


RESEARCH ARTICLE

Rapid and scalable fabrication of ultra-stretchable, anti-freezing conductive gels by cononsolvency effect

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Funding information

China Postdoctoral Science Foundation Grant, Grant/Award Number: 2019M651480; Air Force Office of Scientific Research, Grant/Award Numbers: FA9550-17-1-0311, FA9550-18-1-0449; NSF CAREER award, Grant/Award Number: 1724526

Abstract

With the emergence of soft electronic devices, the requirements for conductive soft materials are unprecedentedly high. Among various soft materials, hydrogels are gaining tremendous attention for their superior softness, wetness, responsiveness, and biocompatibility. However, hydrogels inevitably lose elasticity and ionic conductivity at subzero temperature because of water freezing in the polymer matrices, severely limiting applications at low temperatures. Herein, we propose a rapid fabrication strategy to produce anti-freezing conductive gels with poly(vinyl alcohol) on a large scale within minutes (vs hours/days in conventional methods) using a water/DMSO binary liquid system, which serves as gelation inducer via cononsolvency and anti-freezing solvents simultaneously. The gel with 60 wt% DMSO shows the best anti-freezing performance, remaining unfrozen at temperatures lower than -50°C , while also maintaining the highest mechanical properties with a tensile strength of 1.1 MPa, toughness of 10.9 MJ/m^3 , and elongation of 1500% outperforming the most previous reports. After incorporating H_2SO_4 , the gels exhibit a high ionic conductivity of 5.25 S/m and maintain 1.65 S/m even at -50°C . Furthermore, an all-in-one supercapacitor is fabricated to demonstrate the potential of the anti-freezing gel in soft device applications with good performance at subzero temperatures. A full recyclability of the material was also demonstrated.

KEYWORDS

anti-freezing, conductive, cononsolvency, rapid, ultra-stretchable

1 | INTRODUCTION

As many technologies enter a “soft” era, the innovation on soft material systems has been tremendously increasing for stretchable energy storage devices, wearable sensors, bioelectronics, soft robots, prosthesis devices, medical patches, and many other flexible devices.^{1–9}

Stretchable conductive materials provide an indispensable foundation for these applications. To successfully realize these applications, the key challenge is to design material systems exhibiting excellent mechanical performance and high ionic conductivity simultaneously.¹⁰ Hydrogels, crosslinked networks of hydrophilic polymer chains swollen with water,⁵ have gained considerable

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attention due to their superior softness, wetness, responsiveness, biocompatibility, and bioactivity.⁴ The polymer network provides hydrogels with solid-like mechanical properties, while the aqueous phase in the porous polymer matrix exhibits liquid-like transport properties endowing hydrogels with outstanding flexibility and tailorable mechanical properties.¹¹ Ionic conducting hydrogels, where the gels are incorporated with conductive materials, have already been utilized in many of the applications mentioned previously;^{4,10} however, conventional ionic conductive hydrogels contain pure water and inevitably freeze in subzero-temperature environments, leading to a significant loss in ionic conductivity and stretchability and severely limiting their application in low temperatures.¹² Researchers have proposed several strategies for solving this critical issue, and they can be divided into four categories.¹² First, salts of large amounts such as CaCl_2 and ZnCl_2 can be incorporated into hydrogels to depress the water freezing temperature.^{13,14} The salts can also serve as ionic conductive components. Second, some ionic liquids can remain in the liquid state, with high ionic conductivity, at subzero temperatures because of their low freezing points.^{15–17} Hence, ionic-liquid-based gels can be utilized as conductors tolerating low temperatures. Third, the solvent can be changed from pure water to a mixture of water and organic liquids, such as propylene or ethylene glycol, to form hybrid organo-hydrogels with much larger working temperature ranges.^{18–20} Fourth, the anti-freezing property can be realized through nano-confinement of water molecules.^{21–24} But the anti-freezing performance by nano-confinement is not comparable with the first three strategies.

Tremendous improvements have been made for anti-freezing hydrogels with the aforementioned strategies; however, there remains a common issue for a part of reported works: the anti-freezing mixtures or conductive components are introduced into the gel matrix after the gels synthesized.^{14,19} This process requires long times, from hours to days, because of the slow diffusion of anti-freezing solutions and conductive ions into a bulk gel matrix; this limits the large-scale and rapid fabrication of anti-freezing gels.^{13,25,26} Therefore, it is highly desirable to develop new strategies for producing conductive anti-freezing gels remaining mechanically robust under low temperatures. We propose that this critical demand can be addressed by fabricating gel via the cononsolvency effect, the phenomenon of solubility decrease of a macromolecule in the mixture of two good solvents.^{27–30} This phenomenon has been widely applied in the physico-chemical, green chemical, and pharmaceutical industries.^{27,31} Poly(vinyl alcohol) (PVA) can form a hydrogel in a mixture of water and dimethyl sulfoxide (DMSO) via the cononsolvency effect, attributed to the strong

interaction between water and DMSO molecules.^{28,32–35} On the other hand, the strong interaction between water and DMSO molecules makes the water/DMSO binary system have lower freezing temperature than the pure solvents do.^{36,37} Based on the phase diagram of water-DMSO mixtures, at specific compositions the mixture remains liquid at very low temperatures.³⁶ Some of the reported works also utilized the strong interaction between water and organic solvents to make anti-freezing gels.^{37,38} However, the influences of the binary mixture solvent ratio on the mechanical properties of the anti-freezing gels have yet been investigated.

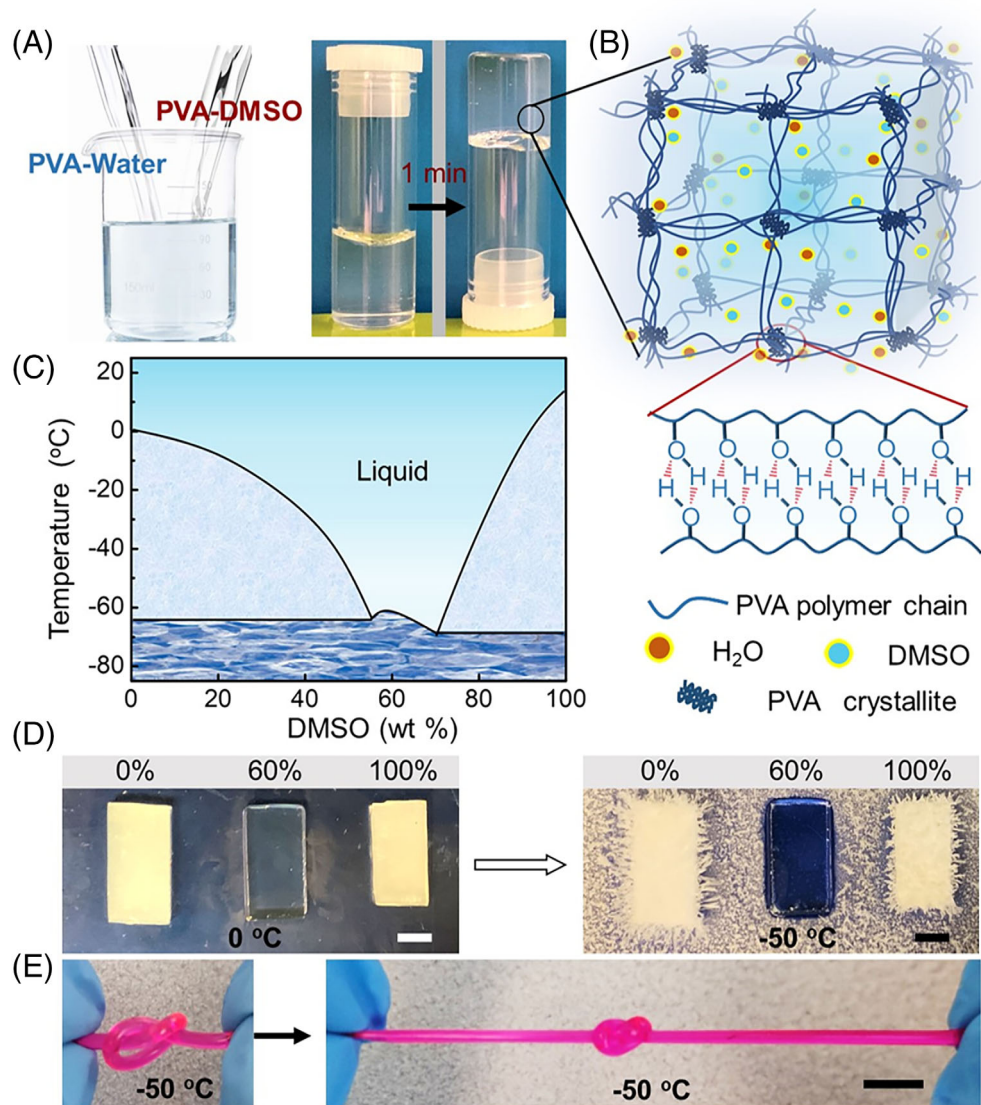
Herein, we utilized the aforementioned two properties, the cononsolvency effect and anti-freezing property of the water/DMSO binary liquid system to fabricate the anti-freezing gel in a rapid and scalable fashion. The gels with 60 wt% DMSO show the best anti-freezing performance, remaining unfrozen at temperatures below -50°C . The ratio of water to DMSO has a significant impact on the mechanical properties of the gels. The gels with 60 wt% DMSO show the best mechanical performances with an ultimate stress of 1.1 MPa, toughness of 10.9 MJ/m^3 , and elongation of 1500%, surpassing most reported anti-freezing gels. After incorporating H_2SO_4 , the gels present a high ionic conductivity of 7.69 S/m and maintains 1.65 S/m at -50°C . Furthermore, an all-in-one supercapacitor is fabricated to demonstrate the anti-freezing gel's potential for soft electronics functional in subzero-temperature environments. This fabrication strategy guarantees the rapid fabrication of conductively anti-freezing gels on a large scale by avoiding the slow diffusion of anti-freezing materials and conductive components. Besides, the as-prepared gel can be fully recycled.

2 | RESULT AND DISCUSSION

2.1 | Fabrication of gels

To fabricate the gels with PVA as an exemplary polymer, DMSO and aqueous solutions with 10 wt% dissolved PVA (Mw 89 000–98 000) were prepared, termed PVA-DMSO and PVA-water respectively. The PVA-DMSO and PVA-water solutions were mixed at different ratios and sonicated for degassing (Figure 1A). The mixtures were put into a freezer at -20°C to facilitate the gelation process. The mixture of 60 wt% DMSO formed a transparent gel very quickly within 1 minute, visually demonstrated by the gel remaining at the bottom of the vial when it was inverted (Figure 1A); meanwhile, at room temperature, the gelation process took longer (~ 30 minutes) and the as-prepared gel was translucent (Figure S1). That was because at -20°C , it facilitated the hydrogen bonding

FIGURE 1 Fabrication and performance of anti-freezing gels. (A) Gelation process of the anti-freezing gels: PVA-DMSO and PVA-water solutions both containing 10 wt % PVA were first mixed and degassed. The mixture was placed in a freezer (-20°C). Within only 1 minute, gelation could be observed when the vial was inverted and the gel remained at the bottom of the vial. (B) Gelation occurred because of the formation of hydrogen bonds due to the cononsolvency effect. (C) Phase diagram of the mixture of DMSO and water. (D) At 0°C , 0 wt% and 100% DMSO gels both froze and became opaque, while the 60 wt% DMSO gel remained unfrozen and transparent even at -50°C . (E) At -50°C , the 60 wt% DMSO gel maintained its stretchability and could be knotted and stretched without any damage. Scale bars in D = 5 mm and scale bar in E = 1 cm



formation between PVA polymer chains resulting in a faster crystallization rate.³⁹ By contrast, solutions with 0 wt and 100 wt% DMSO remained liquid at 20 minutes (Figure S2) and would freeze when they were placed in the freezer for longer times. Both water and DMSO molecules can interact with the PVA; however, in the mixture, the water and DMSO would interact with each other much more strongly than with PVA, which expelled the solvation layer of the polymer chains resulting in hydrogen bond formation between the hydroxyl functional groups on the polymer chains (Figure S3).^{27,40} These hydrogen bonds acted as physical cross-linkers of the gel (Figure 1B). Meanwhile, because of tight bonding between the water and DMSO molecules, a eutectic solvent formed and the freezing temperature was depressed below that of pure water and DMSO, which endowed the gels with anti-freezing capability. The freezing temperature was different depending on the DMSO weight percentage, as shown in the phase diagram in Figure 1C. To

test whether the gel exhibited anti-freezing ability, a gel with 60 wt% DMSO, chosen based on the phase diagram, and two other gels containing pure water (0 wt% DMSO) and pure DMSO (100 wt% DMSO) were placed on a cooling stage. At 0°C , both the 0 wt% and 100% DMSO gels froze and became opaque (Figure 1D), while the 60 wt% DMSO gel remained unfrozen and transparent even when the temperature was lowered to -50°C (Figure 1D). Additionally, the 60 wt% DMSO gel maintained high stretchability and could be knotted and stretched with a large strain at -50°C (Figure 1E).

2.2 | Mechanical properties of the as-prepared gels

The mechanical properties of the as-prepared gels were measured systematically (Figure 2A). When the DMSO content increased from 10 to 60 wt%, the tensile strength

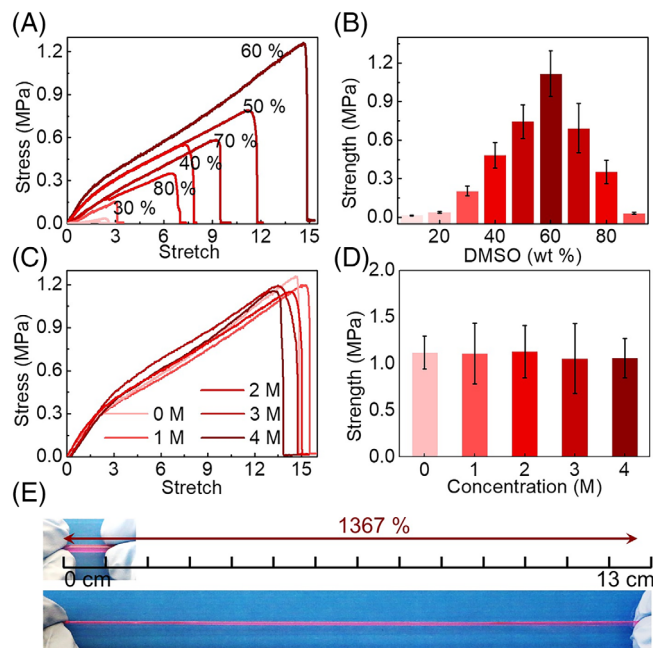


FIGURE 2 Mechanical properties of the anti-freezing gels. (A) Representative stress–strain curves of gels containing different DMSO content. (B) Strengths of the gels with different DMSO content, from 10 to 90 wt%. (C,D) Representative stress–strain curves and the corresponding strengths of gels containing 0, 1, 2, 3, and 4 M H_2SO_4 , all the gels containing 60 wt% DMSO. (E) Photographs of the conductive and anti-freezing gel at the initial length and stretched to 1367% elongation. The gel contains 60 wt% DMSO and 2 M H_2SO_4

and toughness increased from 22 kPa to 1.2 MPa (Figure 2B) and 0.024 to 10.9 MJ/m^3 (Figure S4), respectively. The mechanical properties of gel containing 60 wt% DMSO outperformed the most anti-freezing gels reported by previous reports (Table. S1).^{12,41} Upon further increase of the DMSO content from 60 to 90 wt%, the strength and toughness decreased from 1.2 MPa to 33 kPa (Figure 2B) and 10.9 to 0.036 MJ/m^3 (Figure S4), respectively. The mechanical properties improved because the degree of crystallinity increased when the DMSO content increased from 10 to 60 wt%; however, as the content of DMSO increased further from 60 to 90 wt%, the degree of crystallinity decreased correspondingly (Figure S5). At the molecular level, as the DMSO content increased it tended to form more hydrogen bonds with water, breaking the hydrogen bonding between water and PVA chains; this facilitated the formation of hydrogen bonds between the hydroxyl groups on the PVA chains into crystalline domains (Figure S3).⁴² Once the DMSO content increased above a certain threshold, when all the water molecules formed hydrogen bonds with DMSO already, there were excessive DMSO molecules, which were free to interact with PVA molecules,

inhibiting the hydrogen bond formation between the PVA chains or breaking the existing hydrogen bonding between the chains.⁴³ Here, the mechanical properties of the PVA gel reached the highest level indicating DMSO and water had the maximum association with each other at 60 wt% DMSO, leading to the formation of a highly contracted conformation between PVA chains.^{28,44} The morphologies of the gels with different DMSO content also varied (Figure S6). In the binary mixture, the hydrogen bonds formed between polymer chains leading to the collapse of the gel matrix, indicated by the porous and fibrous structures in the gel matrices.^{31,43,45} Specifically, the 60 wt% DMSO gel presented long fibers (Figure S7) originating from the aggregation induced by the cononsolvency effect, helpful for improving the mechanical properties.⁴⁶ H_2SO_4 was introduced to render the gels ionic conductivity. To fabricate conductive gels, 40 wt% of PVA-water solution containing different concentrations of H_2SO_4 and 60 wt% of PVA-DMSO solution with the same concentrations of H_2SO_4 were mixed, degassed and gelated at -20°C (Figure 3A). The addition of H_2SO_4 did not affect the gelation process, and the gelation still occurred within 1 minute at -20°C . Meanwhile, representative stress–strain curves of the gels and the corresponding strengths of gels containing 0, 1, 2, 3, and 4 M H_2SO_4 indicated that the incorporation of H_2SO_4 did not compromise the mechanical properties of the gels (Figure 2C,D). Figure 2E demonstrated visually the ultra-stretchability of the conductive 60 wt% DMSO gel containing 2 M H_2SO_4 , which could be stretched to 1367% without breaking.

2.3 | Anti-freezing performances

Based on its anti-freezing property and superior mechanical performance, the PVA gel with 60 wt% DMSO was utilized for the fabrication of functional devices via incorporation of H_2SO_4 electrolyte (Figure 3A). Compared with most reported works that rely on the postgelation infiltration of anti-freezing materials or conductive components into the gel matrix, the anti-freezing solvents and conductive electrolyte were added simultaneously before gelation. This allowed a large-size gel to be made within minutes (Figure 3B). The conductivities of the gels with different H_2SO_4 concentrations were measured with an electrochemical workstation. The ionic conductivity of the PVA gel increased from 3.2 to 7.69 S/m as the H_2SO_4 concentration increased from 1 to 4 M (Figure 3C). Then, the conductivities of the 0, 10, 60, and 90 wt% DMSO gels with 2 M H_2SO_4 were measured under different temperatures, from 20 to -50°C (Figure 3D). When the temperature decreased below -5°C , the ionic conductivity of the

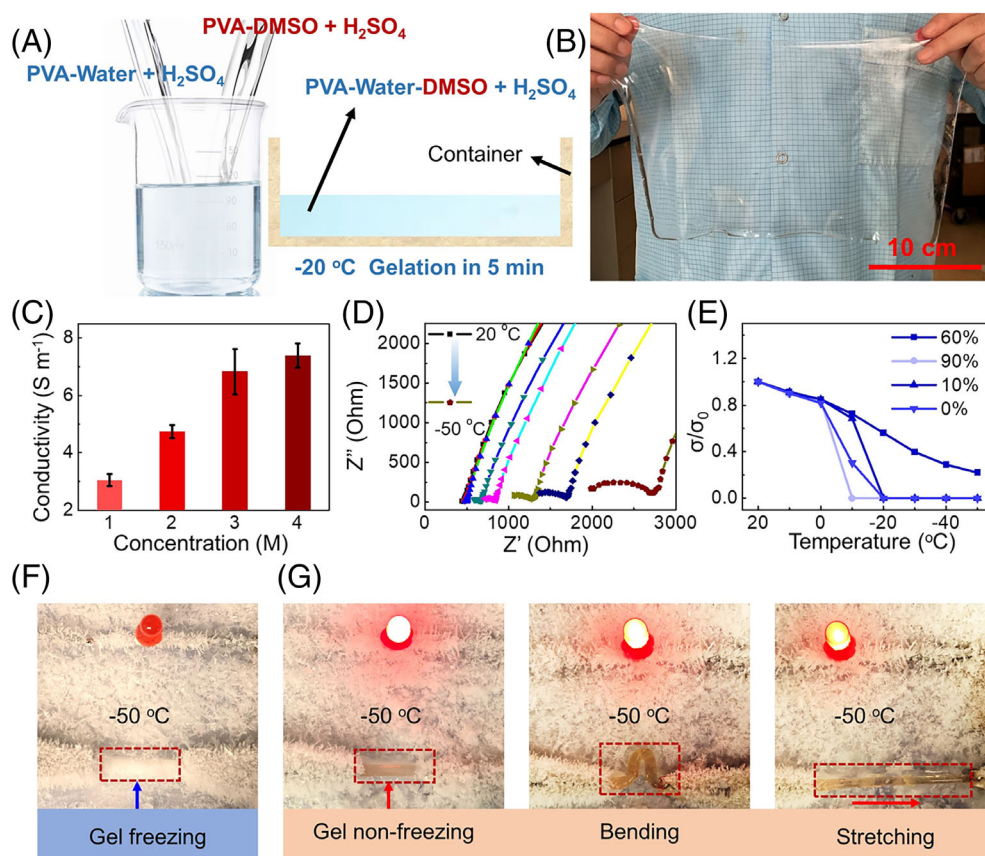


FIGURE 3 Fabrication and conductivities of the conductively anti-freezing gels. (A) Schematic fabrication process of the anti-freezing gels. (B) Optical image of the conductively anti-freezing gel. (C) Conductivities of the 60 wt% DMSO gels with different concentrations of H₂SO₄. (D) The impedances of the 60 wt% DMSO gels with 2 M H₂SO₄ at various temperatures from 20 to -50 °C. (E) Conductivities of the gels under different temperatures; the 0, 10, 60, and 90 wt% DMSO gels were all measured with 2 M H₂SO₄ incorporated. (F,G) The visual demonstrations of the anti-freezing capability of the conductive 60 wt% DMSO gel with 2 M H₂SO₄ at -50 °C. The 0 wt% DMSO gel was frozen, causing the LED to turn off, while the 60 wt% DMSO gel with 2 M H₂SO₄ remained unfrozen, keeping the LED on even during bending and stretching

0 wt% DMSO gel decreased to ~0 S/m; the conductivities of the 10 and 90 wt% DMSO gels decreased dramatically at -20 °C as well (Figure 3E). By contrast, the ionic conductivity of the 60 wt% DMSO gel decreased gradually, but still remained at 40% of the original room-temperature ionic conductivity (20 °C) (Figure 3D,E). An LED was used to demonstrate the ionic conductivity change at subzero temperatures. As shown in Figure 3F, G, at -50 °C, the LED turned off because of the freezing in the 0 wt% DMSO gel. By contrast, the 60 wt% DMSO gel remained unfrozen, and the LED remained on; the gel also remained elastic demonstrated by the lighting of the red LED during bending and stretching (Figure 3G). Besides, the as-prepared gels were crosslinked physically with crystalline domains. As shown in Figure S8, after the gel was cut into pieces, the pieces can be collected and heated to solution once again, as the breaking of the hydrogen bonds in the crystalline domains led to the decrosslinking. Afterward, the solution formed gel once

more, demonstrating the full recyclability of the conductive anti-freezing gel made via cononsolvency effect.

2.4 | Anti-freezing supercapacitor

The anti-freezing performance of the 60 wt% DMSO gel endowed the devices with the ability to function at subzero-temperature environments. A polypyrrole (PPy) foam was synthesized and utilized as electrodes for an all-in-one supercapacitor assembled from the 60 wt% DMSO gel with 2 M H₂SO₄ as the electrolyte (Figure S9). During the assembly of the supercapacitor, the solution of PVA permeated into the PPy foam (Figure 4A) and coated on the porous PPy structures; the PVA gel also formed between the electrodes acting as the gel electrolyte (Figure 4A). As shown in Figure 4B,C, both the electrodes and the electrolyte exhibited porous structures, and PPy particles could still be observed in the electrodes by SEM (Figures 4C and S10).

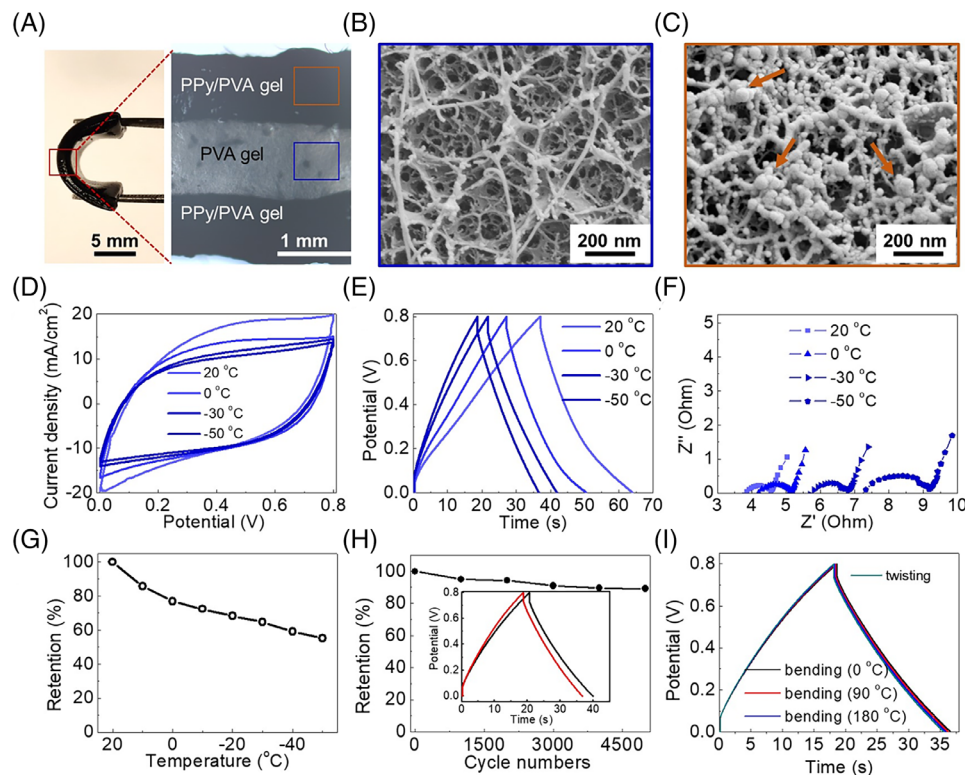


FIGURE 4 Characterizations and the performance of the all-in-one anti-freezing supercapacitor. (A) Optical images of the all-in-one anti-freezing supercapacitor. (B,C) SEM images of the electrodes and gel electrolyte. (D) CV, (E) Galvanostatic charge/discharge curves, and (F) Nyquist plots of the supercapacitor at different temperatures, from 20 to -50°C . Scan rate of CV, 100 mV/s. (G) Capacitance retention at various temperatures. (H) Cycling stability of the supercapacitor at -50°C . (I) GCD curves of the supercapacitor while twisting and bending with various angles. The arrows point to the nanoparticles to aid the viewing

The cyclic voltammograms (CVs) and galvanostatic charge-discharge (GCD) curves were measured systematically from 20°C to -50°C with a home-made temperature-controlling setup (Figure 4D and Figure S12). The CV curves were collected in the range 0 to 0.8 V with different scan rates from 10 to 200 mV/s at different temperatures (Figure S13). Figure 4D shows typical CV curves of the supercapacitors at 20, 0, -30 , and -50°C with a scan rate of 100 mV/s. The CV loops decreased gradually as the temperature decreased from 20 to -50°C , indicating the capacitance decreased correspondingly. The discharging time decreased from 35 to 20 seconds when the temperature was tuned from 20°C to -50°C (Figure 4E). The Nyquist plots of the supercapacitor at different temperatures confirmed the capacitance variation (Figure 4F) and the capacitance maintained 55% of the room-temperature capacitance (Figure 4G). Furthermore, the stability of the supercapacitor was tested at -50°C : after 5000 charging-discharging cycles (Figure 4H and the inset), the anti-freezing supercapacitor exhibited excellent stability with 88.6% capacitance retention. Meanwhile, the PVA- SO_4 supercapacitor showed good capacitance retention under twisting and bending at different angles (Figure 4I).

3 | CONCLUSIONS

Here, we discovered a simple and scalable method of rapidly fabricating anti-freezing gels via cononsolvency

effect utilizing the water/DMSO binary liquid system. The PVA gel made with 60 wt% DMSO shows the best anti-freezing performance, remaining unfrozen at temperatures around -50°C . The water: DMSO ratio plays a significant role in determining the mechanical properties of the gels. The 60 wt% DMSO gel demonstrates the best mechanical performance with a tensile strength of 1.1 MPa, toughness of 10.9 MJ/m^3 , and elongation of 1500%, surpassing most reported anti-freezing gels. The mechanical properties are improved because the degree of crystallinity increases when the DMSO content is tuned from 10 to 60 wt%; as the content of DMSO increases further from 60 to 90 wt%, the degree of crystallinity decreases. After incorporating H_2SO_4 , the gels present high ionic conductivity at very low temperatures. Furthermore, an all-in-one supercapacitor is fabricated with excellent performance at low temperatures, demonstrating high potential for anti-freezing gels in soft electronics applications compatible with subzero-temperature environments. In conclusion, water/DMSO binary liquid system serves as gelation inducer and anti-freezing solvents, which renders the conductively anti-freezing gels with outstanding mechanical properties and excellent anti-freezing performance. This fabrication strategy guarantees the quick fabrication of conductive anti-freezing gels on a large scale by avoiding the slow diffusion of anti-freezing materials and conductive components. Besides, the as-prepared

gel can be fully recycled because of the reversible forming and breaking of hydrogen bonds between PVA chains by tuning the temperature.

3.1 | Experimental section

3.1.1 | Materials

Poly(vinyl alcohol) (PVA) (weight-average molecular weight [Mw] of 89 to 98 kDa; degree of hydrolysis of 99%; Sigma-Aldrich), H₂SO₄ (analytical grade; Sigma-Aldrich) pyrrole (99%; Sigma-Aldrich) FeCl₃ (analytical grade; Sigma-Aldrich) and Rhodamine B were used as received.

3.1.2 | Preparation of the solutions of PVA-water and PVA-DMSO

Then, 10 wt% PVA solutions were prepared by dissolving PVA powder in deionized (DI) water and DMSO, respectively, under vigorous stirring and heating (95°C). After degassing by sonication for 1 hour, clear solutions were obtained. The PVA solutions of DI water and DMSO containing 1, 2, 3, and 4 M H₂SO₄ were made with the same procedures.

3.1.3 | Fabrication of the gels

The gels were made by mixing the PVA aqueous solutions and PVA DMSO solutions with various weight ratios: 1:9, 2:8, ... 9:1. After mixing with a vortex thoroughly, the mixtures were centrifuged with 6000 r/min for 30 seconds to remove the bubbles in the mixtures. Afterward, the mixtures were poured into petri dishes and put in the freezer (−20°C) to gelation. The gels containing H₂SO₄ were fabricated with the same procedures.

3.1.4 | Tensile testing

The gels were cut into dog-bone shaped specimens with gauge width of 2 mm for regular tensile testing. The thickness of individual specimens was measured with a caliper. The force-displacement data were obtained using a Cellscale Univert mechanical tester with a 50 N loading cell installed. The stress-strain curves were obtained by division of an initial gauge cross-section area and an initial clamp distance.

3.1.5 | SEM characterization

For characterization of the micro- and nano- structures of the gels, all gel samples were immersed in DI water for 24 hours before freeze-drying using a Labconco FreeZone freeze drier. The freeze-dried gels were cut to expose the inside and sputtered with gold before carrying out imaging using a ZEISS Supra 40VP SEM.

3.1.6 | Fabrication of all-in-one supercapacitor

To synthesize the PPy foam, the 10 wt% FeCl₃ aqueous solution and 10 wt% pyrrole ethanol solution were prepared and these two solutions of equal volume were mixed fast and poured into a Petri dish. The PPy hydrogel formed within 30 minutes. Then the PPy hydrogel was soaked and washed with plenty of DI water to remove the ions. Afterward, the PPy hydrogel was freeze-dried to obtain the PPy foam. At last, the PPy foams were utilized as electrodes and the supercapacitor was assembled using the setup as shown in Figure S9. The all-in-one supercapacitor was cut into dimensions 1.0 cm × 1.0 cm for the following characterizations.

3.1.7 | Characterizations

The electrochemical tests were performed via two-electrode method on a CHI660E electrochemical workstation (CH instrument). The CV measurements were examined at scan rates of 10, 20, 50, and 100 mV/s. The GCD curves were measured with various current densities in the potential range of 0 to 0.8 V. The EIS measurement was performed in the frequency range from 1 00 000 to 0.01 Hz, with a voltage perturbation of 5 mV. The cyclic stability test was performed by cyclic charging and discharging at a certain current density. The areal capacitance (C_A) of the anti-freezing supercapacitor was calculated according to equations: $C_A = 2It/U$. All these characterizations were performed with a homemade cooling stage.

ACKNOWLEDGMENTS

Shuwang Wu acknowledges the support of the China Postdoctoral Science Foundation Grant (Grant 2019M651480). Yousif Alsaid, Yichen Yan, Mutian Hua, Dong Wu, Yusen Zhao, and Ximin He acknowledge the support of the NSF CAREER award (1724526), Air Force Office of Scientific Research (AFOSR) Grant FA9550-17-1-0311, and AFOSR award FA9550-18-1-0449.

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SUPPORTING INFORMATION

Additional supporting information may be found online in the Supporting Information section at the end of this article.

How to cite this article: Wu S, Alsaid Y, Yao B, et al. Rapid and scalable fabrication of ultra-stretchable, anti-freezing conductive gels by cononsolvency effect. *EcoMat*. 2021;3:e12085. <https://doi.org/10.1002/eom2.12085>