

# Antifreezing ionotronic skin based on flexible, transparent, and tunable ionic conductive nanocellulose hydrogels

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## Research Article

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# Abstract

Ionic hydrogels with excellent flexibility and good conductivity have great potential in diverse electric devices. However, it remains challenging to improve the biocompatibility of ionic hydrogels. Here, natural and environment-friendly cellulose nanofiber hydrogels were prepared without adding any organic active materials. The cellulose hydrogel networks with free metal ions ( $\text{Li}^+/\text{Ca}^{2+}/\text{K}^+$ ) were obtained by soaking in ion aqueous solution of different concentrations in order to endow tunable conductivity, thus a new kind of transparent ionic hydrogels with both excellent sensing performance obtained by a simple, low-cost and harmless process. The free metal ions locked in the negatively charged nanocellulose network through electrostatic interaction provided adjustable conductivity and sensing performance. Hydrogels doped with  $4 \text{ mol L}^{-1}$  lithium ions exhibited the best sensing performance with the conductivity of  $4.36 \times 10^{-4} \text{ S cm}^{-1}$ , and the current response value was as high as 127%. It was worth noting that the strain-sensitive performance of calcium ions was generally excellent even at low temperatures ( $-30^\circ\text{C}$ ). The antifreezing of the hydrogel improved its service under extreme environment. This kind of hydrogel has great application prospects in artificial intelligence products, such as human healthy monitoring equipment and soft robotics at subzero temperature.

## Introduction

Retractable, wearable (Darabi et al. 2017), flexible strain sensors (Huang et al. 2018) are widely used in the field of electronic devices (Amjadi et al. 2016), such as health monitoring (Wan et al. 2017), human-computer interaction (Zhao et al. 2017). Capacitive sensor (Xu et al. 2020; Tao et al. 2017) and piezoresistive sensor (Kwon et al. 2016) present advantages of simple device construction and higher sensitivity (Song et al. 2020; Wang et al. 2014; Qiu et al. 2018; Lin et al. 2016). Sun and co-workers first proposed the concept of ionic skin and used polyacrylamide hydrogel as the ionic conductor, which could be stretched to about six times and the capacitance of the sensor changed as strain (Sun et al. 2019; Yan et al. 2014). Conductive hydrogels (Cao et al. 2020) are concerned as a promising material for ionic skin and bio-sensors due to their hydrophilicity. Flexible strain sensors were required to have good mechanical properties and high conductivity. Ding and co-workers described a novel type of transparent ionic gel with a conductivity of up to  $2.4 \text{ S m}^{-1}$  by locking a free ionic liquid into a charged poly (2-acrylamido-2-methyl-1-propanesulfonic acid) (PAMPS)-based double networks (Ding et al. 2017). Cai and co-workers designed a hydrogel with excellent mechanical properties, which can withstand strains of up to 1000%. It was a stretchable self-healing varistor strain sensor made up of single-walled carbon nanotube, borax and polyvinyl alcohol (Cai et al. 2017). It proved that the combination of matrix material and active conductive material could enhance the sensitivity and irritation response behavior of hydrogel (Bae et al. 2016; Hao et al. 2018). Liao and co-workers successfully developed a freeze-resistant ( $-40^\circ\text{C}$ ), self-healing and conductive nanocomposite hydrogel by the method of soaking MXene nanocomposite hydrogel in ethylene glycol solution to replace the water molecules (Liao et al. 2019). It illuminated that it was feasible to convert hydrogel to organic gel to enhance its frost resistance, inevitably decreasing its biocompatibility.

It is significant to design a low-cost conductive hydrogel with simple process, strong hydrophilicity, high strength and marvelous frost resistance. Flexible sensors usually consist of stretchable matrixes and conductive materials. Polymers or copolymers were commonly used to fabricate stretchable matrix materials, but they are not easy to degrade (Li et al. 2020). Biocompatible materials should not negatively affect the human body. Biomass materials (Chen et al. 2020; Wang et al. 2020) such as cellulose had the characteristics of degradability, good biocompatibility, low price and easy availability (Klemm et al. 2005; Klemm et al. 2011; Roh et al. 2015; Zhou et al. 2017; Yin et al. 2020). Nanocelluloses usually provided reinforcement in the materials of films, hydrogels, aerogels, 3D printing ink and foams. This kind of ecofriendly, lightweight material is suitable for structural, (opto) electronic, photonic, and medical applications (Yang et al. 2020). 2,2,6,6-tetramethylpiperidiny-1-oxyl (TEMPO) was used as the oxidant to catalyze oxidation wood pulp to obtain TEMPO-oxidized cellulose nanofibrils (TOCNs) with carboxyl groups on the surface which could be individually dispersed in water (Isogai et al. 2011; Isogai et al. 2018; Yang et al. 2018). TOCNs possessed high aspect ratio, high modulus, and satisfactory thermal stability (Xu et al. 2019, 2020; Zhan et al. 2019). TOCN hydrogel was regarded as an appropriate matrix material, which was flexible, stretchable and corrosion-resistant (Xie et al. 2020). The active materials employed to enhance the conductivity of flexible sensors commonly included ion conductors (Ding et al. 2017), carbon-based nanomaterials (Xu et al. 2020), metal-based nanomaterials (Son et al. 2018) and conductive polymers (Han et al. 2017). Carbon-based nanomaterials such as carbon nanotubes (CNTs) and graphene were widely reported. However, it has been a challenge for researchers to fabricate high purity and good dispersion carbon-based nanomaterials. The activating treatment of carbon-based nanomaterials was also quite complicated, which made CNTs suffer from large resistance. Metal-based nanomaterials with high properties such as silver nanowires tended to be expensive. Therefore, it is necessary to seek cheaper active materials that were easier to disperse. Morelle and co-workers conducted research on coordinating hard polyacrylamide-alginate double network hydrogel with calcium chloride aqueous solution. The obtained hydrogel could be cooled to  $-57^{\circ}\text{C}$  without freezing (Morelle et al. 2018). Doping metal ions with hydrogels was a simple and efficient method to obtain conductive hydrogels (Zhao et al. 2017; Pan et al. 2020; Wu et al. 2019). In addition, the doping of metal ions could lower the freezing point of the hydrogel, so that the hydrogel had antifreezing performance.

In our work, TOCN hydrogels were crosslinked under hydrochloric acid atmosphere. The three-dimensional network structure of TOCN hydrogels led to the high porosity and water content. TOCN hydrogels were immersed in different ionic aqueous solutions and then assembled into ionotronic skin (I-skin) sensor devices. LiCl,  $\text{CaCl}_2$  and KCl were used as active materials to enhance the conductivity of the hydrogels. The sensing performance and the conductivity of each hydrogel were studied and compared.

## Experimental

### Materials

Softwood bleached kraft pulp (SBKP) provided by Nippon Paper Industries in Japan was used to prepare TEMPO-oxidized cellulose nanofibrils. The TEMPO oxidant was purchased from Sigma Aldrich Corporation (Saint Louis, USA). NaClO was obtained from Aladdin (Shanghai, China). LiCl, CaCl<sub>2</sub>, KCl, HCl and other chemicals were analytical grade, bought from Sinopharm Chemical Reagent Co. Ltd (China) and operated strictly as received.

## Preparation of aqueous TOCN dispersion and ionic solution

TEMPO-oxidized cellulose (TOC) was prepared by the TEMPO/NaBr/NaClO system with NaClO content of 5.0 mmol g<sup>-1</sup>-cellulose in aqueous solution at pH 10 followed by addition of 1 wt% NaBH<sub>4</sub> to convert the small amounts of C6-aldehydes and C2/C3-ketones to be complete hydroxyl groups following the previously reported method (Shi et al. 2015; Takaichi et al. 2014). The obtained TOC was washed with deionized water until neutral. Then, TOC slurry aqueous solution was prepared with a mass fraction of 0.5 wt%. The TOC slurry solution was put into a high-pressure homogenizer to prepare a TOCN dispersion. Since the surface of TOC contained a large amount of carboxylate groups, it was easy to obtain a transparent and uniform TOCN dispersion under the action of high-pressure mechanical shearing.

LiCl was dissolved in water to prepare aqueous solution with LiCl concentration of 2, 4, 8, and 16 mol L<sup>-1</sup>. 4 mol L<sup>-1</sup> CaCl<sub>2</sub> and KCl aqueous solution were also obtained as above.

## Preparation of ionic conductive TOCN hydrogel I-skin

The beaker containing 10 ml 36% hydrochloric acid and the 24-well plate containing 48 g TOCN dispersion were sealed in the same sealed bag to prepare TOCN hydrogels. TOCN hydrogels were cross-linked under hydrochloric acid atmosphere for 48 h, followed by washing and preservation in the deionized water. These hydrogels were then immersed in LiCl, CaCl<sub>2</sub>, and KCl aqueous solutions with various concentrations, respectively, to endow TOCN hydrogels with ionic conductive properties. The hydrogels were immersed into the ion solutions for 48 h, and the ion solutions were refreshed every 6 h. The process and possible mechanism were shown in Fig. 1. The large amount of metal ions throughout the cellulose nanofibrils could be utilized to prepare conductive hydrogel I-skin.

The hydrogels had the properties of electrical conductivity and sensing property after being immersed in metal ions solutions. Tin foil was used as an electrode material respectively, and was attached to both ends of the hydrogel bulks when the voltage was applied. Each experiment was repeated three times to ensure the accuracy of the data. The hydrogels crosslinked with hydrochloric acid were named as H<sup>+</sup>-TOCN. The hydrogels immersed in metal ions were named as Li<sup>+</sup>-TOCN, Ca<sup>2+</sup>-TOCN, K<sup>+</sup>-TOCN respectively. The hydrogels obtained by immersion in lithium ions solutions with LiCl concentration of 2, 4, 8, and 16 mol L<sup>-1</sup> were named as 2Li<sup>+</sup>-TOCN, 4Li<sup>+</sup>-TOCN, 8Li<sup>+</sup>-TOCN, and 16Li<sup>+</sup>-TOCN, respectively. The hydrogel obtained by immersion in 4 mol L<sup>-1</sup> CaCl<sub>2</sub> solutions was named as 4Ca<sup>2+</sup>-TOCN, and immersion in 4 mol L<sup>-1</sup> KCl solution was named as 4K<sup>+</sup>-TOCN.

# Analysis

Scanning electron microscope (SEM) (Hitachi S-4800, Japan) with an accelerating voltage of 5 kV was used to observe the cross-sectional morphology of hydrogels. The hydrogels used for the SEM test were solvent-exchanged with ethanol and *t*-butanol, fractured to expose the cross section in liquid nitrogen and then vacuum freeze-dried. Fourier transform infrared (FTIR) spectra was analyzed by a FTIR spectrometer (Nicolet 6700, USA) in the wavenumber ranging from 4000 to 500  $\text{cm}^{-1}$ . The freeze-dried samples of unoxidized cellulose, TOCNs and  $\text{Ca}^{2+}$ -TOCN hydrogels were cut into powders, and then mixed with KBr for measurement. Four-point probe instrument (ST2258C) was utilized for the conductivity data of the 12×12 mm square samples with a thickness between 80–90  $\mu\text{m}$ . Five parallel samples were chosen to ensure the accuracy of the conductivity data with corresponding test parameters. The hydrogels with a height of 10 mm and a diameter of 10 mm were prepared for testing the mechanical properties by an electromechanical universal testing machine (MTS Exceed E44, China), following the standard of GB/T 1040:2006. The parameters were set by the initial grip distance of 10 mm and speed of 1  $\text{mm min}^{-1}$  while 5 specimens were selected for parallel experiments. Sensor performance was represented by the electrochemical workstation with type of CHI 660E (China) to measure the I-t curve in real time with an applied voltage of 2 V DC. When the metal wire was connected, tin foil was used as electrode material and the hydrogel was applied equal pressure to observe the current change.

## Results And Discussion

### Structures of ionic conductive TOCN hydrogels

The SEM images in Fig. 2(a) showed the cross-sectional morphologies of  $\text{Li}^{+}$ -TOCN, which were proved to exhibit the three-dimensional network structure. The interior of hydrogels presented a three-dimensional highly porous network structure formed by interconnected nanofibers. The pores were between several nanometers and tens of nanometers in size, and the overall three-dimensional network structure showed in Fig. 2(a) was relatively uniform. The nanofibers demonstrated a large surface area, which made it easier for metal ions to enter the cellulose network, thus providing conditions for improving the conductivity of the hydrogels. The excellent internal network structure benefited to the easier shuttle of conductive ions inside the hydrogels, thus giving the hydrogel excellent sensing performance.

The unoxidized cellulose, TOCNs,  $\text{H}^{+}$ -TOCN,  $\text{Ca}^{2+}$ -TOCN were analyzed by infrared spectroscopy. The FTIR spectra were shown in Fig. 2(b). It could be seen from the Fig. 2(b) that the four samples had relatively obvious absorption bands near 3400  $\text{cm}^{-1}$ , which were attributed to the stretching vibration absorption band of hydroxyl group on cellulose. The strong band corresponding to the hydrogen-bonded hydroxyl of unoxidized cellulose was observed at 3356  $\text{cm}^{-1}$ . The bands at 2890  $\text{cm}^{-1}$  of each sample corresponded to the stretching vibration of the C-H bond on cellulose; the bands at 1020  $\text{cm}^{-1}$  represented the stretching vibration of C-O on the backbone of cellulose macromolecules (Yue et al. 2021). Compared with the unoxidized cellulose, the spectra of TOCNs and  $\text{Ca}^{2+}$ -TOCN exhibited asymmetric -OCO-

stretching bands at 1607 and 1604  $\text{cm}^{-1}$ , respectively. In the spectra of unoxidized cellulose and  $\text{H}^+$ -TOCN, the bands of 1645  $\text{cm}^{-1}$  and 1636  $\text{cm}^{-1}$  were attributed to the absorption of the water which was not completely dried in the nanocellulose (Yue et al. 2019; Zheng et al. 2020). In addition,  $\text{H}^+$ -TOCN exhibited a new characteristic absorption band at 1724  $\text{cm}^{-1}$  which was attributed to the vibration absorption band of -COOH. Under the circumstances of hydrochloric acid cross-linking, part of the free sodium ions in the nanocellulose network were replaced by the hydrogen ions in hydrochloric acid, facilitating the  $\text{H}^+$  in the solution and the  $\text{COO}^-$  on the cellulose macromolecular skeleton combined to form a carboxylic acid. The band at 1724  $\text{cm}^{-1}$  disappeared after the replacement of  $\text{Ca}^{2+}$  ion solution, indicating that the structure of carboxylic acid -COOH was broken and the hydrogen ion on the carboxylic acid was replaced by part of the calcium ion. Calcium ions and carboxylate groups were re-complexed and coordinated, which enabled the network structure of hydrogels to be more stable while improving its mechanical properties (Fig. S1) and electrical conductivity.

**Figure 2** (a) Cross-sectional SEM image of  $4\text{Li}^+$ -TOCN, (b) FTIR spectra of  $\text{Ca}^{2+}$ -TOCN,  $\text{H}^+$ -TOCN, TOCN dispersion, and unoxidized cellulose

## Mechanical properties of ionic conductive TOCN hydrogels

The compressive stress-strain curves of the TOCN hydrogels which were immersed in various ions aqueous solutions were shown in Fig. S1.  $\text{Li}^+$ ,  $\text{Ca}^{2+}$  and  $\text{K}^+$  were introduced to prepare the metal ion-immersed conductive hydrogels. As shown in Fig. S1(a) and Table 1, there was no obvious difference among  $\text{H}^+$ -TOCN,  $4\text{K}^+$ -TOCN,  $4\text{Ca}^{2+}$ -TOCN, and  $4\text{Li}^+$ -TOCN hydrogels. The compressive strength of  $4\text{Ca}^{2+}$ -TOCN was 54 kPa, and the stain was 67%. Compressive stress-strain curves of  $\text{Li}^+$ -TOCN hydrogels with different  $\text{Li}^+$  concentrations were shown in Fig. S1(b). The Fig. S1(b) indicated that the mechanical properties of the  $\text{Li}^+$ -TOCN hydrogels did not decrease compared with the  $\text{H}^+$ -TOCN hydrogel blank sample. On the contrary, the mechanical properties of the hydrogels were improved to a certain degree after the replacement of  $\text{Li}^+$  solutions.  $8\text{Li}^+$ -TOCN exhibited best among the samples which presented outstanding compression strength of 72.4 kPa. Lithium ions can enhance the interaction of water molecules in hydrogels (Ge et al. 2020). In addition, the compressive strain of the nanocellulose conductive hydrogels with ultrahigh water content and high porosity prepared by this method was about 60%. Its satisfactory mechanical properties profoundly broadened the application prospects of the conductive hydrogel I-skin.

## Sensing properties of ionic conductive TOCN hydrogels

Figure 3 presented the schematic design of ionic hydrogels. The cellulose nanofibers network possesses negative charges due to the carboxyl groups on the nanofibers. Cellulose nanofiber network also has strong hydrogen bonds, which provides the basis for the excellent mechanical properties of hydrogels. After the hydrogels were immersed in metal ions solutions, metal ions were locked in hydrogel network, and electrostatic interaction formed between carboxyl groups in the TOCN networks and metal cations. Meanwhile, part of the hydrogen bonds between the cellulose molecules were broken by the doping ions.

The doping of metal ions improved the electrical conductivity of the hydrogels. As shown in Fig. 3(c), the metal cations and anions in TOCN network could transport freely under applied voltage. Under the condition of external force, the migration ability of various cations was the primary reason for the current variation of the assembled I-skin sensor.

The  $I-t$  curves of the TOCN hydrogels immersed in  $4 \text{ mol L}^{-1} \text{ Ca}^{2+}$ ,  $\text{K}^+$ , and  $\text{Li}^+$  solutions were shown in Fig. 4, which reflected the sensitivity of each sample. The larger fluctuation range of the output signal of the sample was corresponded to more excellent sensing performance under the equal slight pressure. The hydrogels became deformed when pressed, and the resistance changed accordingly. The hydrogels were pressed with the equal force repeatedly to obtain the corresponding current curves with time after connecting the power. The strain-sensitive performance of the hydrogels was attributed to the fact that electronically charged ions could penetrate in the network. Compressive stress changed the electrical resistance of the hydrogel. The sensing performance of  $\text{H}^+$ -TOCN hydrogels was lower than the  $\text{Li}^+/\text{Ca}^{2+}/\text{K}^+$ -immersed hydrogels. Under the condition of exerting the same stress, the current fluctuation range of  $\text{H}^+$ -TOCN was  $3.7\text{--}4.5 \mu\text{A}$  in Fig. S1, the current fluctuation range of  $4\text{Li}^+$ -TOCN was approximately  $5.3\text{--}6.6 \mu\text{A}$  in Fig. 4(a), current of  $4\text{Ca}^{2+}$ -TOCN fluctuated in the range of  $4.9\text{--}5.5 \mu\text{A}$  in Fig. 4(b) and  $4\text{K}^+$ -TOCN fluctuated within  $4.2\text{--}4.7 \mu\text{A}$  in Fig. 4(c). The  $4\text{Li}^+$ -TOCN hydrogel exhibited the widest range of current response according to Fig. 4(d), which was as high as 23% and about twice as much as those of  $4\text{K}^+$ -TOCN and  $4\text{Ca}^{2+}$ -TOCN. As shown in Fig. 4(e), the conductivity of  $4\text{Li}^+$ -TOCN was about  $4.36 \times 10^{-4} \text{ S cm}^{-1}$ , while  $4\text{Ca}^{2+}$ -TOCN of  $1.61 \times 10^{-4} \text{ S cm}^{-1}$  and  $4\text{K}^+$ -TOCN of  $1.29 \times 10^{-4} \text{ S cm}^{-1}$  were lower. Comparing the radii of these three ions ( $\text{Li}^+ < \text{Ca}^{2+} < \text{K}^+$ ), which demonstrated that the smaller the radius, the better for ions to penetrate the holes in the three-dimensional network structure of nanocellulose hydrogels under homogeneous force. These identically figured out that diverse conductive ions had conspicuous effect on the sensing performance. Therefore, the sensing performance of  $\text{Li}^+$ -TOCN was recognized as the optimal.

**Figure 4** Sensing properties of nanocellulose hydrogels with different replacing methods.  $I-t$  curves of (a)  $4\text{Li}^+$ -TOCN. (b)  $4\text{Ca}^{2+}$ -TOCN, and (c)  $4\text{K}^+$ -TOCN. (d)  $\Delta I/I_0-t$  curves of  $4\text{Li}^+$ -TOCN,  $4\text{Ca}^{2+}$ -TOCN, and  $4\text{K}^+$ -TOCN. (e) The conductivity of  $4\text{Li}^+$ -TOCN,  $4\text{Ca}^{2+}$ -TOCN,  $4\text{K}^+$ - and TOCN

It was significant to explore the influence of lithium ions with different concentrations on the sensing performance of the hydrogels, because  $\text{Li}^+$ -TOCN performed the best among these three ions. The sensor performance of  $\text{Li}^+$ -immersed hydrogels with the solution concentration of 2, 4, 8, and  $16 \text{ mol L}^{-1}$  were shown in Fig. 5 and Fig. 6.  $\text{Li}^+$ -TOCN hydrogels with different concentrations showed regularity when applied the equal pressure, and the higher concentrations of lithium ions could make the better initial current value and conductivity. The current fluctuation range of  $2\text{Li}^+$ -TOCN,  $4\text{Li}^+$ -TOCN,  $8\text{Li}^+$ -TOCN, and  $16\text{Li}^+$ -TOCN were  $4.2\text{--}5.2 \mu\text{A}$ ,  $5.3\text{--}6.6 \mu\text{A}$ ,  $5.8\text{--}7.1 \mu\text{A}$ , and  $7.1\text{--}8.3 \mu\text{A}$  respectively. This phenomenon confirmed that increasing the concentration of the immersed solution was capable of augmenting the charged ions inside the hydrogels, impelling it easier for the ions to form a current under the action of

voltage. Immersing the hydrogels in the ionic solutions to enhance the conductivity, the stable localization of metal ions was promoted through electrostatic action based on the negative charge of TOCN hydrogel network. Simultaneously, metal ions shuttled and transported in the hydrogel network freely under an applied voltage, leading to the hydrogels a higher ion conductivity and excellent responsiveness.

**Figure 5** Sensing properties of TOCN hydrogels immersed by different concentrations LiCl aqueous solutions. I-t curves of (a) 2Li<sup>+</sup>-TOCN, (b) 4Li<sup>+</sup>-TOCN, (c) 8Li<sup>+</sup>-TOCN, and (d) 16Li<sup>+</sup>-TOCN

Fig. 6(a) shows the responsiveness of Li<sup>+</sup>-TOCN. The current fluctuation range value would not continuously increase as different ion concentrations under the same pressure but reached the maximum rate of current change ( $\Delta I/I_0 = 23.8\%$ ) at 4Li<sup>+</sup>-TOCN, which illustrated that the effect of increasing ion concentrations on the sensing performance of hydrogels was limited. The conductivity of Li<sup>+</sup>-TOCN behaved better when the concentration of the ions increased, and 16Li<sup>+</sup>-TOCN met the highest conductivity of 5.21 S cm<sup>-1</sup> in Fig. 6(c). Furthermore, different pressure was applied to 4Li<sup>+</sup>-TOCN for the purpose of demonstrating the maximum current change caused by the ion-immersed hydrogels. Figure 6(b) presented the fantastic current change of 127% under a larger force. The rate of current change fluctuated between 5%-127%. This suggested that hydrogels were highly sensitive to the changes in pressure.

**Figure 6** Sensing properties of Li<sup>+</sup>-TOCN. (a)  $\Delta I/I_0$ -t curves of 2Li<sup>+</sup>-TOCN, 4Li<sup>+</sup>-TOCN, 8Li<sup>+</sup>-TOCN, and 16Li<sup>+</sup>-TOCN. (b)  $\Delta I/I_0$ -t curves of 4Li<sup>+</sup>-TOCN under different pressure. (c) The conductivity of 2Li<sup>+</sup>-TOCN, 4Li<sup>+</sup>-TOCN, 8Li<sup>+</sup>-TOCN, and 16Li<sup>+</sup>-TOCN

## Antifreezing performance of ionic conductive TOCN hydrogels

The Ca<sup>2+</sup>-TOCN hydrogel was selected for the freezing-resistance experiment due to its satisfactory sensing performance and human-friendly. Figure 7(a) indicated that there was no significant decrease at low temperature, and the current fluctuation range of 4Ca<sup>2+</sup>-TOCN hydrogels at -30°C was similar 4.9–5.4  $\mu$ A. Figure 7(b) revealed that the current fluctuation range of 4Ca<sup>2+</sup>-TOCN hydrogels at 25°C were 4.9–5.5  $\mu$ A.  $\Delta I/I_0$ -t curves of 4Ca<sup>2+</sup>-TOCN hydrogels in Fig. 7(b) behaved similarly at different temperature, which demonstrated the antifreezing performance of 4Ca<sup>2+</sup>-TOCN hydrogels. The high conductivity at low temperatures might due to the fact that the salt solutions successfully displaced the water inside the hydrogels, and the addition of salt lowered the hydrogel's freezing point. Due to the presence of metal ions, the hydrogels possessed considerable frost resistance. The mechanical property had no obvious change at -30°C as shown in Fig. 7(c), demonstrating that the 4Ca<sup>2+</sup>-TOCN hydrogels would not freeze at -30°C. The conductivity hydrogels were capable of detecting body signals such as the bending of fingers in Fig. 7(d), and the detected current changes increased with the increase of finger bending angle. Figure 7(e) displayed a picture of a transparent and intact 4Ca<sup>2+</sup>-TOCN hydrogel, which lighted a small

LED under applied voltage at 25°C and -30°C. Compared with the 4Ca<sup>2+</sup>-TOCN at room temperature, the morphology of the hydrogels at -30°C was almost the same. Figure 7(e) showed the electrical conductivity of the 4Ca<sup>2+</sup>-TOCN at -30°C almost same as the 4Ca<sup>2+</sup>-TOCN at 25°C, and Fig. 7(f) was the schematic diagram of lighting LEDs. These results confirmed that the hydrogels immersed in calcium chloride solution could maintain equal sensing performance, electrical conductivity and mechanical properties at -30°C. The prominent performance immensely can broaden the application range of this ion-conductivity hydrogels, confirming that it could be utilized in low temperature environments.

**Figure 7** Low temperature resistance of 4Ca<sup>2+</sup>-TOCN. (a) I-t curves of 4Ca<sup>2+</sup>-TOCN at -30°C. (b)  $\Delta I/I_0$ -t curves of 4Ca<sup>2+</sup>-TOCN at 25°C and -30°C. (c) Compressive stress-strain curves of 4Ca<sup>2+</sup>-TOCN at 25°C and -30°C. (d)  $\Delta I/I_0$ -t curves of 4Ca<sup>2+</sup>-TOCN with the finger bending. (e) LEDs were lighted under a series circuit of the DC power supply. (f) Schematic diagram of lighting LEDs

## Conclusions

The convenient and low-cost method of adding metal ions to the TOCN hydrogels to obtain the antifreezing, high-conductivity, and transparent piezoresistive I-skin was employed in this work. The SEM images indicated that the nanocellulose hydrogels still maintained a three-dimensional network structure with high porosity after immersion. The hydrogels doped with metal ions exhibited better strength and toughness. The mechanical properties of ion-immersed TOCN hydrogels did not decrease compared with H<sup>+</sup>-TOCN hydrogels. Under the same concentration of the Li<sup>+</sup>/Ca<sup>2+</sup>/K<sup>+</sup>-immersed hydrogels, the conductivity of Li<sup>+</sup> was the best, followed by Ca<sup>2+</sup>. As the Li<sup>+</sup> concentration reached 16 mol L<sup>-1</sup>, the conductivity was up to  $5.21 \times 10^{-4} \text{ S cm}^{-1}$ . The current response changes of 4Li<sup>+</sup>-TOCN, 4Ca<sup>2+</sup>-TOCN, and 4K<sup>+</sup>-TOCN were 23.7%, 12.5%, and 12% respectively under equal pressure. Increasing the concentration of the ions could enhance the sensing performance to a certain extent, and 4Li<sup>+</sup>-TOCN hydrogels was optimal. The sensitivity test demonstrated that 4Li<sup>+</sup>-TOCN hydrogels presented the considerable responsiveness of 127%. The low-temperature tests indeed successfully proved that the calcium ion-immersed hydrogels still maintained high conductivity, acceptable mechanical properties and sensing performance at -30°C, which provided possibilities for low-temperature applications in wearable electronics, artificial intelligence, and medical health.

## Declarations

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## Compliance with Ethical Standards

**Conflict of Interest:** The authors declare that they have no conflict of interest.

**Human and animal rights:** The study was approved by the Ethics Committee of Wuhan University of Technology. All procedures performed in studies involving human were in accordance with the ethical standards of the institution or practice at which the studies were conducted.

**Informed consent:** Informed consent was obtained from all individual participants included in the study.

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