Multifunctional Ionic Skin with Sensing, UV-Filtering, Water-Retaining, and Anti-Freezing Capabilities

Jie Wen, Jia Tang, Huiming Ning,* Ning Hu,* Yuanyuan Zhu, Youkun Gong, Chaohe Xu, Qiannan Zhao, Xiaoping Jiang, Xiaolin Hu, Ling Lei, Dan Wu, and Tao Huang

Conductive polymer hydrogels are receiving considerable attention in applications such as soft robots and human-machine interfaces. Herein, a transparent and highly ionically conductive hydrogel that integrates sensing, UV-filtering, water-retaining, and anti-freezing performances is achieved by the organic combination of tannic acid-coated hydroxyapatite nanowires (TA@HAP NWs), polyvinyl alcohol (PVA) chains, ethylene glycol (EG), and metal ions. The highly ionic conductivity of the hydrogel enables tensile strain, pressure, and temperature sensing capabilities. In particular, in terms of the hydrogel strain sensors based on ionic conduction, it has high sensitivity ($GF = 2.84$) within a wide strain range (350%), high linearity ($R^2 = 0.99003$), fast response ($\approx 50 \text{ ms}$) and excellent cycle stability. In addition, the incorporated TA@HAP NWs act as a nano-reinforced filler to improve the mechanical properties and confer a UV-shielding ability upon the hydrogel due to its size effect and the characteristics of absorbing ultraviolet light waves, which can reflect and absorb short ultraviolet rays and transmit visible light. Meanwhile, owing to the water-locking effect between EG and water molecules, the hydrogel exhibits freezing resistance at low temperatures and moisture retention at high temperatures. This biocompatible and multifunctional conductive hydrogel provides new ideas for the design of novel ionic skin devices.

1. Introduction

Ionic skin is regarded as most attractive candidates that can replace human skin.[1] It has similar functions to human skin, such as being able to sense different types of forces (tensile force and pressure) and temperature changes. Moreover, it also has functions that human skin does not have, such as the ability to perceive changes in ultrasound and humidity, and the ability to cause photochromism.[2] In the field of ionic skin, conductive hydrogels have gradually become a hot research topic. It mainly has the following advantages: 1) The elastic modulus of hydrogel is similar to that of human skin (1–100 kPa),[3] so it exhibits tissue-like softness; 2) It has high flexibility and transparency, low toxicity, and great self-repair and self-adhesion abilities and biocompatibility;[4] 3) The combination of raw materials is variable, and different types of polymers can be combined to form a double network (DN), a triple network (TN), an interpenetrating network (IPN), etc., which can significantly improve the mechanical properties;[5] 4) The structure design is flexible and versatile, and the hydrogel can be conveniently and quickly made into a device with changeable styles for use in specific scenes.[6]

Conductive hydrogels can be divided into electronic conductive hydrogels and ionic conductive hydrogels according to different transfer media.[7] The former is doped with conductive metal nanomaterials (e.g., Ag nanoparticles,[8] and Ag nanowires[9]), conductive carbon or carbide/nitride nanomaterials
In the ultraviolet spectrum, UVA in the 320–400 nm band is believed to damage DNA, accelerate cell aging, and even cause skin cancer. Hence, the need for transparent-based UV-protective underwear, UV-protection glass, and sunscreen hydrogels with both transparency and UV-filtering function. However, it is very challenging to fabricate integrated conductive hydrogels that integrate sensing, UV-filtering, water-retaining, anti-freezing and biocompatible performances, which could be used as ionic skin. In this strategy, 1D nanofiller TA@HAP NWs, AlCl₃ and PVA are uniformly dispersed in the binary solvent of ethylene glycol (EG) and water (W). In this combination, TA@HAP NWs played a role in ultraviolet filtering and improved the mechanical properties. At the same time, the binary system of EG and water alleviates water freezing at subzero temperatures and water evaporation at high temperatures, and the free movement of Al³⁺ in the molecular-level water channel makes it more sensitive to strain changes. As a result, the optimized hydrogel showed sensing, UV-filtering, water-retaining, anti-freezing performance, as well as high electrical conductivity (1.00 × 10⁻² S cm⁻¹), good transparency and biocompatibility. The most prominent features of the TA@HAP NWs-PVA(EG/W) hydrogel are that when this ion skin is used as a strain sensor, it has a wide linear sensing range (350%) and high sensitivity (GF = 2.84), which is at the leading level in the same research field. Meanwhile, compared with pure PVA (EG/W) hydrogel, its ultimate tensile strength, ultimate tensile strain and toughness are increased by 100%, 180%, and 330%, respectively. These excellent properties show that the ion conductive hydrogel we developed has an important role in promoting the construction of a new multifunctional ion skin.

2. Results and Discussion

2.1. Synthesis of Ion-Conductive TA@HAP NWs-PVA(EG/W) Hydrogel

The specific synthesis route and design strategy of TA@HAP NWs-PVA(EG/W) hydrogel are shown in Figure 1. Firstly, the ultra-long HAP nanowire was synthesized via one-step hydrothermal reaction. As shown in Figure S1 (Supporting Information), all XRD peaks are well consistent with that of hydroxyapatite (JCPDS 09–0432); no impurity peaks are detected, indicating the hydroxyapatite phase was successfully synthesized. The morphology and microstructure of the as-obtained HAP nanowire were characterized by scanning electron microscope (SEM), as shown in Figure S2 (Supporting Information). The lengths and diameters of these HAP nanofibers are about ~100 μm and ~500 nm, respectively, revealed by high magnifications SEM. The high length to diameter ratio could ensure good mechanical flexibility. Secondly, TA@HAP NWs slurry was synthesized. TA is a polyphenolic substance extracted from the gallnut, which maintain the hydrogel’s flexibility and original conductivity at −20 °C. Lu et al. also used a glycerin/water binary solvent to widen the working temperature range of the hydrogel to −20–60 °C. Liu et al. used the dependence of Li⁺ compounds to inhibit the growth of ice crystals, so that the hydrogel could maintain its mechanical properties basically unchanged at −36 °C. In short, the strategy of using polyol/water binary solvent instead of water solvent can achieve the environmental stability of hydrogel. Although significant advances have been achieved in the research of multifunctional hydrogels, it is still very challenging to construct new flexible ionics skins combining all the critical features described above.

Herein, we developed a transparent and highly ionic conductive hydrogel that integrates sensing, UV-filtering, water-retaining, anti-freezing and biocompatible performances, which could be used as ionic skin. In this strategy, 1D nanofiller TA@HAP NWs, AlCl₃ and PVA are uniformly dispersed in the binary solvent of ethylene glycol (EG) and water (W). In this combination, TA@HAP NWs played a role in ultraviolet filtering and improved the mechanical properties. At the same time, the binary system of EG and water alleviates water freezing at subzero temperatures and water evaporation at high temperatures, and the free movement of Al³⁺ in the molecular-level water channel makes it more sensitive to strain changes. As a result, the optimized hydrogel showed sensing, UV-filtering, water-retaining, anti-freezing performance, as well as high electrical conductivity (1.00 × 10⁻² S cm⁻¹), good transparency and biocompatibility. The most prominent features of the TA@HAP NWs-PVA(EG/W) hydrogel are that when this ion skin is used as a strain sensor, it has a wide linear sensing range (350%) and high sensitivity (GF = 2.84), which is at the leading level in the same research field. Meanwhile, compared with pure PVA (EG/W) hydrogel, its ultimate tensile strength, ultimate tensile strain and toughness are increased by 100%, 180%, and 330%, respectively. These excellent properties show that the ion conductive hydrogel we developed has an important role in promoting the construction of a new multifunctional ion skin.
has the ability to polymerize and deposit in situ and chelate with metal cations in an alkaline environment.[30] Therefore, TA can be polymerized and deposited on the surface of HAP NWs in situ to improve its physical and chemical properties. Generally, the phenolic hydroxyl group in TA is easily oxidized by oxidants (Fe$^{3+}$, IO$_4^{-}$), and the color will change from light yellow to black. Hence, in order to maintain the transparency of the hydrogel, an alkaline environment ($\text{pH} = 8.0$) is used to moderately induce the oxidative polymerization of TA, and HAP NWs provide physical and chemical sites for the in-situ deposition of TA. As shown in Figure S3 (Supporting Information), the HAP NWs suspension showed complete precipitation after standing for 30 min, while the TA@HAP NWs suspension had only a little precipitation at the bottom after standing for 2 h. It can be inferred that TA was deposited on HAP NWs, which made the suspension more uniform. This will help HAP NWs be uniformly dispersed in PVA and improve the mechanical properties of PVA. In addition, as shown in Figure S4a and Table S2 in the Supporting Information, the energy-dispersive X-ray spectroscopy (EDS) of TA@HAP NWs shows that the C element content is 13.87%. However, all C elements belong to TA, which means that TA has been oxidized and deposited on the surface of HAP NWs in situ. Meanwhile, the element mapping image of the C element shows that TA is evenly distributed on the surface of HAP NWs. Moreover, as shown in Figure S4b (Supporting Information), the characteristic bands for TA@HAP NWs were observed at 1716 cm$^{-1}$ (C=O stretching), 1446 cm$^{-1}$ (O–C=O stretching), and 1197 cm$^{-1}$ (O–C=O stretching, C-O–H in-plane bending).[31] These characteristic peaks can also be observed in TA. Similarly, it has characteristic peaks of hydroxyapatite at 1036 and 566 cm$^{-1}$.[32] In addition, TA@HAP NWs have phenolic-OH groups and –OH groups of hydroxyapatite in the range of 3600–3000 cm$^{-1}$.[31b,32,33] All these peaks show that TA has been successfully wrapped on HAP NWs. Next, TA@HAP NWs, PVA and AlCl$_3$ powder were added to the pre-prepared binary solvent of EG and water, and stirred at 95 °C for 4 h. AlCl$_3$ can be completely ionized in water, but not in EG, which helps Al$^{3+}$ move freely in the molecular level ion water channel separated by EG molecules. Moreover, when comparing ions with the same molar concentration in different valence states, the valence state was higher, whose conductivity was stronger. Hence, we used metal salt ions with high valence state as the ion conductor. As shown in Figure S4c (Supporting Information), the low-frequency part in the AC impedance diagram is almost linear, which is a non-Faraday process with no matter or charge crossing the interface, indicating that the conduction mechanism between the conduction process and electrons is different.[6] The ionic conductivity of $1.00 \times 10^{-2}$ S cm$^{-1}$ can be calculated from the AC impedance diagram, which shows that TA@HAP NWs-PVA(EG/W) hydrogel has very high conductivity. It is beneficial to improve the sensitivity of the sensor. More importantly, compared with Fe$^{3+}$, Al$^{3+}$ has a lighter color. There is no need to worry about excessive oxidation of TA by Fe$^{3+}$ to turn black. Finally, three freeze-thaw cycles were used to obtain the multifunctional hydrogel with transparency, UV filter, low temperature anti-freezing, high temperature moisture retention, strong mechanical properties, wide linear range sensitivity, sensing performance and biocompatibility. Similarly, the preparation methods of PVA(W) and PVA(W/EG) ion-conductive hydrogel are introduced in Section S1.3 in the Supporting Information. For convenience, unless otherwise specified, the conductive hydrogel with a content of 4 wt% TA@HAP NWs was used for all tests.

**Figure 1.** Schematic diagram of the synthetic route of TA@HAP NWs-PVA(EG/W) hydrogel. a) Preparation of ultra-long hydroxyapatite nanowire (HAP NWs) precursors. b) Preparation of HAP NWs solution via hydrothermal reaction, and addition of TA in alkaline environment. c) TA-coated HAP NWs synthesized by in-situ oxidation deposition, and addition of PVA and AlCl$_3$. d) Pouring molding of TA@HAP NWs-PVA(EG/W) slurry. e) Preparation of transparent hydrogels via three freeze-thaw (F-T) cycles.
2.2. Sensor for the Detection of Strain, Pressure, and Temperature

At present, the sensors which can only detect one type of physical signal do not meet the development trend of new sensors, and the development of multipurpose sensors has gradually become a new hot spot of sensor development. The TA@HAP NWs-PVA(EG/W) hydrogel-based sensor with ionic conduction has excellent linear response to physical signals such as tensile deformation, pressure and temperature. In short, high sensitivity, wide linearity and multipurpose sensing are the core performance of hydrogel-based sensors. The ionic conductivity in TA@HAP NWs-PVA(EG/W) hydrogel comes from the free migration of metal cations, and its ionic conductivity is $1.00 \times 10^{-2}$ S cm$^{-1}$, which is comparable to the ionic conductivity of liquid electrolytes.\[^{34}\] The high ionic conductivity is beneficial to reduce resistance and improve the sensitivity. The sensing principle of ion hydrogel-based strain sensors mainly relies on the change of ion concentration per unit volume during the deformation process and the change of the conductive path length, which leads to the corresponding resistance change.\[^{15}\] As shown in Figure 2a, the relative resistance change rate increases with the increase of tensile strain (the maximum strain is 350%), showing a linear proportional relationship (linearity $R^2 = 0.99003$). Strain sensitivity is one of the core performance indicators of strain sensors, which can be defined as gauge factor (GF) = $(R’ - R_0)/R_0) / \varepsilon$. It can be obtained that GF = 2.84 in the strain range of 0–350%. More importantly, in terms of linearity, strain range and GF, it is better than most reported data in the literature (Figure 2b). These specific details can be queried in Table S3 (Supporting Information). Compared with most elastomer-based electronic conductive strain sensors, the TA@HAP NWs-PVA(EG/W) hydrogel-based ionic conductive strain sensors generally have lower sensitivity.\[^{36}\] However, for the hydrogel-based ionic conductive strain sensors, their comprehensive properties (i.e., sensitivity,

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**Figure 2.** a) Relative resistance change rate-strain curve. b) A scatter diagram showing the gauge factor within the strain of 600% of some typical reported strain sensors (see details in Table S3, Supporting Information). The reference numbers in the figure are from Table S3 (Supporting Information). (1–6,8–13,17–20,23,24), [This work]: Ionic conduction;[26,27,3,7,14,15,16,21,22,25–30] Electronic conduction. c) The loading-unloading curves of 6000 s (300 cycles).
linearity and working range) are more attractive. This excellent wide linearity of strain and high sensitivity may be related to the molecular-level ion water channel separated by EG molecules. When being stretched, the molecular-level ion water channel will change rapidly, and the metal cation chelated by TA will also move quickly, which will cause the ion concentration per unit volume to drop rapidly, and thus the resistance increases sharply. According to the high ionic conductivity and strain sensing characteristics of TA@HAP NWs-PVA(EG/W) hydrogel, it can be used as a wire with variable resistance in the circuit, that is, the resistance in the circuit can be controlled by changing its length. As shown in Figure S5 and Movie S1 in the Supporting Information, TA@HAP NWs-PVA(EG/W) hydrogel can be used as a wire to light up LED lights, and the brightness of the LED lights gradually decreases as its length increases. Similarly, cycle stability is also one of the core indicators for stable operation of the sensor. As shown in Figure 2c, when the strain is 50% and the extension rate is 100 mm min⁻¹, the TA@HAP NWs-PVA(EG/W) hydrogel-based strain sensor can work stably for 6000 s (300 cycles), indicating its excellent stability.

As can be seen from the illustration in Figure 2c, the loading-unloading curves at 0 s (initial cycle), 3000 s (150 cycles), and 6000 s (300 cycles) are similar. However, the loading-unloading curve shows an overall upward shift with time. The small drift in the resistance-strain curve can be attributed to the fact that during long time cyclic stretching of hydrogels, the water is squeezed out of the polymer network and distributed on the surface of hydrogels to form small water droplets, which are gradually lost during the test. As a result, some ions are lost with water, resulting in an increase in electrical resistance. Although there is a certain resistance deviation, the resistance curve is always similar, indicating that our hydrogel sensor has high durability in practical applications. Figure 3a displays relative resistance change rate-strain curve of TA@HAP NWs-PVA(EG/W) hydrogel-based strain sensor under stepped cyclic stretched strain. It can be found that the relative resistance change rate at different strains (50%, 100%, 200%, and 300%) almost completely recovers to the initial value, showing an excellent strain-sensing reversibility. Particularly, as shown in Figure 3b, when applying cyclic loading and unloading up to

![Figure 3.](image-url)
300% strain, the relative resistance change rate-strain curve of loading and unloading keeps almost the same trend, indicating that the hysteresis of our ionic sensor is very low (2.4%). Meanwhile, as shown in Figure 3c, the sensor works for 10 cycles of loading-unloading with a strain of 300%. The results show that the error area of the relative resistance change rate-strain curve of each cycle is small, indicating that the sensor’s signal is stable and repeatable. The responding time of human skin is about 100 ms. In the 50% tensile strain-time curve and the corresponding resistance-time curve, the responding time for loading and unloading are 51 and 59 ms (Figure 3d), respectively, which are only half of that of human skin, indicating that TA@HAP NWs-PVA(EG/W) hydrogel has fast signal responsiveness and is promising as a substitute for human skin sensing function.

The TA@HAP NWs-PVA(EG/W) hydrogel tensile strain sensor has excellent performance in detecting large strains of human finger joints, elbows and knees, as shown in Figure 4a-c. It can recognize the bending of finger joints and elbows at 45°, 90°, and 180°. It can also recognize the half-bending state and the fully bending state of knees (maintaining the bent state for 3 s). Interestingly, it can also be used to detect changes in facial micro-expression, such as slightly open mouth, wide open mouth, 4 types of tones of “ah”, blinking, frowning, and angrying, as shown in Figure 4d and Figure S6a-d (Supporting Information). The specific application details of the TA@HAP NWs-PVA(EG/W) hydrogel tensile strain sensor can be found in Movies S2-S4 (Supporting Information). These practical applications have proved the powerful potential of the TA@HAP NWs-PVA(EG/W) hydrogel tensile strain sensor in the field of ionic skin.

Because of its good compression performance and high conductivity, the TA@HAP NWs-PVA(EG/W) hydrogel can be used as a tactile pressure sensor, which has a positive effect on the construction of human-computer interaction technology. Generally, pressure sensors can be manufactured by the principle of parallel plate capacitors, that is, conductive hydrogel is used as parallel conductive plates on both sides, and commercial VHB tape can be used as an elastomer and a dielectric layer. The capacitance can be calculated using the following formula: $C = \varepsilon_0 \times \varepsilon_r \times A \times d^{-1}$, where $C$ is the capacitance value, $\varepsilon_0$ is the vacuum dielectric constant (8.854187817×10^{-12} F m^{-1}), $\varepsilon_r$ is the relative permittivity of the dielectric layer (acrylic acid), $A$ is the area of one side parallel to the conductive plate, and $d$ is the thickness of the dielectric layer (that is, the distance between the parallel plate conductive layers). When the external pressure is applied, due to its excellent compressibility, the surface area of the parallel conductive plates will increase, and the distance $d$ will decrease, eventually leading to an increase in capacitance. The relative capacitance change as a function of applied pressures is shown in Figure 4e. The sensitivity of the pressure sensor was calculated to be 0.0085 kPa⁻¹, and the linearity $R^2$ was 0.99086. These results show that TA@HAP NWs-PVA(EG/W) hydrogel can be used for pressure detection, and has a high degree of linearity and high sensitivity.

Since TA@HAP NWs-PVA(EG/W) hydrogel relies on the free migration of metal cations in the water medium to conduct electricity, the diffusion rate of free ions increases with the increase of the ambient temperature, which leads to an increase in conductivity (a decrease in resistance accordingly). Therefore, the ion conductivity of ionic hydrogel is temperature-dependent and can be used for temperature sensors. The relationship between the diffusion rate of free ions in hydrogels and the temperature can be explained by Fick's first law and Arrhenius equation, $J = -D \times \frac{dc}{dx} = -D_0 \times \exp\left(-\frac{Q_D}{RT}\right) \times \frac{dc}{dx}$, where $J$ is the diffusion flux, $D$ is the diffusion coefficient, $D_0$ is a constant independent of temperature, $Q_D$ is the activation energy of diffusion, $R$ is the gas constant, $T$ is the absolute temperature, and $dc/dx$ is the concentration gradient. The relative resistance change as a function of temperature is shown in Figure 4f. The temperature sensitivity is calculated to be 0.00536 °C⁻¹, and the linearity $R^2 = 0.99367$. Although the hydrogel-based temperature sensor will gradually melt when the temperature exceeds 80 °C, it is sufficient for daily applications. Therefore, the TA@HAP NWs-PVA(EG/W) hydrogel-based temperature sensor has great potential in the field of temperature sensing.

As shown above, the sensors based on ionic hydrogel have both strain sensing property and temperature sensing property, therefore, the combined interaction of strain and temperature cannot be ignored in practical applications. The anti-interference of the present sensor’s strain sensing function to temperature variation should be further clarified by the relative resistance change rate-strain curve at different temperatures. As shown in Figure S7 (Supporting Information), each curve has the same trend with only a small error (6% of GF error) at different temperatures, indicating that the temperature has a small effect on strain sensitivity. This is because the resistance change caused by applied strain is much more sensitive than that caused by temperature variation. Therefore, the strain sensing responses of our ionic hydrogel sensor at different temperatures are stable and reliable. It is also simple to remove this small temperature effect on the sensor’s strain sensing performance by implementing another calibration sensor without applied strain under the same environment.

In summary, TA@HAP NWs-PVA(EG/W) hydrogels have great advantages in sensing tensile strain, pressure and temperature. This advantage comes from wide linearity and high sensitivity of the sensors, especially the strain sensors, which have high stable cycle working ability and fast time response. Moreover, the human body sensing also perfectly verified its feasibility in practical applications. This design idea opens up a new path in the field of multipurpose sensing. The ionic hydrogel material not only has excellent sensing functions, but also has outstanding mechanical, UV-filtering, water-retaining and anti-freezing properties, which are discussed in detail as follows.

2.3. Mechanical Properties of the TA@HAP NWs-PVA(EG/W) Hydrogel

Excellent mechanical properties are one of the necessary conditions to ensure normal stretching or compression of conductive hydrogels. Generally speaking, the Young’s modulus of human skin is in the range of 1–100 kPa, so the hydrogel-based ionic skin should also have the same range of mechanical properties. TA@HAP NWs filler plays a crucial role in strengthening and
toughening the entire PVA network, as shown in Figure 5a-c. Within a certain range (0–4 wt%), ultimate tensile strength, ultimate tensile strain and toughness of conductive hydrogel increased with the increase of the TA@HAP NWs content, which reached the maximum (ultimate tensile strength (0.36 MPa), ultimate tensile strain (480%) and toughness (937.403 KJ m\(^{-3}\))) when the content of TA@HAP NWs was 4 wt%. Compared with pure PVA (EG/W) hydrogel, its ultimate

**Figure 4.** Demonstration of tensile strain sensing in human body, such as a) The bending of finger joints at 45°, 90°, and 180°, b) The bending of elbows at 45°, 90°, and 180°, c) Half-bending state and the fully bending state of knee (maintaining the bent state for 3 s), d) Slightly open mouth and wide open mouth (see details in Movies S2–S4, Supporting Information), e) Relative capacitance change rate-pressure curve of pressure sensor, f) Relative resistance change rate-temperature curve of temperature sensor.
tensile strength, ultimate tensile strain and toughness are increased by 100%, 180%, and 330%, respectively. In addition, although the tensile modulus of the hydrogel decreased with the increase of TA@HAP NWs content, the tensile modulus reached 80 kPa when the content of TA@HAP NWs was 4 wt%. The modulus value still meets the requirements of Young’s modulus required by human skin. Meanwhile, the TA@HAP NWs-PVA(EG/W) hydrogel has very good flexibility and can withstand large deformations, such as twisting, bending, knotting and stretching, as shown in Figure 5f. These mechanical behaviors indicate that it can adapt to various complex mechanical conditions. In short, the TA@HAP NWs filler can significantly improve the mechanical properties of PVA-based hydrogels. This improvement may be related to the formation of a large number of hydrogen bonds among TA@HAP NWs, PVA and EG, so that there is an interaction between the TA@HAP NWs network and the PVA network. Due to the formation of the double network structure, it is greatly beneficial to the improvement of mechanical properties. As shown in Figure S8 (Supporting Information), TA@HAP NWs are dispersed in TA@HAP NWs-PVA(EG/W) hydrogel, which is conducive to the formation of dual networks and cooperates to dissipate external energy. Similarly, the same conclusion can be obtained in the stress-strain relationship curve in the compression test, as shown in Figure 5d. That is, when the TA@HAP NWs content is 4 wt%, the compressive strength (80% compressive

Figure 5. Tensile and compressive mechanical properties of PVA(W), PVA(EG/W) and x wt% TA@HAP NWs-PVA(EG/W) hydrogels, where the value of x is 2, 4, 6, and 8. a) Tensile stress–strain curve diagram. b) A mean and standard deviation diagram of tensile stress and tensile strain. c) A mean and standard deviation diagram of elastic modulus and toughness values. d) Compressive stress–strain curve diagram. e) Stress–strain curve at different tensile rates. f1–f4) Various mechanical behaviors (torsion, bending, knotting, and stretching) of 4 wt% TA@HAP NWs-PVA(EG/W) hydrogel.
strain) reaches the maximum value (1.90 MPa). For convenience, unless otherwise specified, the conductive hydrogel with a content of 4 wt% TA@HAP NWs was used for all tests. Interestingly, as shown in Figure 5e, the 4 wt% TA@HAP NWs hydrogel exhibits obvious viscoelastic behavior, that is, as the stretching rate increases, its elastic modulus also increases. In short, TA@HAP NWs-PVA(EG/W) with good mechanical properties has a huge advantage in the field of ionic skin.

2.4. Excellent UV Light Filtering Capabilities and Live Mouse Demo of the Hydrogel as UV-Shielding Skin Patch

High transparency is an excellent characteristic of ionic skin. When the conductive hydrogel is used for skin sensing, transparent hydrogel can facilitate the processes of arrangement and repair of related electronic circuits. However, transparent hydrogels usually do not have the function of reflecting ultraviolet rays, which greatly limits their application in high altitude areas with a thin ozone layer, and deep space exploration. Therefore, a conductive hydrogel that has both transparency and UV protection can greatly expand its application fields. UVA (320–400 nm) in the ultraviolet spectrum is considered to be the strongest radiation wave that causes skin cancer. In the visible light spectrum (400–780 nm), the wavelength of 350 nm is the most sensitive to human vision. Therefore, in the study of UV protection and transparency, 365 and 550 nm bands were selected, respectively.

TA@HAP NWs is able to effectively reflect and absorb ultraviolet light and allow longer wavelengths of visible light to pass through. As depicted in Figure 6a-c, for the characteristic wavelength of 550 nm, the transmittance of PVA(W), PVA(EG/W), and TA@HAP NWs-PVA(EG/W) hydrogels are 40%, 89%, and 60%, respectively. Although TA@HAP NWs-PVA(EG/W) hydrogel has a reduced transmittance compared with PVA(EG/W) hydrogel, it can also be regarded as a transparent hydrogel. As shown in Figure S9 (Supporting Information), when TA@HAP NWs-PVA(EG/W) hydrogel is placed on the school badge, the content on the school badge can be clearly distinguished. For the characteristic wavelength of 365 nm, the transmittance of PVA(W), PVA(EG/W) and TA@HAP NWs-PVA(EG/W) hydrogels are 32%, 72%, and 3.6%, respectively. Compared with PVA(W) and PVA(EG/W) hydrogels, TA@HAP NWs-PVA(EG/W) hydrogels have very strong ultraviolet filtering performance, which can reflect and absorb almost all ultraviolet light. Although TA@HAP NWs are inherently non-transparent, they have a suitable nano-scale diameter, which is at the same level as the short-wavelength ultraviolet light. Therefore, the short-wavelength ultraviolet light will be reflected (size effect) and absorbed multiple times by TA@HAP NWs. When natural light passes through the material, only a small amount of ultraviolet light remains, while visible light with long-wavelength can pass through smoothly. As shown in Figure S10 (Supporting Information), it is worth noting that TA@HAP NWs has obvious absorption ability to ultraviolet light waves, which may be related to the catechol in tannic acid. In addition, due to the chelation between TA and metal cations and the evenly dispersed nature of TA-coated HAP NWs, HAP NWs are distributed uniformly in the PVA network without agglomeration. Therefore, TA@HAP NWs-PVA(EG/W) hydrogel is transparent to the naked eye and has the function of filtering ultraviolet rays (Figure 6d).

More importantly, since TA@HAP NWs-PVA(EG/W) hydrogel has excellent UV-filtering performance, it can also be used to filter ultraviolet skin patch, so as to protect the skin from UV burns. In the demonstration of the hydrogel as an UV-shielding skin patch in Figure 6e, two adjacent areas were selected on the back of the BALB/c mice as the hydrogel skin patch protection area of the experimental group and the unprotected area of the control group, respectively. UV lamps (40 mW cm$^{-2}$, 365 nm) were used to irradiate the experimental group and the control group for 1 h. In the visual observation of the experimental group and the control group, it can be intuitively observed that the area protected by the hydrogel skin patch was normal, while the skin of the unprotected area showed obvious burns. The skin structure of the experimental group was complete and clear; the cells were clearly divided; the cell composition and number were moderate; the epidermis, dermis and basal layers were closely connected. However, in the control group, there were obvious epidermal ruptures, breakages, and local continuity interruptions. The thickness of the stratum corneum increased, and nuclear pyknosis and deformation were occasionally seen; and neutrophil infiltration was occasionally seen in the dermis. In the transparent layer, the collagen fibers were locally broken, their integrity was destroyed, and their continuity was interrupted (elliptical area). In brief, the TA@HAP NWs-PVA(EG/W) hydrogel with excellent UV-filtering function and transparency is more suitable for ionic skin and can effectively protect the skin from UV lights.

2.5. Water-Retaining Properties of the TA@HAP NWs-PVA(W/EG) Hydrogel

Conductive hydrogels are very easy to lose water at room temperature, which greatly reduces the service life of hydrogels as various devices. Therefore, water retention at room temperature, even at higher temperatures, is particularly important. As shown in Figure 7a, in order to simulate human body temperature and extremely dry environment, moisture retention test was conducted at 37 °C and 40% relative humidity for 10 d. It can be observed from the moisture retention curve that the water loss weight of PVA(W/EG) hydrogel and TA@HAP NWs-PVA(W/EG) hydrogel was in a state of convergence on the 4th day; PVA(W/EG) had a high weight retention rate of 71 wt%, and TA@HAP NWs-PVA(W/EG) also had a high weight retention rate of 72 wt% on the 10th day. However, the PVA(W) hydrogel converged on the 2nd day, and only had a low weight retention rate of 15 wt% on the 10th day. In a high temperature and extremely dry environment, the high moisture retention originated from the formation of many strong hydrogen bonds among PVA, EG molecules and water molecules, as shown in Figure 7b. The water-locking effect formed by these interactions can ensure that free water molecules are not easily evaporated, and inhibit freezing of free water molecules at low temperatures. Similarly, TA@HAP NWs-PVA(W/EG) hydrogel was tested for water retention at different temperatures. As shown in Figure S11a (Supporting Information), the weight retention
Figure 6. a) Visible spectrum transmittance graph. b) Ultraviolet spectrum transmittance graph and c) Transmittance histogram of 365 and 550 nm spectral bands of PVA(W), PVA(EG/W) and 4 wt% TA@HAP NWs-PVA(EG/W) hydrogels. The thickness of each group of samples is 1.5 mm. d) The mechanism diagram of TA@HAP NWs reflecting ultraviolet light and transmitting visible light. e) Demonstration of the conductive hydrogel as UV-shielding skin patch.
Figure 7. a) Weight change rate curve of PVA(W), PVA(EG/W) and 4 wt% TA@HAP NWs-PVA(EG/W) hydrogel (ambient temperature 37 °C, relative humidity 40%). b) Schematic diagram of the moisturizing and anti-freezing mechanism of TA@HAP NWs-PVA(EG/W) hydrogel. c) Differential scanning calorimetry (DSC) of the PVA(W), PVA(EG/W) and 4 wt% TA@HAP NWs-PVA(EG/W) hydrogels from -100 to 30 °C. d) Lighting LED lights of 4 wt% TA@HAP NWs-PVA(EG/W) at -30 °C (see details in Movie S1, Supporting Information). Before the demonstration, the conductive hydrogel was stored at -30 °C for 24 h. e) Demonstration of the conductive hydrogel as an anti-freezing skin patch.
rate of the hydrogel decreases with the increase of temperature at the same storage time. The weight retention rates of the hydrogel at 0, 20, 37, and 60 °C are 98%, 81%, 72%, and 65% respectively at the 7th day, as shown in Figure S11b (Supporting Information). The results show that although the water retention will become worse with the increase of temperature, the water retention capacity of our hydrogel is sufficient when exposed to a room temperature environment for a long time or a short-term high temperature environment. These results indicate that, compared to traditionally conductive hydrogels, the moisture retention of TA@HAP NWs-PVA(W/EG) has been significantly improved.

2.6. Outstanding Anti-Freezing Capabilities and Live Mouse Demo of the Hydrogel as Anti-Freezing Skin Patch

Human skin is often exposed to the external environment, and sometimes contacts with extreme environments, such as below zero temperature. In order to better apply conductive hydrogels to the skin, the problem of low temperature freezing should be overcome. When the free water in the hydrogel freezes, the free metal cations will lose the transmission medium, which will greatly reduce the conductivity of the hydrogel. In the designed hydrogel, the strong hydrogen bonds formed among PVA, EG molecules and water molecules will inhibit the tendency of water molecules to freeze. The anti-freeze property of the conductive hydrogel can be analyzed by differential scanning calorimetry (DSC), as shown in Figure 7c. In the range of -100 to 30 °C, PVA(W) hydrogel exhibits an exothermic peak at -21 °C, which is attributed to the condensation of free water. However, neither PVA(EG/W) hydrogel nor TA@HAP NWs-PVA(EG/W) hydrogel showed any exothermic peaks, indicating that both have excellent anti-freeze properties. In the anti-freeze demonstration of Figure S12 (Supporting Information), TA@HAP NWs-PVA(EG/W) hydrogel can be mechanically deformed with various patterns (twisting, stretching, folding and knotting) at -30 °C. Furthermore, TA@HAP NWs-PVA(EG/W) hydrogel still has high ionic conductivity (9.21 × 10⁻³ S cm⁻¹) at -30 °C, as shown in Figure S13 (Supporting Information). Although the conductivity is slightly lower than that at room temperature (1.00 × 10⁻² S cm⁻¹), it can normally maintain rapid ion transmission at low temperatures. It also exhibits strain sensitivity at a low temperature of -30 °C. When it is used as a wire with variable resistance, as the tensile strain increases, the LED light becomes darker, as shown in Figure 7d and Movie S1 (Supporting Information). These phenomena indicate that TA@HAP NWs-PVA(EG/W) hydrogel still has excellent mechanical, electrochemical properties and strain sensitivity at extremely low temperatures. The reason is that strong hydrogen bonds are formed among PVA, EG molecules and water molecules, which will inhibit the tendency of water molecules to freeze (Figure 7b).

Considering that TA@HAP NWs-PVA(EG/W) hydrogel has excellent anti-freezing properties, it can also be used in skin patch to protect the skin from frostbite. In the demonstration of the conductive hydrogel as an anti-freezing skin patch in Figure 7e, two adjacent areas were selected on the back of Sprague Dawley (SD) rats, including the hydrogel skin patch protection area of the experimental group and the unprotected area of the control group. Two stainless steel sheets that were previously cooled in liquid nitrogen were placed on these areas, and kept for 1 min. It can be visually observed that the area protected by the hydrogel skin patch was normal, while the skin of the unprotected area showed obvious frostbite. Analysis of the histological section showed that the area protected by the hydrogel skin patch had a continuous and complete epidermal layer, tightly connected collagen fibers and evenly distributed hair follicles. In the unprotected area, local thinning and continuous interruption of the epidermal stratum corneum were observed, the local collagen fibers in the dermis were ruptured and damaged, and the hair follicle (elliptical area) was damaged. In conclusion, TA@HAP NWs-PVA(EG/W) hydrogels with excellent anti-freeze properties can be used as skin patch under extremely low temperature environments without adverse effects on the mechanical and electrochemical properties.

2.7. Biocompatibility of the TA@HAP NWs-PVA(W/EG) Hydrogel

As an ion skin, biocompatibility is undoubtedly an essential prerequisite. The RAW 264.7 cells were cultured with TA@HAP NWs-PVA(W/EG) hydrogel extracts at different volume concentrations (0, 10, 20, 50, and 100 vol%), and the toxicity of RAW 264.7 cells was determined at 6, 12, 24, and 48 h. As shown in Figure S14 (Supporting Information), as the culture time increases, the conductive hydrogel has little toxicity on cells. The inhibition rate of the conductive hydrogel at the highest concentration on RAW 264.7 cells after 48 h was only 12%. These results indicate that TA@HAP NWs-PVA(W/EG) hydrogel has excellent biocompatibility and can be in contact with the human body for a long time.

3. Conclusion

We synthetized TA-coated biomass HAP NWs, which were evenly dispersed in the PVA network and showed the enhanced mechanical properties. Meanwhile, the molecular level ion water channel constructed by the binary solvent and the chelation of TA and metal cations can realize the rapid diffusion of ions during the straining process, thereby greatly improving the sensing sensitivity. It is worth mentioning that the conductive hydrogel has sensing performance for a variety of physical quantities (tensile strain, pressure, and temperature). There is a linear response relationship in strain sensors, pressure sensors and temperature sensors. In particular, the strain sensor has high sensitivity within a wide strain range (GF = 2.84), high cycle stability, and fast response (~50 ms). Simultaneously, the hydrogel-based strain sensor can be used to monitor large strains such as human joints, and it also has excellent sensitivity to facial microexpressions. In addition, the TA@HAP NWs filler has a suitable nanometer size (size effect) with the function of absorbing ultraviolet light waves. It can reflect and absorb shorter ultraviolet light waves and transmit longer visible light waves to achieve transparency and UV-filtering. A network of hydrogen bonds...
was formed among EG molecules, PVA molecular chains and water molecules, which leads to a strong water-locking effect. Therefore, TA@HAP NWs-PVA(W/EG) hydrogel can realize the functions of low temperature anti-freezing and moisture retention. Importantly, TA@HAP NWs-PVA(W/EG) hydrogel has excellent biocompatibility, which allows it to be in long-term contact with human skin or tissue. In summary, this new type of conductive hydrogel can achieve the purpose of medical protection and human motion detection in harsh environments. We believe that this new hydrogel design idea paves a new development path for flexible wearable sensors and ionic skin.

Supporting Information
Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest
The authors declare no conflict of interest.

Data Availability Statement
Research data are not shared.

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