

Ultrastretchable Polyaniline-Based Conductive Organogel with High Strain Sensitivity

Yucheng Zhang, Yusen Zhao, Zihang Peng, Bowen Yao, Yousif Alsaid, Mutian Hua, Dong Wu, Yu Qiu, Qibing Pei, Xinyuan Zhu, Zhiyuan He,* and Ximin He*



ABSTRACT: Strain sensors, as a key component of wearable/stretchable electronics, typically exhibit an intrinsic conflict between large strain (>100%) and high sensitivity (gauge factor > 10). This Letter reports a solution to this trade-off by creating a high-conductivity thin layer of polyaniline (PANi) percolated through the outer surface of a polymethyl acrylate organogel. The highly robust, conductive organogel can achieve both high gauge factor and large strain via the mismatch between the fragile PANi and the elastic polyacrylate blending layer. The high gauge factor over the entire strain range of 2000% enables its broad sensing range from human pulse to massive deformation. The water-free conductive organogel provides purely electronic conductivity and allows for working under extreme conditions, which typical conductive hydrogels cannot withstand. These merits allows the sensor to present high sensitivity for both subtle movement (8% resistance change for pulse detection) and large strain (a gauge factor of 376 at 460% strain). Such a conductive organogel also demonstrated great sustainability under harsh operating conditions, as demonstrated by a dielectric elastomer actuator based on it, capable of generating a horizontal displacement of 15.7 mm (46% of the total length) at -12 °C, as a substitute for conventional hydrogels as the electrode.

onductive organogels have recently attracted the attention of researchers because they can overcome the intrinsic drawbacks of conventional conductive hydrogels used in wearable electronics, energy storage, robots, and health monitoring.^{1–10} The main reason is that hydrogels contain water that causes poor tolerance of their mechanical and electrical properties to the atmospheric changes. This hinders the application of hydrogels as stretchable conductors under long-term or extreme conditions.^{11–13} For example, exposure to an equilibrium environment of unsaturated water vapor or freezing at subzero temperature makes these materials rapidly dehydrate. This effect is further compounded under repetitive deformations, for example, within actuators or strain

sensors. Furthermore, the ionic conductivity from mobile ions of water as a solvent will inevitably contribute to the conductivity from the conducting components of the hydrogel. In this respect, a potential electrochemical reaction or water electrolysis may severely impair the performance of related

Received: June 26, 2021 Published: September 8, 2021



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Figure 1. (a) Schematic of the preparation of conductive organogel based on the abnormal swelling process in polyacrylate matrix. (b-d) SEM images of (b) external polyaniline top layer surface, (c) internal polyacrylate matrix, and (d) polyaniline layer (upper layer)/polyacrylate matrix interface. (e) Sheet resistance of the conductive organogel as a function of percentage by weight of aniline in the precursor. (f) Stress-strain curves of poly(methyl acrylate)-*co*-(butyl acrylate) conductive organogel as a function of molar ratio of methyl acrylate in the precursor.

devices such as DC voltage appliances.^{14,15} To prevent this shortcoming, organohydrogels or organogels has been recently developed by employing a nonvolatile organic solvent. Organohydrogels are usually produced by one-step method in which a preprepared hydrogel is directly immersed in an organic solvent to partially remove the water. Examples include nondrying cryoprotectant-based Ca-alginate/PAAm tough organohydrogels¹² and MXene organohydrogels with excellent low-temperature tolerance, which can be obtained by mixing ethylene glycol (EG) and water as a gel medium.¹³ The synthesis of pure organogels includes a complementary evaporation process to remove the residual water and further reduce the contribution of ionic currents to the conductivity of the final product. For example, Lee et al. used the mixture of EG and water to replace the latter inside a PEDOT:PSS/ acrylamide conductive hydrogel,¹⁴ and water was afterward selectively evaporated to form the conductive organogel instead of the organohydrogel. However, the hydrophilic polymer matrix rather absorbs water than organic solvents, which makes the fabrication process time-consuming. Additionally, organogels based on hydrophilic monomers quickly revert back to organohydrogels, or even hydrogels, when exposed to moisture.

The conductors used in detecting dynamic movements, such as robotics and health monitoring, place high demands on strain sensing performance. On the one hand, high sensitivity (i.e., gauge factor (GF)) generally requires faster and more accurate detection and reducing the threshold of detection allows one to measure subtle movements such as human pulse.¹⁶ On the other hand, stretchability determines the application scope of sensors. Large stretchability (i.e., strain above 100%) is essential in physiology and kinesiology applications.¹⁷ There is a trade-off between high sensitivity and high stretchability in common strain sensors due to the fact that high sensitivity necessitates considerable structural deformations upon stretching, whereas high stretchability needs morphological stability under significant stretching. In that regards, achieving both features through simple thin-film structures is a challenge.^{18–21} In traditional hydrogels, the conductive component, such as mobile ions, metallic nanowires, carbon-based nanomaterial, or polymer, can be homogeneously distributed across a gel matrix. However, this approach reduces the sensitivity mainly due to the geometrical and percolation effects that are strain-insensitive.^{22,23} Another route is the lamination of the conductive material on a resilient matrix. Although the high sensitivity can be realized by forming



Figure 2. Photos of the conductive organogel working in a LED circuit at (a) 26 °C under tension (above) and twisting (below), (b) -22 °C under tension (above) and twisting (below), and (c) -22 °C encapsulated in ice. (d) Resistance percent as a function of temperature for conductive polyacrylate organogel and typical ionic PVA hydrogel. (e) Weight percentagevs. air exposure time for the conductive polyacrylate organogel after ultrasonication in water and for a typical ionic ally conductive PVA hydrogel.

disconnected microcracks during deformation of the device, the physically adsorbed conductive layer results in a mechanically unstable structure that is prone to fracture under large strain.^{24,25}

In this work, a conductive organogel was produced based on a hydrophobic polyacrylate matrix to improve the stability in an ambient environment. Surface percolation networks of conductive PANi served as the sensing components. The PANi formation within the subsurface region of the polyacrylate matrix was facilitated by the "abnormal swelling" of the hydrophobic matrix upon the absorption of its nonsolvent water on its surface, a phenomenon observed earlier in acrylate-based organogels explained by the formation of a semipermeable skin layer from rapid phase separation.²⁶ The presence of a middle stretchable polyacrylate component made the PANi-coated organogel highly deformable. The resistance of the obtained material was found to be as low as 50 Ω /sq at room temperature and its conductivity remained unchanged even at subzero temperatures (-22 °C). Furthermore, thanks to a facile UV curing process, this stretchable composite has a great potential for various applications. As an example, highly sensitive strain sensors were fabricated from organogels, exhibiting exceedingly high gauge factors with substantial deformation capability. Besides, the change in resistance measured by a designed organogel-based sensor was impressively high (8%) when detecting the human pulse. Benefiting from the unique advantages of the organogel, the latter was successfully utilized both as the electrode and as a passive layer of a dielectric-elastomer-based actuator with a simplified structure. Finally, the high electrical conductivity and softness of the organogel enabled the appliance to operate

under subzero temperatures (down to -12 °C) at maintaining 45% of total length bending displacements and 8200 V of the working voltage.

PANi/polymethyl acrylate conductive organogels were synthesized by oxidizing the aniline monomers as the components of the solvent (DMF) inside the as-prepared hydrophobic polymethyl acrylate matrix (Figure 1). The APS solution permeated into the subsurface region of the organogel along with the nonsolvent water to oxidize aniline into PANi (Figure 1a-1d), forming a 150- μ m-thick conductive layer of PANi blend within the surface of polymethyl acrylate (Figure 1d). The diffusion of the aqueous solution into organic solvent occurs due to abnormal swelling, which originates from the osmotic pressure difference between the organic solvent inside the polyacrylate matrix and the APS aqueous solution outside the matrix. The resistance of organogel can be modulated by changing the ratio of aniline to organic solvent in the precursor. According to Figure 1e, an increase in the weight percent of aniline from 5.52% to 27.61% resulted in a decrease in sheet resistance from about 400 000 to 50 $\Omega/sq.$ On the other hand, the weight percent above 27.61% caused the insolubility of aniline in the polymer matrix. Comparing to the pure polymethyl acrylate organogel, the samples with conductive PANi layer have a larger Young's Modulus in the strain range from 0% to 100% (Figure S5). However, the PANi layer's impact on the mechanical properties is not substantial in general because, unlike the inner polymethyl acrylate layer, the fragile conductive layer cannot restore its original shape once stretched (Figure S3). In turn, tunable mechanical properties can be achieved by mixing methyl acrylate monomer with butyl acrylate monomer in various proportions. As seen in Figure 1e,



Figure 3. (a) Schematic illustration of the tunneling conduction model as the conductive mechanism of the polyaniline layer under significant strain. (b) SEM characterization of surface morphology at (b1) 0% and (b2) 100% strain. (c, d) Resistance percent (red) as a function of strain and the corresponding logarithmic plot (blue) at (c) 25 °C and (d) -12 °C. (e–h) Human movement sensors based on the conductive organogels. Detection of (e) pulse and (f) human voice at the artery on the neck. Repetitive detection of finger bending (g) with increasing bending angle and (h) at a fixed angle.

an increase in the methyl acrylate monomer content ratio led to a rise in Young's modulus of the conductive organogel, which can be extrapolated from the slope of the stress-strain curve at the beginning. Moreover, according to Figure 1f, the stretchability of organogel was not hindered by the high aniline concentration because polyaniline was entirely concentrated on the outer surface, whereas the inner polyacrylate layer remained unaffected. In general, organogels exhibited higher toughness (222 kpa) than traditional hydrogels (~25 kpa),¹¹ which enabled one to enhance their stability when applied in related devices.

According to Figure 2d, the conductivity of ionic PVA hydrogel drastically decreased as the temperature had dropped below 0 °C, where the gel was frozen and unstretchable. On the contrary, the organogel remained resistant to even lower temperatures down to -20 °C, maintaining mechanical softness and electrical conductivity. As a simple demonstration of antifreezing, organogels in the initial, extended, twisted, and encapsulated-in-ice states were set up in series in a blue LED circuit under various temperature conditions (see the photos in Figure 2a-2c). A more intuitive relationship between the resistance percent and the temperature (Figure 2d) shows how the resistance responds to the change in temperature. It is evident that a decrease in the temperature from 8 to -20 °C exerts no noticeable impact on the resistance of the conductive organogel. This is because the conductivity of the latter is determined by the electrons hopping in PANi rather than by

the mixture of ionic and electronic conductivities. For comparison, the conductivity of a typical ionic conductive PVA hydrogel with a sodium sulfate solution inside rapidly decreases as the temperature drops below 0 °C, which is due to the solidification of a solvent. Even in the room-temperature open-air environment, the unstable electrical properties of conductive hydrogels, caused by water loss, remain an issue, restricting their long-term applications. According to Figure 2e, the weight percent of the conductive organogel and PVA hydrogel changed with time after both were removed from the water and placed under open-air conditions with 60% humidity. A nearly 20% weight loss in the organogel was mainly owing to the release of water adsorbed on the PANi layer. In contrast, the weight loss of PVA hydrogel takes origin from the water wastage from the solvent inside the matrix, leading to a fatal change in shape and resistance of the composite.

This conductive organogel is found to ensure both large stretchabilities from the internal polyacrylate matrix and high sensitivity from a thin external conductive PANi layer when working as a strain sensor. In previous reports, a trade-off between "high sensitivity" and "stretchability" was mentioned for the majority of resistive-type strain sensors.^{5,18} In general, high stretchability comes with a typical lower GF < 30. In our material, a high GF of 376 was enriched at 460% strain (Figure 3a), which was caused by the tunneling effect.^{27–29} The initial morphology of the PANi layer under no external strain is

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Figure 4. (a) Graphic structure of a dielectric elastomer bending actuator. (b) Displacement of the DEA bottom as a function of time. (c) Displacement of the DEA bottom as a function of applied voltage at 25 °C and -12 °C, respectively. (d) Real photos of bending DEA movements at 25 °C (top) and -12 °C (bottom), corresponding to panel c under the applied voltage from 6800 to 8200 V at a constant interval of 200 V.

shown in Figure 3a, where the conductive polymer clusters are closely connected with one another forming consecutive electron transporting channels. When increasing strain is applied on the organogel, some of the clusters start to detach from others, inducing the resistivity change. The corresponding materials surface morphology is shown in Figure 3b. The resistance of organogel increased exponentially with the linearly increasing strain (Figure 3c, d), which corresponds well with the established relationship between tunneling resistivity and the square root of energy barrier height (Figure S3). From the viewpoint of quantum mechanics, the tunneling effect arises at excessive strain starting from 50%, which creates a barrier, allowing the electrons with the energy lower than the barrier height to have some probability of hopping. In addition, the conductive organogels contain a highly stretchable internal polymer matrix, whereas the external polyaniline layer remains fragile under severe strain. The mechanical mismatch of the two layers promotes the formation of disconnected microcracks, which further contribute to the high-strain sensitivity.

Figure 3d displays the strain-stress characteristics of organogel at a subzero temperature, where it observes the same exponential trend as the sample under room temperature but with a far smaller strain elongation at the break about 250%. The damping factor for the antifreezing property, in this case, is the polymer chains that become more rigid as the temperature approaches the glass transition value, macroscopically resulting in the lower elongation at break for the organogel.

High sensitivity of the organogels to strain makes the latter promising for sensor applications. As an example of the excellent sensory ability of organogel, Figure 3g depicts a signal obtained from the bending of a finger at different angles. It is obvious that an increase in the bending angle from 0° to 25° causes an increase in the resistance of the organogel by 50%. A further increase in the bending angle to 70° leads to a progressive increase in the signal by 15 times over the initial value, evidencing ultrahigh responsiveness (>1500%) of produced organogel compared to other reported fingerbending sensors (Figure S1). A repetitive bending at a fixed angle confirmed the strain sensing stability of the organogel (Figure 3h). Besides, the conductive organogel was afterward designed as a pulse sensor attached to a human neck (Figure 3e), demonstrating impressive regular responsiveness of an 8% change in resistance. Furthermore, keeping the sensor at the same position on the human neck enabled one to detect the human vocal cord vibration with a responsivity even higher than that of a pulse (Figure 3f).

Recently, instead conductors such as carbon grease, using hydrogels as electrodes contributes nearly no constraints to help with the deformation of the dielectric layer in dielectric elastomer actuator (DEA).³⁰ Although hydrogels are promising candidates as compliant conductors as they can be patterned and integrated into solid-state devices with excellent stretchability,³¹ the presence of water inside results freezing and unstable electrical behavior. In that regard, conductive organogels enable one to avoid these shortcomings at maintaining the advantages of hydrogels working as electrodes in DEAs.

To show the advantages of organogels in the bending sensors, a typical bending DEA was fabricated using conductive organogel as the positive electrode, carbon grease as the negative electrode, and a dielectric layer sandwiched by the two electrodes (Figure 4a). The bending performance of the DEA was evaluated at 25 and -12 °C (Figure 4c and 4d). For this, the distance between the bottom part of the actuator and its original position was defined as the displacement. According to Figure 4c, the displacement at room temperature increased rapidly from 8.5 to 15.7 mm with increasing applied voltage from 6800 to 8200 V, which took up to 46% of the total length of the actuator. For the same sample at a subzero temperature, where traditional hydrogel-based DEAs cannot function, this bending actuator still performed well with a 13.1

mm displacement at 8000 V, making up to 38.6% of the total length. The optical images of displacements at 25 and -12 °C under the same input voltages are given in Figure 4d. While there was no noticeable difference between the displacements at lower input voltages (6500-7000 V), a further increase in voltage led to more pronounced displacements at room temperature. This can be explained by the rigidity of polymer chains under low temperatures, which was consistent with resistance-strain data (Figure 3d). Finally, a relationship between the displacement and time in the on-off one-time voltage mode shows the responsivity of this bending actuator (Figure 4b). The displacement reaches its maximum within 5 s after the voltage is on and takes about 10 s to recover to the initial state.

In conclusion, an antifreezing PANi-polyacrylate organogel was fabricated through a typical abnormal swelling process in the polyacrylate matrix. Compared to previously reported conductive organohydrogels/organogels, the conductive organogel obtained in this study exhibited high stability both in the electrical properties and physical shape under extreme conditions and ultrahigh sheet resistance. The strain sensor based on this organogel was shown to achieve simultaneously high stretchability and elevated gauge factor, resulting in ultrahigh sensitivity when used for human motion detection. The conductive organogel is also promising as the electrode and elastomer (VHB) of the dielectric elastomer bending actuator with simplified structure, intended for operation under harsh conditions.

EXPERIMENTAL SECTION

Fabrication of PANi-Based Organogel Using Polymethyl Acrylate with DMF. First, precursor solution A was prepared by mixing methyl acrylate monomer (1.2 mL) with PEGDA (20 μ L) as the cross-linker and Darocur 1173 (15 μ L) as the photoinitiator. Then precursor solution B was obtained by mixing aniline (3.650 mL) with dimethylformamide (5 mL). After that, precursor solution C was produced by dissolving APS (3600 mg) into a mixture of water (45 mL) and HCl (2.8 mL). Finally, precursor B (0.8 mL) was carefully dissolved in precursor A, and the blend was injected into the designed mold for further exposure to UV photopolymerization for 90 s, resulting in a transparent gel with light yellow color. The surface of the fabricated gel quickly turned black after being immersed into precursor C for 2 h, successively transforming into a wet conductive organogel. To make sure that physically adsorbed polyaniline was removed from the surface, a complementary 2-h ultrasound treatment was conducted on the black gel. At last, the organogel was dried in air for 10 h prior to further tests.

Conductive hydrogels were fabricated as the control samples using the ionic conduction mechanism.

Fabrication of Dielectric Elastomer Bending Actuator. First, commercialized VHB (3MTM VHBTM Adhesive Transfer Tape F9473PC) was sliced with a laser into 7×60 mm sheets serving as dielectric elastomers. After that, the polyimide (PI) strips (0.5×7 mm) were adjusted onto one side of the VHB sheets to direct the actuation shape, so that their dimensions were $4 \times 20 \times 0.5$ mm. The strip-aligned VHB sides were afterward laminated with organogel to get the electrodes. Finally, a protective layer of VHB was applied onto organogel and another side of strip-aligned VHBs was coated with carbon grease to obtain a compliant electrode. The copper wires were used to connect electrodes to a high-voltage power supply.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsmaterialslett.1c00368.

Tunneling effect, supplemental SEM figures, and supplemental stress-strain test (PDF)

AUTHOR INFORMATION

Corresponding Authors

- Zhiyuan He Key Laboratory of Green Printing, Institute of Chemistry, Chinese Academy of Sciences, Beijing 100190, China; orcid.org/0000-0001-7942-8605; Email: hezy@ iccas.ac.cn
- Ximin He Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States; orcid.org/0000-0001-8845-4637; Email: ximinhe@ucla.edu

Authors

- Yucheng Zhang Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States
- **Yusen Zhao** Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States
- Zihang Peng Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States
- Bowen Yao Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States; School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China
- Yousif Alsaid Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States
- Mutian Hua Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States
- **Dong Wu** Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States
- Yu Qiu Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States; © orcid.org/0000-0002-2707-3993
- **Qibing Pei** Department of Materials Science and Engineering, University of California, Los Angeles, California 90095, United States; orcid.org/0000-0003-1669-1734
- Xinyuan Zhu School of Chemistry and Chemical Engineering, State Key Laboratory of Metal Matrix Composites, Shanghai Jiao Tong University, Shanghai 200240, China; orcid.org/0000-0002-2891-837X

Complete contact information is available at: https://pubs.acs.org/10.1021/acsmaterialslett.1c00368

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Y.Z., Y.A., M.H., D.W., and X.H. acknowledge NSF CAREER award 1724526, AFOSR awards FA9550-17-1-0311, FA9550-18-1-0449, and FA9550-20-1-0344, and ONR awards N000141712117 and N00014-18-1-2314. Z.H. acknowledges National Natural Science Foundation of China (21875261), Youth Innovation Promotion Association CAS (2018044).

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