3D Printed Mechanical Robust, Anti-swellable Cellulose derived Liquid-free Ionic Conductive Elastomer for Multifunctional Underwater Electronic Skin

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Abstract

Ionic gel-based wearable electronic devices with robust sensing performance have gained extensive attention. However, the development of mechanical robust, multifunctional, and water resistance ionic gel-based wearable sensors still is a challenge because of their intrinsic structure weakness such as swelling-induced function degradation in a water environment. Herein, we first report the preparation of 3D printed cellulose derived ionic conductive elastomers (ICEs) with high mechanical toughness, multifunctional, and water/organic solvent resistance through one-step photo-polymerization of polymerizable deep eutectic solvents. The well-defined structural design combining multiple hydrogen bonds with strong coordination bonds allows the ICE to be stabilized in aquatic environments. The introduction of polyaniline modified carboxylate cellulose nanocrystals (C-CNC@PANI) not only yields a high conductivity (58.7 mS/m) but also contributes to constructing dense networks to achieve extremely high mechanical strength (4.4 MPa), toughness (13.33 MJ*m⁻³), elasticity and improved anti-swelling performance. Given these features, the ICE-based multifunctional sensor is used for real-time detecting human motions, respiration, and body temperature. More importantly, the ICE-based sensor shows reliable underwater mechanosensing applications for accurately monitoring human movements in aqueous environments. This work provides a promising strategy for designing the new generation of strong, tough, multifunctional, and water-resistant wearable electronic devices that required multi-scene applications.

Summary

3D printed Cellulose-derived ionic conductive elastomers with well-defined structural design combining multiple hydrogen bonds with strong coordination bonds are fabricated by in-situ radical polymerization of PDES/C-CNC@PANI mixture. The ionic conductive elastomers with the features of high conductivity, mechanical toughness, elasticity, and water resistance showed promising practical applications in multifunctional sensors for human health monitoring and underwater mechanosensing.

1. Introduction

Recently, the rapid development of internet of things and artificial intelligence has greatly promoted the research of intelligent wearable sensing devices to a new level[1, 2]. Various wearable sensing devices based on hydrogel, ionic gel, composite graphene/carbon nanotube fiber, etc. with high flexibility, conductivity, and sensing sensitivity have been reported and applied in real-time health monitoring, human motion detection and electronic skin[3–5]. Ionic gel with the characteristics of high ionic conductivity, electrochemistry stability, flexibility and mechanical toughness has been widely applied to fabricate the wearable sensor[6–8]. Importantly, the ionic gel could avoid the risk of sudden failure of the sensing functionality caused by the water evaporation or freezing that often occurs in the hydrogel-based wearable sensors, which allowed the ionic gel to long-time stable work in dry/cold environments[9, 10].
Deep eutectic solvents (DESs) as a new type of green, non-volatile, and low-cost ionic liquid have attracted extensive attention as precursors for the fabrication of next-generation ionic gel-based wearable sensor[11–13]. Recently, researchers developed polymerizable deep eutectic solvents (PDES) by introducing the acrylic or methacrylic monomer into the DES system[14–16]. Up to now, the pioneers have made great efforts to fabricate various PDES-based ionic gels with excellent mechanical toughness, elasticity, and wide working temperature window for promising applications in wearable sensors[17–21]. However, the working conditions of the sensor inevitably involve sweating, humidity, and underwater environments in practical application. The inherent structural features of hydrogen bond crosslinking and rich hydrophilic groups made the PDES-based ionic gel easily undergo swelling at hydrated environment, thus leading to unwanted deformation, structural failure and functional deterioration[22, 23]. Therefore, the development of PDES-based ionic gel with the well-define chemical structure to avoid unwanted swelling deformation underwater environment was very crucial.

To date, the researchers have developed several strategies (such as strong coordination interactions, hydrophobic association, high crosslinking density, etc.) for fabricating anti-swelling conductive gels used as underwater wearable sensors[24–27]. For instance, Qin et al. developed an anti-swelling ionogel based on polymerization-induced phase separation and used as a wearable sensor to detect movements in a wet environment[28]. Lv et al. designed an anti-swelling ionic conductive hydrogel based on the electrostatic repulsion for underwater strain sensors.[29] And sun et al. fabricated a bio-inspired, ultra-tough, anti-swelling conductive hydrogel strain sensor by the combination of inter/intra-molecular hydrogen bonding and strong ionic coordination interactions[30]. Despite the abovementioned gels possessed improved anti-swelling and underwater sensing performance, the mechanical strength of most of these gels hardly exceeded 1 MPa. These gels, mainly based on the hydrogels, were only sensitive to strain changes, and also showed poor environmental stability under high-temperature conditions even at room temperature due to the tendency of water evaporation, which limited their further applications in multifunctional sensing, such as humidity and temperature monitoring[31, 32]. Therefore, the development of PDES-based ionic gels integrating with excellent mechanical toughness, conductivity, anti-swelling and multifunctional sensing properties is extremely desirable but remained greatly challenging.

Cellulose, the most abundant biopolymer, possessed strong intramolecular and intermolecular hydrogen bonds formed by abundant polar hydroxyl groups, which made cellulose hardly swollen in water[33, 34]. Cellulose nanocrystals (CNCs), as a special form of cellulose, with the advantages of high mechanical strength, nano-scale, and high surface charge could not only enhance the mechanical strength of the gels but also promote the ion movement[17, 35]. More inspiringly, CNCs were often used as a biotemplate for the in-situ polymerization of the aniline or pyrrole to further enhance the conductivity of the gels[36, 37]. Thus, we hypothesize that DESs as green solvents could be used to disperse the polyaniline-modified carboxylate cellulose nanocrystals (C-CNC@PANI), and the obtained PDES/C-CNC@PANI mixture could be in-situ polymerized to fabricate the mechanical robust, anti-swellable cellulose-derived liquid-free ICEs for multifunctional sensing.
Herein, a cellulose derived PDES-based ionic conductive elastomer (ICE) named as PDES/C-CNC@PANI ICE simultaneously with mechanical toughness, high ionic conductivity, 3D printability, water resistance and multifunctional sensing performance was first fabricated by combination of multiple hydrogen bonds and strong coordination interactions. The PDES/C-CNC@PANI ICE was composed of choline chloride (ChCl), acrylic acid (AA), AlCl$_3$, and C-CNC@PANI. The PDES/C-CNC@PANI ionic conductor was featured with dense hydrogen bonding network formed between the ChCl, PAA, and C-CNC@PANI and strong coordination interactions of AlCl$_3$ and AA, and demonstrated excellent mechanical toughness, elasticity, and anti-swelling performance at water and organic solvent environments. C-CNC@PANI was obtained from in-situ polymerization of aniline using carboxylate cellulose nanocrystals (C-CNC) as a biotemplate. The introduction of C-CNC@PANI yielded a high conductivity and further enhanced the mechanical properties. Additionally, the ICEs possessed wide working temperature windows (-20 °C to 60 °C). These features ensured the long-term stability of the ICEs in wearable sensors for detecting various human motions. Moreover, the ICEs showed sensitive and stable responses to temperature and humidity changes. Particularly, the ICEs with excellent anti-swelling capability maintained satisfactory sensing performance at underwater environments. This work paved a new strategy for the fabrication of ultra-strong, anti-swelling and multi-functional PDES-based ionic conductors for next-generation flexible and wearable devices.

2. Experimental Section/Methods

2.1 Materials

Choline chloride (ChCl), AlCl$_3$, diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (photo-initiator TPO), aniline, ammonium persulfate, and p-Toluenesulfonic acid were purchased from Macklin Biochemical Co., Ltd and used as received. Acrylic acid (AA) was purchased from Sinopharm Chemical Reagent Co., Ltd and used as received. Carboxylate cellulose nanocrystals (C-CNC, carboxyl content: 1 mmol/g) was purchased from Qihong Technology Co., Ltd and used as received, and the C-CNC@PANI was synthesized according to previous reports\[32, 36\], the content of PANI in C-CNCs@PANI was calculated to be 27.3 wt% according to the results of elemental analysis, and the synthesis process was provided in supporting information.

2.2 Synthesis of photosensitive PDES/C-CNC@PANI mixture

The ICE ChCl/PAA/C-CNC@PANI$_{1\%}$ was used as an example, and the fabrication process was as follows. Briefly, a mixture of ChCl 2 g (0.014 mol) and C-CNC@PANI (1wt% to AA) was added into a round-bottom and heated at 120 °C for 1 h to remove the water. Then, the AA 2.02 g (0.028 mol) and AlCl$_3$ 0.202 g (10 wt% to AA) were added to the mixture and continued stirring for 2 h at 95 °C. Following the photo-initiator TPO 0.0808 g (4 wt% to AA) was added to the PDES mixture and stirred for 10 min. After that, the
photosensitive PDES/C-CNC@PANI mixture was successfully prepared. The PDES/C-CNC@PANI mixtures with different C-CNC@PANI contents were prepared in a similar procedure.

2.3 Fabrication of PDES/C-CNC@PANI ICEs

To fabricate the PDES/C-CNC@PANI ICE, the photosensitive PDES/C-CNC@PANI mixture was poured into a PTFE mold. And then the mixture was cured under the irradiation of UV light for 20 min at 25 °C and 50% relative humidity.

2.4 Fabrication of 3D printed PDES/C-CNC@PANI ICEs

A commercial 3D printer (CREALITY, LD-002, China) was utilized to print the ICE through UV-induced free radical polymerization of photosensitive PDES/C-CNC@PANI mixture. Then, the printed ICE was washed with ethanol to remove unreacted monomer and subjected to post-curing in a UV oven (365 nm) for 1 min.

2.5 Characterization of materials

Fourier transform infrared spectroscopy (FT-IR) was recorded on Thermo Scientific Nicolet iS5 spectrometer apparatus. X-ray photoelectron scattering (XPS) spectroscopy analysis was carried out on an AXIS Ultra DLD X-ray photoelectron spectrometer. The microscopic morphology and element distribution were characterized by scanning electron microscope (Regulus 8100, HITACHI, Japan) and transmission electron microscope (JEM-1400, JEOL). The conductivity was measured by Electrochemical impedance spectroscopy (EIS) using an electrochemical working station (CHI760E, Shanghai Chenhua). The rheological properties of composite hydrogel were characterized using an RS6000 rheometer (HAAKE, Germany). Stress sweep tests were performed at a frequency of 1 Hz and in the shear stress range of 0.01–100 Pa. The mechanical properties tests were performed on a UTM6503 universal testing machine at a speed of 50 mm/min. DSC was carried out on a DSC214 (NETZSCH, Germany) at a rate of 20 K/min. TGA was carried out on a TG 209 F1 Libra (NETZSCH, Germany). The resistance of the ICE was recorded by Keysight 34461A (Keysight Technologies, USA). The IR images were recorded by Hikvision H13 IR camera.

All experiments performed in this work involving human volunteers were carried out in full compliance with all local laws and institutional ethical guidelines. The wearable sensors were attached on human subjects’ skin with their approval.

3. Results and discussion

3.1 Preparation and structure of the PDES/C-CNC@PANI ICEs

The ionic conductive elastomers with multiple hydrogen bonds and strong coordinate bonds were fabricated via one-step polymerization of the PDES/C-CNC@PANI mixture. Importantly, the PDES/C-
CNC@PANI mixture with highly photosensitive allowed it to fabricate various 3D objects with complex shapes by digital projection lithography (DLP) 3D printing technology. Figure 1 shows the schematic illustration of the 3D printing process and the chemical structure of the ICEs. Patterned UV light that emitted by a laser projector initiated the localized photopolymerization of the PDES/C-CNC@PANI mixture into a patterned solid layer with a thickness of 50 µm. As the printing platform moved upward, the predesigned 3D objects were constructed layer by layer (Fig. 1a). In the PDES/C-CNC@PANI mixture, AA was used as a monomer, the TPO as a photoinitiator, and the ChCl as conductive ionic salt could form a stable conductive network with PAA and C-CNC@PANI through hydrogen bonding interaction, which could avoid the leakage risk of traditional ionic liquids and endow the ICEs with intrinsic conductivity. The ICEs showed excellent 3D printability, which could be printed to various 2D or 3D shapes, such as 2D school badge and circuit, and 3D chess pieces, which allowed to preapred the wearable sensor devices with complex shapes. All the details of the 3D-printed objects could be clearly observed, indicating the high printing resolution. The 3D printed specimen possessed excellent conductivity, when the ICE connected in series to a circuit with a LED and battery, the LED bulb was successfully lit (Fig. 1b).

Different from previously reported PDES ionic gels, the unique design strategy of the introduction of the C-CNC@PANI and Al\(^{3+}\) in the PDES system could simultaneously construct the well-defined dense multiple hydrogen bonds and strong coordination bonds, which endowed the ICEs with excellent mechanical properties and anti-swelling performance. To demonstrate the construction of the strong coordination bonds, the ICE was soaked in a solution with a pH of 1.0, and the ICE was dissolved due to the strong acid conditions disrupting the strong coordination bonds. In contrast, the ICE soaked in deionized water still maintained its original shape (Figure S5). Meanwhile, the C-CNC@PANI as conductive fillers could further improve the conductivity of the ICE about 9.2 times as well as enhance the mechanical toughness about 1.4 times of the PDES-based ionic gel ChCl/PAA/C-CNC, and the ICE could lift a burden of about 3300 times its weight without any obvious defects (Fig. 1b and Figure S7). This novel ICE simultaneously with excellent mechanical toughness, conductivity and water/organic solvent resistance performance had promising applications in more harsh environments.

The construction of the hydrogen bonds and coordination bonds was demonstrated by temperature-dependent FT-IR and XPS. As shown in Fig. 2a, the region 1750 – 1625 cm\(^{-1}\) was attributed to the stretching vibration of C = O of ICEs. It should be noted that the bands at 1729 cm\(^{-1}\) showed a blue-shift upon heating, and the peak intensity of the hydrogen-bonded C = O groups at 1650 cm\(^{-1}\) sharply decreased, which was associated with that the breakage of hydrogen bonds of related groups generated “free” groups upon heating. This result demonstrated the formation of the hydrogen bonds. The O 1s and Al 2p XPS spectra of ChCl/PAA/C-CNC@PANI\(_{1\%}\) were shown in Fig. 2b,c. The high-resolution O 1s spectrum of the control sample without adding AlCl\(_3\) could be divided into three peaks of C-O, -O-C = O, and -OH appearing at 530.66 eV, 532.00 eV, 532.52 eV, respectively. Compared with the control sample without adding AlCl\(_3\), the C-O, O = C-O, and -OH peaks of ChCl/PAA/C-CNC@PANI\(_{1\%}\) shifted to higher binding energy 531.16, 532.21 and 532.77 eV. And the peak localized at around 74.57 eV correspond to the Al-OH state, which demonstrated the formation of coordination bonds.
The SEM image in Fig. 2d indicated the uniform and smooth surface morphology of the ICE. The energy-dispersive Xray spectrometry (EDS) mapping in Fig. 2e-g revealed the even distribution of Cl (ChCl), Al and S (C-CNC@PANI) among the ICE. The uniform distributions of ChCl and C-CNC@PANI contributed to enhancing the conductivity of the ICEs. As shown in Fig. 2h, the conductivity of the ICEs was gradually improved with the increase of C-CNC@PANI content, and the conductivity of the ICE ChCl/PAA/C-CNC@PANI\textsubscript{1\%} reached 58.7 mS/m, which was higher than that of most previously reported PDES-based ICEs (the details see Figure S8\cite{16, 20, 38–41}). In addition, another control sample ChCl/PAA/PANI\textsubscript{1\%} was also prepared to investigate the important role of the C-CNC in the conductivity of the ICEs. As shown in Figure S9, the conductivity of the ChCl/PAA/PANI\textsubscript{1\%} only was 13.23 mS/m, which was much lower than that of the ChCl/PAA/C-CNC@PANI\textsubscript{1\%}. The reason for this result was that the C-CNC with carboxylic acid group was beneficial to act as a biotemplate for the in-situ polymerization of aniline and could avoid the aggregation of PANI which significantly improved the conductivity of the ICEs.

The viscoelastic performance of the ICEs was evaluated by a rheometer under stress sweep mode. As shown in Fig. 2i, the storage modulus (G') of ChCl/PAA/C-CNC@PANI\textsubscript{1\%} was higher than the loss modulus (G'\textsuperscript{\prime}). Particularly, the G' and G'\textsuperscript{\prime} remained constant as the stress increased, indicating the solid-like behavior of the ICE. And the storage modulus (G') was gradually improved with the increase of C-CNC@PANI content (Figure S10), suggesting an improvement in the elastic property. Furthermore, the thermal properties of the ICEs were evaluated by DSC and TGA. As shown in Figure S11, the glass transition temperature (T\textsubscript{g}) of the ICEs was decreased from 14.6 °C to 5.3 °C with the increase of the C-CNC@PANI content, and the low T\textsubscript{g} suggested their potential applications in cold environments. Figure 2j shows the TGA curves of the ICE ChCl/PAA/C-CNC@PANI\textsubscript{1\%}. The temperature at 5% weight loss and the temperature at maximum degradation rate were 211°C and 264°C, indicating of the satisfactory thermal stability of the ICE.

3.2 Mechanical properties of the ICEs

The outstanding mechanical properties are critical for the ICEs in practical application. Figure 3a showed that the ICEs could be easily stretched, twisted and crimped, indicating the excellent flexibility and deformability of the ICEs. The mechanical properties of the dumbbell-shaped ICEs with different C-CNC@PANI contents were investigated by monotonic tensile tests and cycle tensile tests. As shown in Fig. 3b, the C-CNC@PANI showed a significant enhancement effect on mechanical properties due to the high crystallinity and rigidity of C-CNC, and the mechanical strength of the ICE ChCl/PAA/C-CNC@PANI\textsubscript{1\%} was measured to be as high as 4.4 MPa. Meanwhile, the ICE with low C-CNC@PANI content showed excellent stretchability, and the elongation at break of ChCl/PAA/C-CNC@PANI\textsubscript{0.5\%} was high up to 1186%.

It was worth noting that the ICE also possessed extremely high toughness of 13.33 MJ*m\textsuperscript{-3} (Fig. 3c). Compared with the previously reported conductive gels (Fig. 3d, and the details see Table S1, Supporting Information), this ICE integrating with hydrogen bonds and coordination bonds crosslinking network exhibited significant advantages in mechanical strength, toughness, and environment stability. In addition, the mechanical properties of the control sample ChCl/PAA/PANI\textsubscript{1\%} were also investigated and
presented in Figure S12. Compared with ChCl/PAA/C-CNC@PANI_{1\%}, the ChCl/PAA/PANI_{1\%} showed lower mechanical strength and toughness of 2.26 MPa and 9.34 MJ*m^{-3}, which was associated with the rigid C-CNC with abundant carboxyl groups could construct a denser crosslinking network to further improve the mechanical properties of the ICEs.

Furthermore, the sequential cyclic tensile test was performed to investigate the elastic property and fatigue resistance of the ionic elastomer, and the ICE ChCl/PAA/C-CNC@PANI_{1\%} with the best toughness was used as a representative sample. Figure 3e shows the cyclic stress-strain curves of ChCl/PAA/C-CNC@PANI_{1\%} with increased stain. The ICE showed an obvious hysteresis loop in given cycle, indicating the effective energy dissipation through the broken of sacrificial bonds of hydrogen bonds and coordination bonds. The hysteresis loop was gradually increased with the increase in maximum tensile strain, suggesting that the dissipation energy was increased at high strains. Meanwhile, the elastic recovery (ER) rates also increased with the tensile strain increasing, and the ER rates were as high as 95%. Moreover, the fatigue resistance of the ICE was evaluated by 10 consecutive loading-unloading cycles at a strain of 150% and relaxing for 5 min (Fig. 3f). The first loading-unloading cycle curve showed a large hysteresis loop, suggesting a significant energy dissipation (0.16 MJ m^{-3}). The hysteresis loop in the second cycle was much small than that in the first cycle, and the energy dissipation decreased to 0.03 MJ m^{-3}, which was associated with the broken sacrificial bonds without enough time to restore to the original state during the consecutive cyclic tensile tests[42]. As the broken and re-association of the sacrificial bonds reached a dynamic balance, the dissipated energy was almost coincided in the subsequent cyclic tensile tests (Fig. 3g). It was worth noting that when the ICE specimen was allowed to relax for 5 min at room temperature and then carried out the 11th cyclic tensile test. The 11th loading-unloading curve was almost coincided with the 1st cycle, and the recovery efficiency of the dissipated energy and stress reached 86.1% and 100.7%, respectively, indicating the full reconstruction of the hydrogen bonds and coordination bonds and the excellent fatigue resistance property of the ICEs. Additionally, all the ICEs with different C-CNC@PANI contents also showed excellent fatigue resistance (Figure S13 and Figure S14), and the elastic recovery performance was gradually improved with the increase of the C-CNC@PANI content due to the formation of denser crosslinking networks. Importantly, the ICE also showed better elastic recovery performance than the control samples of ChCl/PAA/PANI_{1\%} and ChCl/PAA (Figure S15), which further demonstrated the important role of C-CNC in improving elasticity.

3.3 Strain sensing property of the ICEs

The ICEs integrated with excellent mechanical toughness, elasticity and conductivity allowed it to be used as a strain sensor. Figure 4a shows the relative resistance change (ΔR/R_0) curves corresponding to the applied strain, thereby demonstrating the possibility of the ICEs serving as strain sensors. The ΔR/R_0 was increased monotonically with the increase of the applied strain, and the ΔR/R_0 reached 450% at 300% strain, indicating the wide sensing range of the strain sensor. The sensitivity of the strain sensor at different strain ranges was evaluated by gauge factors (GFs, slope of the ΔR/R_0), and the GF of the strain
sensor was divided into two regions. The GF in the strain range of 0-125% and 125–300% were 1.06 and 1.85, respectively. Particularly, compared with the control sample of ChCl/PAA/PANI1% and ChCl/PAA, the ICE showed the best sensing sensitivity (Figure S16).

Figure 4b, c shows the sensing performance of the ICE-based strain sensor under small strains (1%, 2.5%, 5%, 10%, 15%) and large strains (20%, 50%, 100%, 150%, 200%). Obviously, the ICE-based strain sensor produced highly reliable and repeatable signals to both the small and large strains over the 10 consecutive cycles. The detection limit of the strain sensor was as low as 1% strain, and the values of \( \Delta R/R_0 \) corresponding to different strains were matched with the results of Fig. 4a, suggesting the excellent stability and sensing sensitivity of the strain sensor. In addition, the effect of tensile speed on the sensing performance was also investigated. As shown in Fig. 4d, the strain sensor outputted almost independent \( \Delta R/R_0 \) signals with the tensile speed, indicating its superb reliability and promising application in wearable sensors for monitoring various human motions. The strain sensor also possessed fast and stable responsiveness for applying strain and removing strain, and the response times were 206 ms and 346 ms under 50% and 100% strain, respectively, which ensured the real-time monitoring of strain changes (Fig. 4e). Additionally, the fabricated strain sensor also displayed excellent long-term reliability. The \( \Delta R/R_0 \) exhibited periodic variations and no apparent fluctuations were observed during more than 2400 loading-unloading cycles at 50% strain (Fig. 4f).

On the basis of the sensitive and reliable strain sensing performance, the ICE-based strain sensor was used as a wearable flexible sensor for detecting human motions. As shown in Fig. 5a, a wearable strain sensor was assembled by attaching the 3D-printed strain sensor on the VHB adhesive film. Then the wearable strain sensor was glued to the different joints (such as fingers, elbows, knees, etc.) to motor human motions. As shown in Fig. 5b, the wearable sensor was first allowed to detect finger movements. When the finger was sequentially bent to 30°, 60°, and 90°, the \( \Delta R/R_0 \) showed stepwise increase from 0–31%, and the \( \Delta R/R_0 \) maintained stabilized when the finger was held at a specific angle. Meanwhile, the \( \Delta R/R_0 \) was gradually returned to its original value as the finger gradually straightened. In addition, the wearable sensor produced a real-time and stable response corresponding to the finger rapidly bending to different angles (Figure S17). Additionally, the wearable sensor was used to monitor the wrist movements (Fig. 5c), the sensor produced a differentiated electrical signal corresponding to the different bending angles. Particularly, the sensor could not only detect the bending angles of the wrist but also distinguish the movement direction of wrist-down/up by outputting positive or negative electrical signals. Similarly, the wearable sensor also could be integrated to the elbow joint for achieving the detection of the elbow swing (Fig. 5d). To detect the intense motions of lower limbs, such as sitting, standing, walking, and running, the wearable sensor was attached to the knee joint (Fig. 5e). When the volunteer sits-down/up, walks, and runs, the sensor displayed stable and rapid responses toward the movements of the knee joint, and the different movements could be distinguished by the shape and frequency of \( \Delta R/R_0 \) curves. In addition to monitoring the movement of single joint, the wearable sensors also could simultaneously detect the movement of multiple joints. As shown in Fig. 5f and Movie S1, five wearable sensors were attached on the hand of the experimenter to monitor the hand motions. When the experimenter made
different gestures, the five wearable sensors produced distinguishable and stable signals with different on/off states and waveforms.

More importantly, the wearable sensor also possessed the capability to accurately monitor subtle motions, such as facial expressions, swallowing, and vocal vibrations. As shown in Fig. 5g-h, the sensor was attached to the forehead of the experimenter to monitor the frowning behavior, and adhered to the neck to detect the swallowing behavior. In addition, the wearable sensor also showed promising applications in sound recording by monitoring throat vibrations. As presented in Fig. 5i, the sensor produced repeatable and distinguishable signals corresponding to the different words spoken by an experimenter, such as one peak for monosyllable “a”, and two peaks for double “aa”, three peaks for triple “aaa”. These results demonstrated the practical application of the ICEs in wearable sensors for monitoring various human motions.

### 3.4 Temperature and humidity sensing properties of the ICEs

The ICEs also could be used as a humidity sensor for detecting the relative humidity (RH) changes of the environment. Figure 6a shows the working mechanism of the ICEs-based humidity sensor. In this ICE, both the ChCl/AA type PDES and Al\(^{3+}\) were hydrophilic. When the ICE was exposed to moist or dry environments, the processes of water molecule adsorption into and desorption from the ICE occurred, which induced resistance changing of the ICE\[52, 53\]. The resistance of the humidity sensor at different relative humidity was recorded (Figure S19). As shown in Fig. 6b, the \(\Delta R/R_0\) gradually decreased from 0% to -78.3% as the relative humidity (RH) increased from 30% RH to 90% RH, indicating the wide humidity monitoring range of the humidity sensor. The humidity sensor also possessed high sensitivity of 2.35 in the humidity range of 55–80% RH. In addition, the real-time dynamic sensing property of the humidity sensor at 11%-32% RH and 11%-57% RH was shown in Fig. 6c. The resistance of the humidity sensor showed stable and periodic changes over 5 cycles, indicating the excellent sensing reliability of the humidity sensor.

The humidity sensor with high sensitivity and reliable sensing performance had a practical application in detecting human respiration. As shown in Fig. 6d, a 3D-printed sensor was attached to the breathing valve of the mask for the health monitoring of human respiration. When the air with high humidity was exhaled from the nose contacted with the humidity sensor, the water vapor molecules were captured by the sensor, which would reduce the resistance of the ICE as well as output a differentiated electrical signal. As shown in Fig. 6e and Movie S2, the sensor produced a faster response for fast breathing compared with normal breathing. For deep breathing with a lower gas flow rate, the sensor had enough time to remain in the high humidity atmosphere, resulting in a longer response time and a wider waveform. Furthermore, when the experimenter held his breath, the sensor outputted a constant electric signal. Particularly, the waveshape and amplitude of the electric signal of different respiratory conditions
showed excellent stability and repeatability, indicating the practical application of the sensor in health detection.

It is well known that the temperature has significant effects on the ion migration rate, which will reflect in the conductivity changes of the ICE. As shown in Fig. 6f, the conductivity of the ICEs was increased from 45.5 ms/m to 344.3 ms/m with the temperature increasing from −20°C to 60°C, and the conductivity versus temperature curve showed two distinct regimes. When the temperature was low than the $T_g$ (0°C) of the ICE, the hindered ion migration led to a decrease in conductivity. As the temperature increased above 0°C, the movement of the molecular chain becomes violent as well as the ion migration rate increased, which greatly enhanced the conductivity of the ICE. Based on the temperature-dependent conductivity, the ICE was used as a temperature sensor to detect the temperature changes of the environment. As shown in Figure S20, the resistance of the ICE was decreased monotonically from 3.55 MΩ to 1.20 MΩ with the temperature increased from 20 to 60°C. And the plot of $\Delta R/R_0$ versus temperature was linearly fitted (Fig. 6g), the temperature coefficient of resistance (TCR) of the temperature sensor was about 1.65%/°C at a range of 20 to 60°C, which was higher than ever reported (the details see Table S2, Supporting Information)[54–57]. In addition, the sensing accuracy and reliability of the temperature sensor were investigated by allowing the sensor to alternate attach on the cup wall with different temperatures. As shown in Fig. 6h, the IR images showed the temperature of the cup walls (23.3°C, 29.1°C, 40.1°C, 49.8°C), when the temperature sensor was sequentially close to different cup walls, the temperature sensor could accurately monitor the temperature differences by outputting stepwise and repeatable signals.

The stable and reliable temperature sensing performance allowed the ICE-based temperature sensor to be applied to detect human temperature. As shown in Figure S21, the temperature sensor was attached on the experimenter’s forehead to monitor the skin temperature changes before and after “artificial fever”. As shown in Fig. 6i, the temperature of the experimenter’s forehead in a healthy state was measured at 36.1°C, and the resistance of temperature sensor was 0.3511 MΩ at this time. When the experimenter was in a fever, the temperature of the experimenter’s forehead increased to 39.3°C. Correspondingly, the temperature sensor displayed a highly distinguishable response resistance of 0.3397 MΩ, demonstrating the promising application of the ICE-based temperature sensor in health monitoring.

### 3.5 Anti-swelling and underwater sensing properties of the ICEs

Different from the previously reported PDES-based ionic conductors with single hydrogen bonds crosslinking network, the introduction of C-CNC@PANI and Al$^{3+}$ was able to construct the strong coordination bonds in the PDES-based ICEs, which endowed the PDES/C-CNC@PANI ICE with excellent anti-swelling performance. As shown in Fig. 7a, the direct visualization of the 3D-printed university badge after soaking in water for 7 days suggested a restricted swelling behavior. The soaked 3D-printed university badge showed high shape fidelity, and all details still could be clearly observed. In contrast, the
control sample without adding AlCl₃ was dissolved in water after soaking for 6h, which confirmed the positive effect of coordination bonds on the anti-swelling performance of the ICEs (Figure S22). Figure 7c shows the swelling kinetics of the ICEs in water by recording the mass changes. The swelling ratio of the ICEs rapidly reached 123% within 0.5h, then the swelling ratio decreased to around 95.0% and maintained equilibrium. It should be noted that the dry weight of the swollen ICE was decreased to 49.9% of the initial weight. The decrease in the weight of ICEs was associated with the breaking of the hydrogen bonds resulting in the leakage of the components of ChCl and little PAA. Especially, the swollen ICEs still maintained a complete coordination bonds network, which was demonstrated by the presence of Al in the result of EDS mapping (Figure S23), the presence of the coordination bonds network achieved the high shape fidelity of ICEs after being soaked. Additionally, the ICE also possessed satisfactory organic solvent resistance performance, and the weight of the ICE specimens had almost no changes after being soaked in tetrahydrofuran (THF), petroleum ether (PE) and ethyl acetate (EAC) for 7 days (Fig. 7c).

The mechanical property of the ICE ChCl/PAA/C-CNC@PANI₁% before and after being soaked in water and organic solvents for 12h was also investigated. As shown in Fig. 7d, e, the ICE ChCl/PAA/C-CNC@PANI₁% after being soaked still maintained excellent mechanical properties. The retention rates of the toughness after being soaked in organic solvents were above 81.9%. It was worth noting that the mechanical strength and stretchability of the ICE after being soaked in water were 2.0 MPa and 776.3%, respectively, which were still higher than that of most reported water resistance gels (the details see Table S3, Supporting Information). The decrease in the mechanical property of the ICE after being soaked in water was attributed to the breaking of the hydrogen bonds. In addition, ICE after being soaked in water and THF maintained high conductivity of 63.4 ms/m and 26.8 ms/m (Fig. 7f). Stretching the ICE specimen that connected in series with a LED bulb and battery at underwater environment, the LED bulb turned dim, indicating the sensitive underwater resistance response of the ICEs (Fig. 7b).

Given the excellent mechanical property and anti-swelling performance, the ICE showed promising applications for monitoring underwater human motions, such as swimming or diving. As shown in Fig. 7g, the ICE-based wearable sensor could accurately monitor the finger movements in a water environment, and the ΔR/R₀ was almost consistent at the same bending angles, suggesting the excellent reliability and stability of the underwater sensing performance. In addition, the wearable sensor also could real-time detect the wrist and elbow movements in the aquatic environment (Fig. 7h and Figure S26), and the movements of the different parts could be identified through the shape and intensity of the ΔR/R₀ curves. And the wearable sensor was still able to accurately recognize different gestures at underwater environment (Fig. 7i). More importantly, the wearable sensor showed a sensitive and stable resistance response to the temperature changes in an aquatic environment (Fig. 7j), the resistance of the wearable sensor was decreased from 57.84KΩ to 28.82KΩ with the water temperature increased from 10°C to 40°C, and the resistance maintained stable at a specified water temperature, demonstrating the promising application of the ICE for underwater health monitoring.

4. Conclusion
In conclusion, we developed a strong, tough, anti-swelling, multifunctional and customizable cellulose derived ionic conductive elastomer, the photosensitive properties of PDES/C-CNC@PANI mixture contributed to fabricating the ICEs with customized 3D complex shapes by DLP 3D printing. The construction of multiple hydrogen bonds and strong coordination bonds simultaneously improved the anti-swelling and mechanical properties of the ICEs, and the ICE exhibited high mechanical strength (4.4 MPa), high toughness (13.33 MJ*m$^{-3}$), excellent elasticity and high conductivity (58.7 mS/m). Particularly, the introduction of the C-CNC@PANI not only enhanced the conductivity about 9.2 times and mechanical toughness about 1.4 times than most commonly reported PDES-based ionic gel (ChCl/PAA) but also further improved the elasticity and anti-swelling performance of the ICE. The ICEs possessed superb strain sensitivity (GF = 1.85), low detection limit (1% strain), and long-term sensing stability (more than 2400 cycles), which allowed them to be used as wearable strain sensors for detecting and identifying various human motions. Besides, the ICEs also showed sensitive responses to humidity and temperature changes, which allowed them to monitor human breath and temperature. More importantly, the strong coordination bonds endowed the ICE with satisfactory water resistance performance, and the ICE was able to assemble as an underwater strain sensor for real-time underwater sensing applications. This work highlights a new structural design strategy to develop the next-generation multifunctional PDES-based ICE with promising applications in advanced wearable sensors.

**Declarations**

**ASSOCIATED CONTENT**

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**Notes**

The authors declare no competing financial interests.

**Authors Contribution**


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Data availability

The data are available from the corresponding author upon reasonable request.

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**Figures**
Figure 1

Schematic illustration of the fabrication process and chemical structure of ICE.
Figure 2

(a) The FT-IR of the ChCl/PAA/C-CNC@PANI\(_{1\%}\) at 25 °C and 120 °C. (b) O 1s XPS spectra of ChCl/PAA/C-CNC@PANI\(_{1\%}\) and control sample. (c) Al 2p XPS spectrum of ChCl/PAA/C-CNC@PANI\(_{1\%}\). (d-g) SEM and EDS mapping images of the ICE. (h) The conductivity of the ICEs with different C-CNC@PANI contents. (i) The G’ and G” versus stress curves of ChCl/PAA/C-CNC@PANI\(_{1\%}\). (j) TGA curves of ChCl/PAA/C-CNC@PANI\(_{1\%}\).
Figure 3

(a) The images of ICE being stretched, twisted and crimped. (b) Monotonic tensile stress-strain curves of the ICEs with different C-CNC@PANI contents. (c) The toughness and tensile strength of the ICEs. (d) The comparison of the mechanical properties of the ICE with previously reported conductive gel[6,15,18,38,43-51]. (e) The sequential cyclic tensile stress-strain curves of ChCl/PAA/C-CNC@PANI$_{1\%}$. (f) The repeating cyclic tensile stress-strain curves of ChCl/PAA/C-CNC@PANI$_{1\%}$ at 150% strain. (g) The dissipated energy of ChCl/PAA/C-CNC@PANI$_{1\%}$ of each repeating cyclic tensile cycle.
Figure 4

(a) The $\Delta R/R_0$ versus strain curve of ICE. (b)-(c) The $\Delta R/R_0$ of the ICE-based strain sensor under different strains. (d) The $\Delta R/R_0$ of the strain sensor at different tensile speeds. (e) The responsive time of the strain sensor under different strains. (f) The $\Delta R/R_0$ of the strain sensor under 2400 loading-unloading cycles.
Figure 5

(a) The schematic illustration of wearable strain sensor. (b)(c)(d) The $\Delta R/R_0$ under different bending angles of finger, wrist and elbow. (e) The $\Delta R/R_0$ under the knee bending, walking and running. (f) The $\Delta R/R_0$ under different gestures. (g)(h)(i) The $\Delta R/R_0$ response to the frowning, swallowing and speaking.
Figure 6

(a) The working of the ICEs-based humidity sensor. (b) The $\Delta R/R_0$ under different humidity. (c) The resistance of the humidity sensor under repeating humidity changes from 11.3% RH to 32.8 and 57.6% RH. (d) The photos of the humidity sensor for detecting human breath. (e) The $\Delta R/R_0$ under different breath states. (f) The conductivity of the ICE at different temperatures. (g) The $\Delta R/R_0$ versus temperature curve from 20 °C to 60 °C. (h) Sensing stability of the temperature sensor for repeating temperature changes. (i) The application of the temperature sensor in human health detection.
Figure 7

(a) The photos of the ICE before and after being soaked in water. (b) The photos of the ICE in series with a LED at underwater environments. (c) The swelling curves of ICE in different solvents. (d) The stress-strain curves of the ICE after being soaked in water and organic solvent. (e) The mechanical properties retention rate of the ICE after being soaked. (f) The conductivity of the ICE after being soaked. (g)(h) The $\Delta R/R_0$ of the wearable sensor for underwater finger and elbow motion detection. (i) The $\Delta R/R_0$ of the wearable sensor for underwater gesture recognition. (j) The real-time resistance of the sensor for underwater temperature monitoring.

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