In this study, a binary networked conductive hydrogel is prepared using acrylamide and polyvinyl alcohol. Based on the obtained hydrogel, an ultrastretchable pressure sensor with biocompatibility and transparency is fabricated cost effectively. The hydrogel exhibits impressive stretchability (>500%) and superior transparency (>90%). Furthermore, the self-patterned micro-architecture on the hydrogel surface is beneficial to achieve high sensitivity (0.05 kPa⁻¹ for 0–3.27 kPa). The hydrogel-based pressure sensor can precisely monitor dynamic pressures (3.33, 5.02, and 6.67 kPa) with frequency-dependent behavior. It also shows fast response (150 ms), durable stability (500 dynamic cycles), and negligible current variation (6%). Moreover, the sensor can instantly detect both tiny (phonation, airflowing, and saliva swallowing) and robust (finger and limb motions) physiological activities. This work presents insights into preparing multifunctional hydrogels for mechnosensory electronics.

1. Introduction

Electronic skins (E-skins) refer to electronic devices that mimic the flexible and sensory performance of human skins by transducing various external stimuli into electrical signals. They are receiving increasing attention due to their potential applications in smart clothing, biomedical prosthetics, robotics, and so on.1–5 Particularly, skin-like pressure sensors which can detect various external stimuli into electrical signals. They are receiving increasing attention due to their potential applications in smart clothing, biomedical prosthetics, robotics, and so on.1–5. Among their other applications in engineering scaffolds, drug delivery, soft actuators, energy conversion, and so on, due to their high stretchability, bio-compatibility, and environmental-friendliness.15–18 For example, Tai and Yang prepared ionic hydrogel-based pressure sensor for human motion detection.19 Wan and co-workers reported highly stretchable hybrid hydrogels based on cellulose nanocrystals and ferric ion.20 However, single networked hydrogels usually present undesirable elongation and unstable electrical behavior because of the unsatisfactory mechanical properties. Among the methods to increase both the sensing performance and mechanical properties, the construction of binary or trinary networked hydrogels has been demonstrated as an effective approach.21,22 Besides, another strategy is to fabricate microstructured patterns on the surface of the hydrogel film, for instance, wrinkled design has been demonstrated to enhance the sensitivity and stimuli-responsive behaviors.23–27 In addition, the microarchitectures can increase the skin-conformability and the signal-to-noise ratio (SNR) of hydrogels, which enable exquisite sensing and good adhesion on the human skin.28 On the other hand, excellent transparency is still difficult to achieve for hydrogel-based sensors because of the addition of chemicals, such as graphene and carbon nanotubes.29,30

Herein, we have prepared a highly stretchable, biocompatible, and transparent double-networked hydrogel with self-patterned surface microstructure to assemble into a pressure sensor. To form robust and vigorous hydrogel, rigid conductive polymer networks and soft polymer chains entanglement via supramolecular interactions were incorporated. Acrylamide (AM) and polyvinyl alcohol (PVA) were chosen to build the binary networked structure crosslinked by N,N-methylenebisacrylamide (MBAA). The mechanically compliant hydrogel can be stretched up to 500% without breakage. The hydrogel also demonstrates...
excellent adhesiveness and high transparency (>90%). The hierarchically wrinkled microarchitectures and interconnected ridges on the self-patterned hydrogel surfaces can increase the contact area significantly, which endows the hydrogel-based pressure sensor with high sensitivity (0.05 kPa$^{-1}$ for 0–3.27 kPa) and precise sensing capability of dynamic pressures (3.33, 5.02, and 6.67 kPa). It also exhibits fast response (150 ms) and reliable durability up to 500 loading/unloading cycles. Moreover, the versatile hydrogel-based pressure sensor can successfully detect phonation signals, airflow monitoring, and limb motions with high stability and high signal-to-noise ratio.

2. Results and Discussion

The highly stretchable and transparent PVA-polyacrylamide (PAM) hydrogel was prepared through a sol–gel process, which involves in situ polymerization of PAM and formation of PVA-based physically crosslinked network, as shown schematically in Figure 1a. Upon dissolving PVA powder in hot water under agitation, AM monomer was added into the as-prepared solution, followed by addition of chemical crosslinker MBAA and oxidizer ammonium persulfate (APS). Afterward, potassium chloride and N,N,N',N'-tetramethylethylenediamine (TEMED) were added to enhance the conductivity and increase the reaction rate. To form covalent crosslinking, the hydrogel precursor solution was poured into a petri dish and subsequently degassed in a vacuum drier and then exposed to UV light in a dark chamber. After crosslinking for 120 min, the monolithic hydrogel was peeled off from the petri dish and rinsed several times with deionized (DI) water. Hydrogels with different PVA loadings (5, 10, and 15 mg mL$^{-1}$) were synthesized and tested to investigate the influence of composition on its mechanical properties. Covalent crosslinking between PAM long chains helps build tough networks within the hydrogel.$^{[31]}$ In addition to chemical crosslinking, physical crosslinking
comprising node interconnections and hydrogen bonds also play important roles in the tensile performance.\textsuperscript{[20]}

Rigid and robust networks can be generated when the hydrogel precursor was exposed to ultraviolet radiation during the sol–gel process (Figure S1, Supporting Information). The stretchability of the prepared hydrogel is denoted as strain ($\varepsilon = \Delta L / L_0 \times 100\%$), where $\Delta L$ is the length variation upon tensile force and $L_0$ is the original length. As shown in Figure 1b,c, the conductive hydrogel can be stretched up to 400% strain, which is advantageous to many reports.\textsuperscript{[32–34]} Furthermore, the robust hydrogel can even endure a heavy weight of up to 100 g without obvious shape variation (Figure 1d). To further explore the compressive behavior of the hydrogel, finger pressing was exerted to apply deformation on the monolithic hydrogel and 44% compression strain was obtained (Figure S2, Supporting Information). The transparent hydrogel film shows excellent adhesion and toughness on the human epicuticle (Figure 1e), suggesting great potential in practical applications, such as human motion detection. Especially, the freeze-drying treated hydrogel (Figure S3a,b, Supporting Information) can recover to original shape after reabsorbing water for 6 h (Figure S3c, Supporting Information), demonstrating the structural integrity of the polymer matrix within the hydrogel. The unique binary networks composed of both chemically and physically crosslinked segments contribute to the high stretchability, as illustrated in Figure 1f. Specifically, the polymer long chains are randomly coiled within the networks without deformation. Under tensile strain, the dynamic and reversible interactions could increase the flexibility of the network through unwrapping and sliding of polymer chains to dissipate energy.\textsuperscript{[35]} Moreover, the chemical crosslinking between PAM also increased the stretchability of the binary networked hydrogels. Upon tensile force relaxation, the hydrogen bonds between heterogeneous components and twisting chains could recover to the original condition, contributing to a mechanically reversible process.

The sol–gel method holds the potential of cost-effective and large-scale preparation of hydrogel films. As illustrated in Figure 2a, an ultratransparent thin hydrogel film ($\Phi$ 9 cm) was prepared. Scanning electron microscope (SEM) characterization (Figure 2b) reveals that the hydrogel surface possesses uniform self-patterned microstructures containing numerous 3D protruding microchannels with widths 30–90 $\mu$m. This configuration resembles the spinosum microstructure of human epicuticle.\textsuperscript{[24]} These microchannels may result from solvent evaporation during the sol–gel process, which enhances the solution viscosity and forms air bubbles.\textsuperscript{[21]} The presence of the wrinkled microarchitectures and interconnected ridges on the rough surfaces can increase the contact area and sensitivity of the hydrogel-based sensor.

Since PVA molecules can interact with PAM long chains through hydrogen bonding in addition to the self-coiled structure, PVA concentration has great influence on the mechanical performance of hydrogel. As shown in Figure 2c, the increase of PVA content (5, 10, and 15 mg mL$^{-1}$) can increase both the stress and strain properties. In detail, pure PAM hydrogel presents maximal strain of 317.9% with a tensile stress of 88.3 kPa. PAM-PVA$_5$ (PVA, 5 mg mL$^{-1}$) hydrogel film possesses a strain of 469% with a tensile stress of 104.5 kPa, and the elastic modulus within linear ranges ($R^2 = 0.99$) is 62 kPa. The high flexibility is beneficial for shape variation and sensitivity.
enhancement compared to traditional rigid materials. The maximum strain of PAM-PVA$_{10}$ (PVA, 10 mg mL$^{-1}$) composite hydrogel can remain 500% with the tensile stress of 129.5 kPa, whereas the elastic modulus obtained is as high as 79 kPa. More importantly, the ruptured strain of PAM-PVA$_{15}$ (PVA, 15 mg mL$^{-1}$) hydrogel film is 488%, slightly lower than that of PAM-PVA$_{10}$. However, the tensile stress is 183.8 kPa, and the elastic modulus is 87 kPa. The addition of PVA to the PAM building blocks could dissipate enormous energy due to the synergistic effect within the binary networks. Nevertheless, the soft materials become rigid and stiff with massive PVA loading due to strong interactions of two components. The comparison between previous references and this work is presented in Table S1 in the Supporting Information.

Figure 2d exhibits the stress–time curve of the hydrogel film under dynamic tensile condition. Upon mechanical loading (0.63 N, 0.043 Hz), the composite hydrogel can respond accurately to the stretching-releasing deformation, implying remarkable stability. The inset depicts the stress variation upon applied strain within one stretching process. Most polymer-based materials present obvious mechanical hysteresis due to the viscoelastic effect resulting from the interactions of long molecule chains. However, our composite hydrogel film shows negligible mechanical hysteresis, which can improve the performance of sensing devices. Figure S4a in the Supporting Information depicts the mechanical performance under compressing force (8.54 N, 20 mm min$^{-1}$), it is clear that the hysteresis within one compression-recovery procedure is very low (Figure S4b, Supporting Information). In addition, low hysteresis is also presented in the stretching-recovery process (9.2% strain, 20 mm min$^{-1}$, Figure S5, Supporting Information).

Transmittance is of significant importance for wearable circuitry that requires visualization. Figure 2e shows the transmittance spectra of the hydrogel film in the visible range of the electromagnetic radiation spectrum (from 400 to 800 nm). The transmittance at 650 nm wavelength is 92%, which is beneficial for aesthetic visualization. Optical transparency and stretchability are preferable for wearable electronics. However, present materials and devices usually face a trade-off between the two properties. Figure 2f presents the comparison of our sensor with recently reported sensors in terms of transmittance and maximal strain performance. Clearly, our hydrogel-based sensor exhibits both high transparency and high strain performance.

The piezoresistive performance of hydrogel-based pressure sensors were evaluated using a custom-designed intelligent data-acquisition device containing electrical signal analyzer (Keithley 4200-SCS) and a computer-controlled dynamic positioning system (Figure S6, Supporting Information). The long-term monitoring of current output under fixed potential was conducted and shown in Figure S7 in the Supporting Information, a stable current output ($\approx 0.35$ µA, 1 V) can be continuously read (1155s) without obvious deviation, demonstrating the long-term stability of the sensor. Sensitivity is the paramount parameter for a pressure sensor which indicates the electrical response upon pressure and is defined as $S = \delta (\Delta I/I_0)/\delta P$, where $\Delta I$ is the current variation under certain pressure, and $P$ is the pressure loading. The sensitivity of our hydrogel-based pressure sensor is 0.05 kPa$^{-1}$ below 3.27 kPa ($R^2 = 0.95$), and 0.02 kPa$^{-1}$ in the range of 3.27–6.83 kPa ($R^2 = 0.99$), as shown in Figure 3a. The performances of recently reported pressure sensors based on conductive hydrogels are summarized in

![Figure 3. a) Relative current variation versus pressure for the pressure sensor. b) Relative current variation as function of time under different pressures (3.33, 5.02, and 6.67 kPa). c) The frequency-dependent behavior of the pressure sensor under various frequencies (0.24, 0.36, and 0.45 Hz). d) The electrical deviation of the pressure sensor under high dynamic pressure (5.35 kPa). e) The response time of pressure sensor upon pressure on/off. f) The stable current output after application of cyclic pressure.](image-url)
Table S2 in the Supporting Information. Figure 3b shows the current response profiles ($\Delta I/ I_0 (%)$) of the sensor under different pressure at 0.27 Hz. Larger pressure can generate more significant change in conductive pathways, so the current variation was more obvious. Figure 3c demonstrates the frequency-dependent behavior of the pressure sensor. Durable and stable electrical waveforms were obtained upon 1.57 kPa with frequency ranging from 0.24 to 0.45 Hz.

Figure 3d depicts the current variation curve under dynamic pressures (5.35 kPa, 2.31 Hz). Note that 6% deviation is presented in the long-term loading–unloading process. It can be attributed to the inherent viscoelasticity of the polymer-based hydrogel, which causes molecular chain sliding and signal hysteresis upon high pressure. Despite signal deviation, the current profiles were similar. To further explore the effect of pressure on electrical hysteresis, three pressures were imposed on the hydrogel-based sensor (Figure S8, Supporting Information). Small deviation emerged under high pressures. The response time was measured to be around 150 ms and no obvious hysteresis to external stimuli (Figure 3e), which is close to that of human skin ($\approx$100 ms).[49] Stability and durability are two crucial properties for the long-term stability of wearable electronics. Almost consistent current output under 5.63 kPa can be observed within 500 cycles (Figure 3f). The current initially increased after the hydrogel exposed to cyclic pressure because the spacing between conductive channels decreased under pressure. However, irreversible mechanical destruction and water evaporation under repeated application and releasing of pressure can impede the percolation of conductive pathways, which decreased the current after certain pressure cycles.

External pressure can induce resistance decrease due to the diminution of thickness (Figure S9, Supporting Information). The configuration of the sensor under applied pressure is depicted in Figure S10 in the Supporting Information and the total resistance of the device is composed of electrode resistance $R_e$ ($R_{e,1}$ and $R_{e,2}$), hydrogel film resistance $R_f$ and contact resistance $R_c$ ($R_{c,1}$ and $R_{c,2}$)

$$R_{\text{total}} = R_e + R_f + R_c$$  \hfill (1)

Since $R_c$ is much bigger than $R_e$ ($R_c \gg R_e$), and $R_c$ presents more obvious variation in current, the above equation can be simplified as $R_{\text{total}} \approx R_c$. A tiny force can generate huge flattened deformation on the self-patterned surface of the hydrogel film to increase the number of conductive pathways (Figure S11, Supporting Information). Furthermore, the rugged and complicated surfaces with wrinkled microchannels can significantly enhance the sensitivity because the spinosum-like microstructure could provide more contact sites compared to a flat pattern. However, the resistance variation shows tiny change under higher pressure due to the limited contact of conductive ions within the hydrogel. A higher current value can be induced under pressure as shown by the increased brightness of a red light-emitting diode (Figure S12, Supporting Information).

Wearable and flexible sensors are urgently needed for human–machine interactions and detection of physiological signals, including phonation and epicuticle vibration. To demonstrate this potential, the as-prepared hydrogel-based pressure sensor was tested to differentiate the pronunciation of various English words, such as “sensor” and “Institute of Advanced Materials (IAM)” (Figure 4a,b). The sensor showed

![Figure 4. Photographs of pressure sensor used for the detection of tiny human motions: voice recognition of a) “Sensor” and b) “IAM”. c) Blowing process. d) Saliva swallowing process.](image)
similar stable current pattern when the same word was repeated three times, and unique waveforms with characteristic peaks were found for different words, indicating the capability of our sensor for voice recognition and phonation rehabilitation. Figure S13 in the Supporting Information depicts the current variation upon pronouncing "hydrogel". Furthermore, the sensor was capable of detecting the gentle blowing process as well as tiny epicuticle vibrations related to saliva swallowing (Figure 4c,d).

Besides pressure, the flexible sensor also responds to twisting and stretching deformations (Figure 5). Notably, distinctive current–time curves with high signal-to-noise ratio were observed for each mechanical stimulus, proving high reliability and sensitivity of the sensor. The high performance of the pressure sensor can be partially attributed to the self-patterned microstructure on the hydrogel surface. Moreover, the sensor can differentiate the degree of pressing forces (Figure 5a), and it possesses excellent limit of detection as shown in Figure S14 in the Supporting Information.

Apart from tiny human movements, large-scale human motions such as motions of limbs can also be monitored in real time by the hydrogel-based pressure sensor (Figure 6). The sensor was attached onto the back of hand to monitor the motion of fist (Figure 6a). The “M”-like profile with high signal-to-noise ratio in the curve illustrates the grasping and unfolding motions of the hand. The “V” shape of the curve in Figure 6b corresponds to the bending process of the index finger and the current variation extent is related to the degree of finger bending. Furthermore, the hydrogel-based pressure sensor can also monitor elbow stretching-releasing and knee squatting-arising motions (Figure 6c,d). These curves show complicated profiles because of the sensitivity of the sensor toward mechanical motions.

**Figure 5.** Photographs of the current variation in response to finger movements: a) pressing, b) twisting, and c) stretching.

**Figure 6.** a) Current response during making a fist. b) Current output during bending of a finger. c) Current–time curve during elbow motion. d) Current–time curve due to the squatting-arising motion of the human knee.
3. Conclusion

In summary, a highly stretchable (>500%) and transparent (>90%) binary hydrogel has been constructed via in situ polymerization of PAM networks and physical reinforcement of interconnected PVA long chains. This one-step synthetic procedure holds the potential of cost-effective and large-scale preparation. The unique wrinkled spinosum-like structure with microchannels on the hydrogel surface contributes enormously to the impressive stretchability as well as to the increased sensitivity of the sensor. Furthermore, the hydrogel-based pressure sensor presents reliable piezoresistive behavior under dynamic pressures (3.33, 5.02, and 6.67 kPa). Tiny electrical deviation (6%) could be observed due to the viscoelasticity of the hydrogel. The sensor shows fast response (150 ms), which is comparable to the human skin. The sensor exhibits stable and reliable electrical performance up to 500 cycles. Moreover, the hydrogel-based sensor can be used to monitor various human motions, including phonation, swallowing process, finger movements and limb activities, showing great potential for electronic skins (E-skins), soft robotics, biomimetic, and artificial intelligence.

4. Experimental Section

Materials: AM (99%), MBAA, APS, and TEMED were purchased from Sigma-Aldrich. PVA and potassium chloride were purchased from Adamas. All chemicals were used directly without purification.

Synthesis of PAM-PVA Conductive Hydrogel: The highly stretchable and transparent PAM-PVA hydrogels were prepared by in situ polymerization of AM into conductive networks reinforced by PVA chains. Typically, 50 mg PVA in 10 mL of DI water was stirred and heated for 2 h (60 °C) to dissolve PVA. AM (8 wt%), MBAA (0.02 wt%), and APS (0.01 wt%) were mixed in 10 mL of cooled PVA solution under magnetic stirring. To enhance the conductive and piezoresistive performance, potassium chloride (3.5 wt%) was added into the solution.

Before preparing hydrogel films, the mixed solution was placed in a vacuum drier to eliminate air bubbles. After 5 min, TEMED was added to the as-mentioned mixed solution to prepare hydrogel precursor solution. In this reaction system, MBAA was the chemical crosslinker for the formation of AM networks and TEMED acted as accelerator for crosslinking reaction. Thereafter, the reaction precursor solution was poured into a petri dish mold (Φ 55 mm) and exposed to ultraviolet light (BILON-ZCW-1000W) in a dark chamber to trigger cross-linking reaction. After 120 min, a free-standing and highly transparent hydrogel film (Φ 55 × 1.5 mm) was peeled off from the petri dish mold. For large-scale preparation of hydrogel film, a large petri dish mold (Φ 90 mm) was utilized. Care needs to be taken that no vibration occurred during the crosslinking reaction to ensure formation of homogeneous, free-standing, and thin hydrogel films. For further characterization and testing, the thin composite hydrogel membrane was cut into the size of 20 mm × 8 mm × 1.5 mm. Hydrogels with different PVA concentrations (5, 10, and 15 mg mL⁻¹) were fabricated by altering the PVA loading.

Fabrication of Pressure Sensors: The free-standing hydrogel films were cut into strip-like samples. Before manufacturing resistive-type pressure sensors, the hydrogel films were blown by hair drier for 10 min to blow away the residual impurity and improve the mechanical performance. Afterward, two conductive copper wires were tightly adhered to the opposite ends of the stretchable hydrogel films to assemble electrodes. Finally, two pieces of semitransparent adhesive tapes were utilized to encapsulate the hydrogel film into a sandwich-like pressure sensor. Adhesive tapes could minimize the interference from the ambient environment to obtain stable current signals.

Supporting Information

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

Acknowledgements

The work was supported by the National Natural Science Foundation of China (61525402, 61775095, 61728401, and 61775089), Natural Science Funds for Young Scholars of Jiangsu Province (BK20170999), National Postdoctoral Program for Innovative Talents (BX201600072), and Industrial Alliance Fund of Shandong Provincial Key Laboratory (SDKL2016038).

Conflict of Interest

The authors declare no conflict of interest.

Keywords

human motion detection, hydrogels, pressure sensors, stretchable sensors, transparent sensors

Received: April 16, 2018
Revised: May 19, 2018
Published online: June 21, 2018
