increased from 10 wt% to 50 wt% (Fig. 3c). In addition, the conductivities of the PVA hydrogel soaked in 50 wt% KAc were measured at different temperatures, from 20 °C to -60°C (Fig. 3d and Fig. S5). The conductivity of the 50 wt% PVA hydrogel decreased gradually from 8.0 S/m at 20 °C to 1.2 S/m at -60°C . An LED light was used to demonstrate the conductivity change at low temperatures. Figure 3e, f show the LED connected with hydrogels at a low temperature (-30°C). The hydrogel containing no salt was frozen and fractured during stretching, and the LED switched off. However, the hydrogel soaked in 50 wt% KAc remained unfrozen and soft, and the LED connected to it remained on even at -30°C with bending and stretching (Fig. 3f). The relative resistance changes in the PVA hydrogel

soaked in a 50 wt% KAc solution were also studied. As shown in Fig. S6, the relative resistance changes increased linearly with increasing strain.

The PVA hydrogels soaked in 50 wt% KAc showed high conductivity and superior mechanical properties, outperforming many other reported tough and conductive ionic hydrogels (Fig. 4a)^{22,24,34,44–54}. This inspired us to explore the universality of the proposed method in which hydrogels were soaked in KAc solutions. Poly(acrylamide) (PAAm) and poly(2-hydroxyethyl acrylate) (PHEA) were UV polymerized and soaked in a 50 wt% KAc solution for 5 h. As shown in Fig. 4b, the strength and toughness of PHEA increased from 5.7 kPa to 306.5 kPa and from 2.2 kJ/m³ to 1298.2 kJ/m³, respectively (Fig. 4b, c), and the strength and toughness of PAAm increased from 73.9 kPa to 337.6 kPa and from 20.6 kJ/m³ to 1303.2 kJ/m³ (Fig. S7). Figure 4d shows optical images of PHEA hydrogels before and after soaking in a 50 wt% KAc solution. The PHEA hydrogel was transparent and flaccid before soaking but



turned semitransparent and held the shape of a rectangular sheet after soaking. The mechanical properties of the PHEA hydrogels soaked in 50 wt% KAc were measured under subzero temperatures. The stress and strain were reduced as the temperature dropped from 20 °C to –60 °C. However, the hydrogel still exhibited adequate stress (235.7 kPa) and strain (460%) at –60 °C. The dehydration of conductive ionic hydrogels leads to a loss in stretchability, limiting their real-world applications. KAc is a hygroscopic salt, which means it can absorb water molecules from the air. The hygroscopicity of KAc can allow these hydrogels to retain their water content, preventing dehydration issues. The KAc solution-treated hydrogels were kept in under open-air conditions, and their weights were measured over the course of 10 days. As shown in Fig. 4f, the PVA hydrogels containing 0 wt% and 10 wt% KAc lost ~90% of their original weight, indicating the complete dehydration of the hydrogels. The PVA hydrogels soaked in 30 wt% lost significant amounts of weight within the first day but remained at a relatively constant weight for the remaining 9 days. In stark contrast, the hydrogel soaked in 50 wt% KAc maintained 90% of its original weight over all 10 days (240 h), demonstrating excellent anti-dehydration capacity (Fig. 4f). The observed weight fluctuations of the PVA hydrogels were probably due to humidity changes, which ranged from 40% – 70% over the 10 days of testing.

Conclusions

In summary, KAc induces a salting-out effect on PVA, greatly improving the mechanical properties of PVA hydrogels. The mechanical properties can be further optimized by utilizing long polymer chains and high concentrations of KAc. Furthermore, due to the high solubility of KAc, the hydrogels soaked in salt solutions exhibited antifreezing capacities. The resultant 195 kDa PVA hydrogel soaked in 50 wt% KAc solution showed superior mechanical properties, with a tensile strength of 8.2 MPa, toughness of 25.8 MJ/m³, conductivity of 8.0 S/m and freeze tolerance as low as –60 °C. The proposed method in this study addressed the previously observed tradeoff between anti-freezing performance and mechanical properties in other recently reported studies. Furthermore, this method for strengthening hydrogels can be applied to other hydrogels, such as those made of PAAm and PHEA. After soaking in a 50 wt% KAc solution, hydrogel toughness could be increased by as much as two orders of magnitude. Additionally, the as-prepared hydrogels have anti-dehydration properties. We anticipate that the proposed method will further expand the range of conductive hydrogel applications in wearable aqueous batteries, soft robots and ionic skins under low-temperature conditions.

Materials and methods

The reagents consisted of poly(vinyl alcohol) (PVA) (average molecular weight (M.W.) of 27 kDa, 89~98 kDa and 195 kDa; degree of hydrolysis of 99%; Sigma–Aldrich), potassium acetate (ACS reagent, $\geq 99.0\%$, Sigma–Aldrich), acrylamide (analytical standard, Sigma–Aldrich), N,N'-methylenebisacrylamide (99%, Sigma–Aldrich), 2-hydroxyethyl acrylate (96%, Sigma–Aldrich), and lithium phenyl-2,4,6-trimethylbenzoylphosphinate (TPO-Li) (CPS polymers). All chemicals were used as received.

Preparation of PVA and salt solutions

PVA solutions were prepared by dissolving PVA powder in pure water with vigorous stirring and heating (95 °C) for 2 h. After the solutions were degassed by sonication for 1 h, clear solutions were obtained. KAc solutions of different concentrations were prepared by dissolving salts in pure water. After the solutions were sonicated for 10 min, clear salt solutions were obtained.

Fabrication of hydrogel

Fabrication of PVA hydrogels: A total of 20 mL of a 10 wt% PVA solution was poured into a Petri dish and placed in a freezer (−20 °C) for 2 h to completely freeze. The frozen PVA solutions were soaked in specific concentrations of KAc solutions for 96 h.

Fabrication of poly(acrylamide) and poly(2-hydroxyethyl acrylate) hydrogels: To fabricate these two hydrogels, 16 g monomer (acrylamide or 2-hydroxyethyl acrylate), 80 mg crosslinker (N,N'-methylenebisacrylamide) and 100 mg TPO-Li were dissolved in 40 g pure water to prepare the precursor solution. Then, the precursor solution was poured into molds and cured for 15 s under UV illumination. The model of the equipment was DYMAX SILVER, and the power of the UV light was 400 W. Then, the hydrogels were cut into strips (5 cm* 5 mm) and soaked in 50 wt% KAc solutions.

Tensile testing

The hydrogels were cut into strips with widths of 2 mm for regular tensile testing. The thickness of each sample was measured with a caliper. The data for the tough PVA hydrogels were obtained using a Cellscale Univert mechanical tester with a 50 N loading cell installed. The data for the poly(acrylamide) and poly(2-hydroxyethyl acrylate) hydrogels were collected with a 4.5 N loading cell. The stress–strain curves were calculated by dividing the load by the initial cross-sectional area and the initial clamp distance.

SEM characterization

To characterize the structures of the hydrogels, all hydrogel samples were immersed in pure water for 24 h to remove salts. Then, the samples were frozen in liquid nitrogen and freeze-dried using a Labconco FreeZone

freeze drier. The freeze-dried hydrogels were sputtered with gold and observed using a ZEISS Supra 40VP SEM.

Conductivity characterization

The conductivity characterizations were performed according to a previously published method²⁹. Specifically, the conductivities of the hydrogels at different temperatures were measured using two-electrode configurations. The hydrogels were fixed on two gold electrodes connected to an electrical working station (660E, CH Instruments). Then, the samples were placed in sealed plastic bags and immersed in a cooling bath at different temperatures (PSL-1810, Eyela). The conductivities (σ) were measured by EIS spectra at an initial voltage of 0 V with a 5 mV amplitude and a frequency of 10⁴ Hz. The conductivities were calculated according to the following equations:

$$\sigma = l / (R \times w \times d)$$

where R is the measured resistance. *l*, *w*, and *d* represent the length, width, and thickness of the hydrogels, respectively. The dimensions of the hydrogels were measured by a digital Vernier caliper.

DSC characterization

The hydrogels treated with different concentrations of KAc solutions were characterized using a differential scanning calorimeter (DSC-Q8000). The hydrogel samples were sealed in aluminum pans for testing, with an empty pan used as the reference. The samples were equilibrated at 20 °C and then cooled to −70 °C.

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Author contributions

S.W. and X.H. conceived the concept. X.Z. and X.H. supervised the project. S.W. and T.W. conducted the experiments. S.W., Y. D, X.Z. and X.H. wrote the manuscript. All authors contributed to the analysis and discussion of the data.

Data availability

All data are available in the main text or in the supplementary materials.

Competing interests

The authors declare no competing interests.

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