Catechol/Pyrogallol-Modified Chitosan Composite Conductive Hydrogel as Strain Sensor for Human Movement Monitoring

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Summary: Conductive hydrogels have great application and development value in the field of functional materials including flexible wearable devices, electronic skin and health detectors. Herein, chitosan (CS) was firstly modified with 3,4-dihydroxybenzaldehyde and 2,3,4-trihydroxybenzaldehyde, respectively, through the Schiff base reaction and $NaBH_3CN$ reduction, and the resulting products (CCS and PCS) with improved water solubility were then used as the cross-linking agents for polyvinyl alcohol (PVA) to fabricate the corresponding CCS/PVA and PCS/PVA composite hydrogels through the freezing-thawing method. $AlCl_3$ was further introduced into the two composite systems to give the hydrogels good conductivity. As flexible strain sensors, both CCS/PVA/$AlCl_3$ and PCS/PVA/$AlCl_3$ hydrogels could monitor human movements such as finger bending, wrist rotation, elbow bending, foot rotation and nodding. In addition, the conductive hydrogels can also respond regularly to small facial movements such as mouth opening-closing cycle and frowning. In general, the present CCS/PVA/$AlCl_3$ and PCS/PVA/$AlCl_3$ conductive hydrogels are expected to have good application prospect in smart wearable devices and other functional fields.

Keywords: Chitosan; Catechol; Pyrogallol; Conductive hydrogel; Strain sensor; Movement monitoring.

Introduction

In recent years, inspired by biosensors that can convert external stimuli into bio-electronic signals to neurons, brains and muscles, many strain sensors based on soft conductive materials have been developed. The application of strain sensors in wearable devices, flexible robots and artificial skin has attracted great research attention [1-3].

In the strain sensor system, the elastomer acts as a flexible matrix to deform the network of conductive fillers, which leads to the change in its conductivity and resistance, so external pressure and strain are converted into electronic outputs. The performance of a strain sensor usually depends on the performance of its matrix and network and the connection between them. Compared with the traditional sensors based on the rigid semiconductors, metals and ceramics [4], elastomers have advantages in stretchability, which is of great significance for the application of strain sensors in the wearable field [5-7]. However, the elastic body in the strain sensor must have a low modulus close to that of biological tissue, and the conductive filler and the elastic body also needs good compatibility, which are huge challenges for the research of the strain sensor.

Hydrogel is a kind of soft substance with a three-dimensional network structure and rich water content, which can maintain a certain shape in water but not be dissolved by water. It exhibits excellent water absorption, water retention and gel stabilities, and can be used as a good matrix, carrier or skeleton for functional soft materials, which is an ideal material for future flexible electronic devices [8-10]. Conductive hydrogel is a new type of composite hydrogel with good processability, high flexibility and excellent electrochemical performance due to the organic combination of hydrophilic matrix and conductive medium. It is often used in electronic skin, biological sensors, supercapacitors, flexible wearable electronic devices and many other fields, and has broad application prospects [11-17]. For example, Liu et al. constructed a multifunctional double network (DN) hydrogel through the host-guest interaction between β-cyclodextrin and ferrocene and the dynamic borate bond between polyvinyl alcohol (PVA) and borax, and carbon nanotubes was used to impart conductivity to the DN hydrogel. The obtained DN hydrogel has good biocompatibility, tensile ability (436%), breaking strength (41.0KPa), self-repairing ability (repair efficiency of 95%) and high tensile strain sensitivity (specifications). The coefficient is 5.9) [2].

For the strain sensors, adhesion is an important performance that can expand its application range and scenarios. There is a kind of mollusk in the ocean called mussels, and this kind of animal can express protein containing a special amino acid (3,4-dihydroxytyrosine), which can make the mussels tightly adsorb on different places such as rocks and wood [18,19]. Scientists found that modification of molecules with catechol structure to biomass can improve its water solubility, and give it adhesion, etc. [20]. In other words, modifying biomass with polyphenols and applying it to flexible electronic materials can give the materials well adhesion, greatly improve the application range and environment of flexible electronic materials, and compared with other macromolecular structures for modification, the use of small molecules with catechol or pyrogallol structures for modification has the advantages of small steric hindrance, simple reaction, short reaction time, and low price [21-22].

Derived from the exoskeleton of the cell walls of crustaceans, insects and fungi, chitosan (CS) is a deacetylation product of chitin, and because of its good biocompatibility, non-toxic, degradable, antibacterial and antioxidant properties, it has become a research hotspot in recent years [23,24]. As the solubility of chitosan in water is extremely low, which limits the formation of its gel, it is particularly important to chemically modify CS with hydrophilic groups to develop water-soluble CS derivatives. In recent years, there have been several reports on the modification of CS with catechol structure and pyrogallol structure [25-29]. The side chain of CS modified by polyphenols is rich in phenolic hydroxyl groups, which can coordinate to metal ions, such as Al^{3+}, Fe^{3+} et al. Therefore, we can use the coordination of metal ions and phenolic hydroxyl groups to form crosslinking to prepare hydrogels. Since the crosslinking is dynamic, it can give the hydrogel a certain degree of self-healing, pH responsiveness and ionic conductivity, so it has a good application prospect [30-33].

Here, we used 3,4-dihydroxybenzaldehyde and 2,3,4-trihydroxybenzaldehyde, which have the polyphenol structure, to respectively modify CS, and using the Schiff base reaction and $NaBH_3CN$ reduction methods, we got the modified CS products CCS and PCS, and verified the modification results using the ^{1}H NMR and infrared spectroscopy. Subsequently, by blending the modified CS products with PVA, adding $AlCl_3$ to give the hydrogel conductivity, and using the cyclic freezing and thawing method [3], we prepared two kinds of the composite hydrogels named as $CCS/PVA/AlCl_3$ and $PCS/PVA/AlCl_3$. Because both CCS and PCS can form multi-point hydrogen bonds with PVA, the crosslinking density of the hydrogel system was increased, thereby increasing the tensile strength and elongation at break, and because of the modification effect of polyphenols on CS, the hydrogels exhibited good adhesion, and can adhere to human skin, glass, plastics, metal steel and other substances. Finally, by using the composite hydrogels to prepare strain sensors, we found that both hydrogels could well monitor human movements such as finger bending, wrist rotation, elbow bending, foot rotation, and nodding. Notably, the composite hydrogels can also respond regularly to small facial movements such as mouth opening-closing cycle and frowning. In short, CCS and PCS composite hydrogels have the advantages of wide sources of raw materials, low price, and environmental protection, etc. The prepared strain sensors have good mechanical properties and electrical conductivity, which will have good application prospects in smart wearable devices and other fields in the future.

Experimental

Materials

Chitosan (M.W. ca. 100000-500000), polyvinyl alcohol 1799 (PVA, 95.5-96.5% hydrolyzed), 3,4-dihydroxybenzaldehyde, 2,3,4-trihydroxybenzaldehyde and $AlCl_3$ were provided by Chengdu Kelong Chemical Reagent Factory (Chengdu, China).

Instrument

FT-IR spectra were recorded using an ATI Mattson Genesis series FT-IR spectrophotometer in the range of 400-4000 cm^{-1}. ^{1}H NMR spectra were recorded using a Bruker AV II-400 MHz spectrometer at 25 °C and tetramethylsilane was applied as the reference to give the chemical shifts in parts per million (δ, ppm). Differential scanning calorimetry (DSC) curves were obtained using DSC214 (Netzsch, Germany) and the hydrogel sample was heated from 40 °C to 220 °C at a heating rate of 10 °C /min under N_2 atmosphere.

Synthesis of CCS and PCS

CS (0.1 g, 0.62 mmol, 1 equiv) in 40 mL acetic acid solution (1%, w/w) was heated at 50 °C for 30 min to get the transparent solution. 3,4-Dihydroxybenzaldehyde (0.27 g, 1.95 mmol, 3

equiv) dissolved in 10 mL dimethylformamide (DMF) was then added dropwise into the solution, and stirred for 7 h at room temperature (r.t., 25 °C or so). After that, NaBH₃CN (0.3 g, 4.76 mmol, 8 equiv) dissolved in 10 mL deionized water was injected into the resulting mixture, and further stirred at r.t. for another 7 h. The obtained solid product was dissolved in 100 mL hydrochloric acid (HCl) solution (1%, w/w), and the resulting solution was dialyzed against 1% HCl solution for 2 days, followed by the dialysis against deionized water for 2 days. The freeze drying was finally conducted to get the final catechol-modified chitosan (CCS, 0.16g). Similar procedure was used to synthesize the pyrogallol-modified chitosan (PCS, 0.17g) using 2,3,4-trihydroxybenzaldehyde (0.3 g, 1.95 mmol, 3 equiv).

Preparation of hydrogels

PVA solution (10%, w/w) was prepared by heating PVA particles in deionized water at 95 °C for 2 h. CCS (0.03 g, 0.06 g or 0.12 g) was added into 5 mL of the PVA solution, and heated at 95 °C for 1 h to get the transparent mixed solution that was poured into a mold for cooling. The mold was placed at r.t. overnight to remove the foams. Then the mold containing PVA and CCS was frozen at -20 °C for 8 h, and thawed at r.t. for 2 h. This freezing-thawing cycle was repeated two times to get the final CCS/PVA hydrogel. The same procedure was adopted to prepare the PCS/PVA hydrogels and the amount of PCS used were 0.03 g, 0.06 g and 0.12 g, respectively. For the preparation of conductive hydrogels, 50 mg AlCl₃ was added into each solution, and the resulting hydrogels was named as CCS/PVA/AlCl₃ and PCS/PVA/AlCl₃, respectively. Table-1 shows the detailed compositions of the prepared various hydrogels.

Table-1: The compositions of the prepared various hydrogels.

Sample	CCS (g)	PCS (g)	H₂O (mL)	PVA (g)
0.5% CCS/PVA	0.03	–	5	0.05
1% CCS/PVA	0.06	–	5	0.05
2% CCS/PVA	0.11	–	5	0.05
0.5% PCS/PVA	–	0.03	5	0.05
1% PCS/PVA	–	0.06	5	0.05
2% PCS/PVA	–	0.11	5	0.05
PVA	–	–	5	0.05

Characterization of hydrogels

The adhesion strength, tensile strength and elongation at break of hydrogels were recorded using a universal materials test machine (INSTRON5967, America). The size of hydrogel sample was 75 mm × 5 mm × 3 mm, and the extending rate was fixed at 20 mm min⁻¹.

An electrochemical workstation (CHI760E, China) was used to record the electrical signals of CCS/PVA/AlCl₃ and PCS/PVA/AlCl₃ sensors. The size of hydrogel sensor was 75 mm × 5 mm × 3 mm, and its relative resistance change was determined by using the equation of $\Delta R/R_0$ (%) = $(R-R_0) \times 100/R_0$. In this equation, R_0 is the resistance of sensor without strain, while R is the resistance of sensor with the applied strain. During the electrical tests, the testing voltage was fixed at 5 V.

Results and Discussion

Characterization of CCS and PCS

The synthesis routes of CCS and PCS are shown in Fig. 1. There are two reactions for the preparation of CCS and PCS. The first is the Schiff base reaction between the amino groups (-NH₂) of CS and the aldehyde groups (-CHO) of 3,4-dihydroxybenzaldehyde (or 2,3,4-trihydroxybenzaldehyde). The second is the reduction reaction by NaBH₃CN in which the C=N bonds were transferred into C-NH bonds. The successful formation of CCS and PCS was confirmed by their FT-IR and ¹H NMR spectra. As shown in Fig. S1, compared with the FT-IR spectrum of CS, both the FT-IR spectra of CCS and PCS provide new peak at 1530 cm⁻¹ that can be attributed to the stretching vibration of C=C bond in benzene ring. The appearance of this peak clearly confirms the successful grafting of catechol and pyrogallol structures to the side chains of CS. Results of ¹H NMR (Fig. S2) further confirm this point. In the ¹H NMR spectrum of CCS, the multiplet peaks at 6.6-6.9 ppm should be assigned to the protons in benzene ring, while the single peak at 4.16 ppm is attributed to the CH₂ protons close to the benzene ring. In the ¹H NMR spectrum of PCS, the peaks corresponding to the protons of benzene ring are found at 6.62 and 6.36 ppm, while the peak for the CH₂ protons close to the benzene ring is located at 4.19 ppm. Comparing the ¹H NMR spectrum of CS, we can draw a conclusion that the catechol and pyrogallol groups containing benzene ring were successfully grafted to the side chains of CS. Furthermore, the grafting rates were calculated by using the ¹H NMR spectra of CCS and PCS. Concretely, the integration for benzene protons at 6.6-6.9, 6.62 and 6.36 ppm were used to compare with the integration of C-2 protons at 3.0 ppm or so. The obtained grafting rates were 73% for CCS and 60% for PCS, respectively.
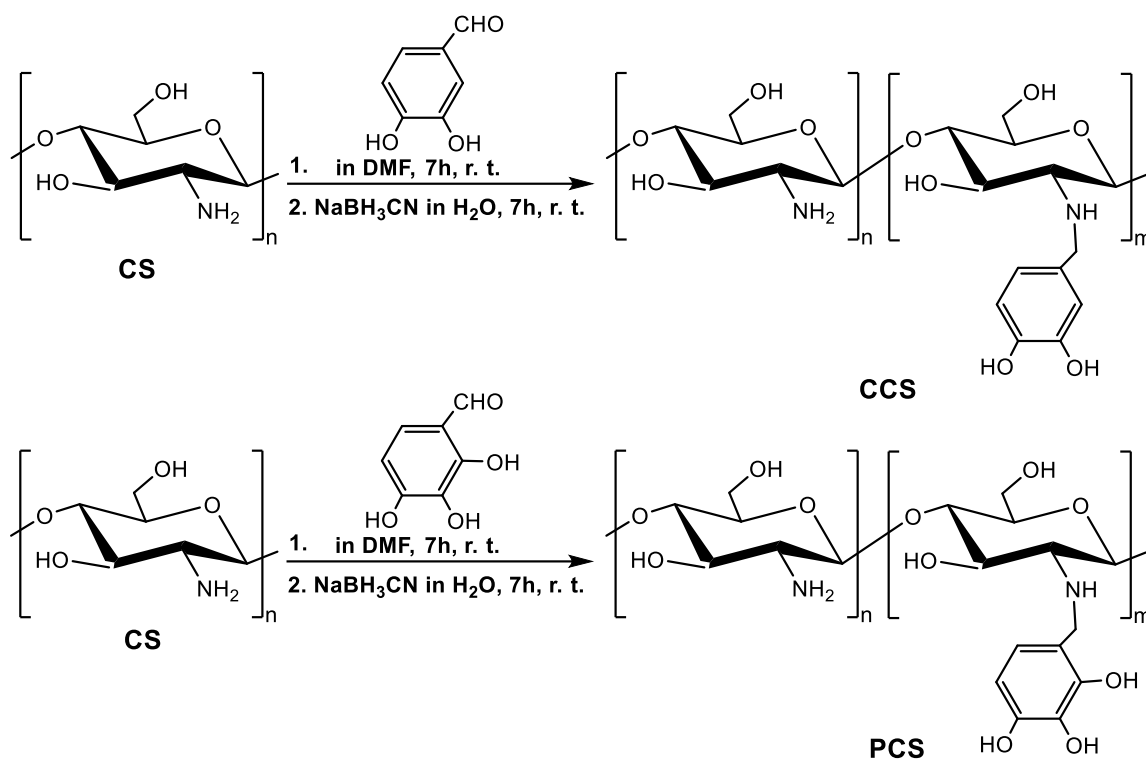
Fig. 1:   Synthesis routes of CCS and PCS.

Mechanical properties of CCS/PVA and PCS/PVA hydrogels

The tensile tests were carried out to investigate the influence of the dosages of CCS and PCS on the mechanical properties of the resulting composite hydrogels. Fig. 2 provides the tensile stress-strain curves of CCS/PVA and the control pure PVA hydrogels. The dosages of CCS were 0.5%, 1% and 2%, respectively. The pure PVA hydrogel showed the tensile strength of 0.14 MPa with the elongation at break of 280 %. The addition of CCS could improve both the tensile strength and the elongation at break of the resulting hydrogel. Concretely, when the dosage of CCS was 0.5%, the obtained CCS/PVA hydrogel has the tensile strength of 0.17 MPa with the elongation at break of 295%. The increase of CCS dosage to 1% led to the improved tensile strength (0.23 MPa) and prolonged elongation at break (300%) of the resulting hydrogel. When the dosage of CCS was further increased to 2%, the tensile strength and elongation at break were improved to 0.28 MPa and 400%, respectively. The increase in both the tensile strength and the elongation at break could be explained by the fact that CCS can increase the cross-linking density of hydrogel system owing to its multi-point hydrogen

bonding to the PVA chains. Especially, the ortho-phenolic hydroxyl groups in CCS could act as electron donors or receptors to form hydrogen bonds with the OH groups of PVA [3,22].
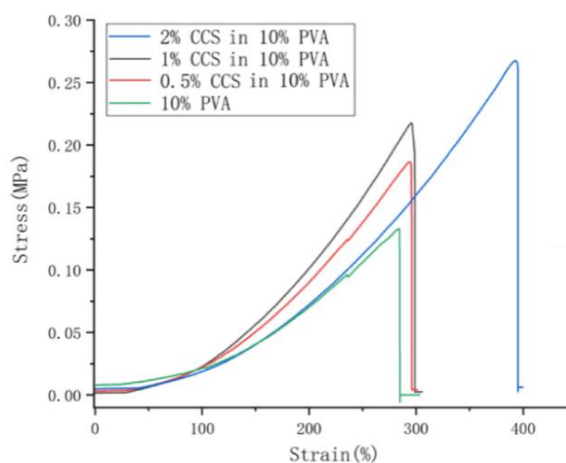

Fig. 2: The tensile stress-strain curves of CCS/PVA hydrogels.

PCS containing pyrogallol groups also has the similar influence on the mechanical properties of the resulting PCS/PVA hydrogels. Fig. 3 gives the tensile stress-strain curves of PCS/PVA hydrogels. When the dosage of PCS was 0.5%, the obtained PCS/PVA hydrogel has the tensile strength of 0.24 MPa with the elongation at break of 200%. When the dosage of PCS was increased to 1%, the tensile strength of the resulting hydrogel was improved to 0.36 MPa and its elongation at break was improved to 250%. When the dosage of PCS was further increased to 2%, the tensile strength of the resulting hydrogel was improved to 0.51 MPa and its elongation at break was improved to 290%. Notably, the addition of PCS could significantly improve the tensile strength of hydrogel, and the more the dosage of PCS used, the larger the tensile strength of the resulting hydrogel. However, compared to the pure PVA hydrogel, the PCS/PVA hydrogels with the low dosages (0.5% and 1%) of PCS have the decreased elongation at break, and only when the dosage of PCS was improved to 2%, the elongation at break of PCS/PVA hydrogel is comparable to that of pure PVA hydrogel. Like the case in CCS, there are multi-point hydrogen bonding between PCS and PVA. The phenolic hydroxyl groups in PCS could act as electron donors or receptors to form hydrogen bonds with the OH groups of PVA [3, 22].
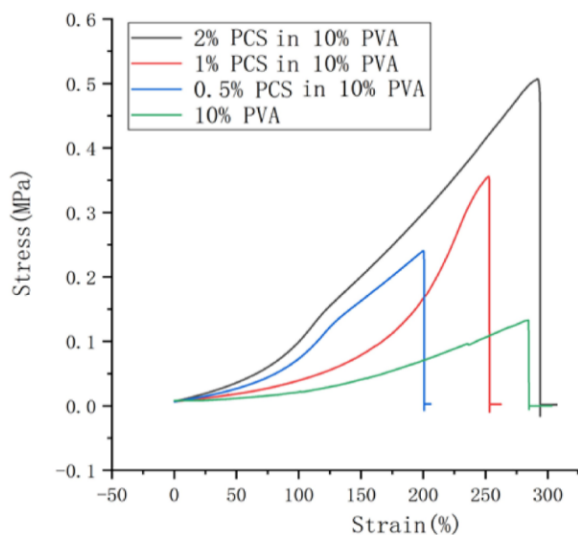

Fig. 3: The tensile stress-strain curves of PCS/PVA hydrogels.

For both CCS and PCS, the increased dosage (>2%) are tried, but they cannot totally be dissolved in the resulting system. Thus, the optimal dosages of

CCS and PCS were fixed at 2% to get the corresponding CCS/PVA and PCS/PVA hydrogels with the best mechanical property.

DSC of CCS/PVA and PCS/PVA hydrogels

Fig. 4 shows the DSC curves of PVA, CCS/PVA and PCS/PVA hydrogels. For each DSC curve, only one peak is observed in the temperature range of 40-200 °C, and can be assigned to the thermal denaturation temperature of PVA chains [11]. The peak temperatures are 113.0 °C for the pure PVA hydrogel and 114.3 °C for both CCS/PVA and PCS/PVA hydrogels. These results indicate that the multi-point hydrogen bonding between CCS (or PCS) and PVA is beneficial to improve the thermal stability of the resulting hydrogels.
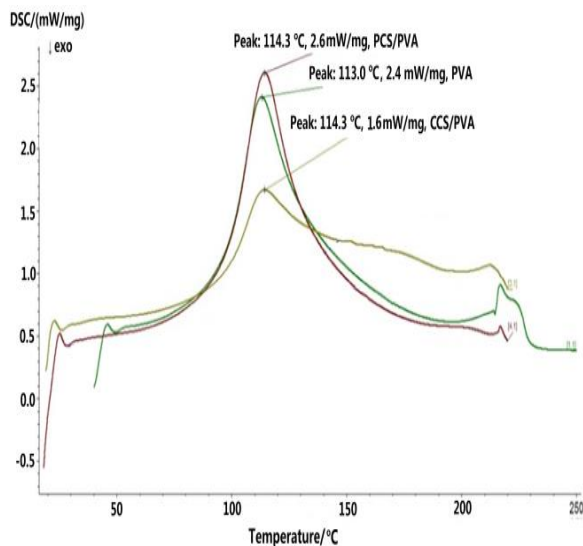

Fig. 4: DSC curves of PVA, CCS/PVA and PCS/PVA hydrogels.

Adhesion properties of CCS/PVA and PCS/PVA hydrogels

Owing to the presence of catechol structures in CCS and pyrogallol groups in PCS, the obtained CCS/PVA and PCS/PVA hydrogels are expected to have good adhesive properties, and the actual results also confirm this conjecture. As shown in Fig. 5, both CCS/PVA and PCS/PVA composite hydrogels can adhere to human skin, glass beaker, plastic culture dish, and metal steel ruler surface. It can be seen that for different types of substrates, both CCS/PVA and PCS/PVA composite hydrogels can exhibit strong

adhesion. The adhesion mechanisms of both CCS/PVA and PCS/PVA hydrogels could be attributed to the abundance of phenolic hydroxyl groups (-OH) in CCS and PCS. These groups can take place hydrogen bonding, hydrophobic interaction, and coordination bonding to different substrates [18-20]. In order to specifically quantify the adhesion strengths of the two hydrogels to these substrates, the tensile adhesion tests were carried out by using the lap shear testing method [14]. It can be seen from Fig. S3 that the adhesion strengths of CCS/PVA hydrogel to porcine skin, glass, plastic and steel are 2.1, 4.2, 5.6 and 4.7 kPa, respectively, while the adhesion strengths of PCS/PVA hydrogel are 2.2 kPa for porcine skin, 4.3 kPa for glass, 6.0 kPa for plastic and 4.9 kPa for steel. Overall, PCS/PVA hydrogel shows better adhesion strengths than CCS/PVA hydrogel, which is probably explained by the fact that PCS containing pyrogallol units possesses more phenolic hydroxyl groups than CCS bearing catechol structures. The feature of being able to firmly adhere to human skin also provides a practical basis for the subsequent application as strain sensors, thus they will not fall off due to the change in the motion amplitude when monitoring various types of motion, and this can also be proved by the subsequent motion monitoring images.
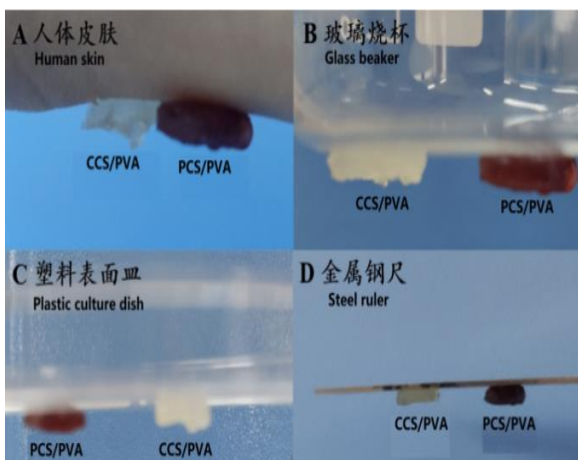

Fig. 5: Pictures showing the adhesive properties of CCS/PVA and PCS/PVA hydrogels.

Sensing properties of conductive CCS/PVA/AlCl$_3$ and PCS/PVA/AlCl$_3$ hydrogels

Both CCS/PVA/AlCl$_3$ and PCS/PVA/AlCl$_3$ conductive hydrogels have good stretchability and adhesion properties that are required to construct strain sensors. Among the materials for preparing hydrogels, we also chose materials such as CS and

PVA, which are relatively harmless to organisms. These all provide a basis for strain sensors with good comprehensive performance and a wide range of applications. And the introduction of AlCl$_3$ in the system gives the hydrogel with the key conductivity needed for strain sensors.

As shown in Fig. 6, we took PCS/PVA/AlCl$_3$ composite hydrogel as an example, and used it to conduct preliminary conductivity experiment. Connecting the composite hydrogel to an ordinary DC circuit containing a small bulb, the small bulb is lightened, and comparing with a bulb that is not connected to the circuit, it can be seen that the small bulb can still emit a clear green light in a bright environment. This phenomenon indicates that the PCS/PVA/AlCl$_3$ composite hydrogel possesses the conductivity required for strain sensors and can be used as a conductor. The same result was also obtained for the CCS/PVA/AlCl$_3$ composite hydrogel.
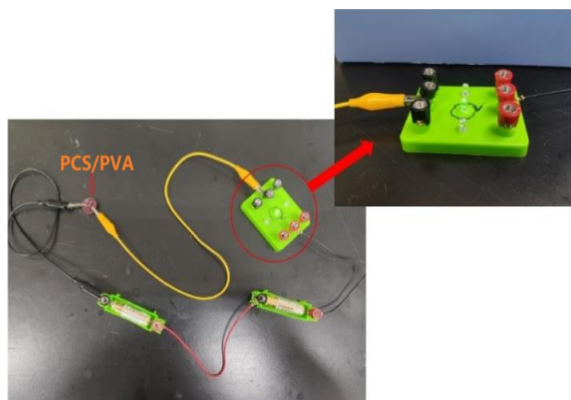

Fig. 6: Picture showing the conductivity of PCS/PVA/AlCl$_3$ hydrogel.

To quantitatively investigate their conductive properties, the electrical conductivities of CCS/PVA/AlCl$_3$ and PCS/PVA/AlCl$_3$ were tested by using the electrochemical workstation, and the obtained values are 3.197 S/m for hydrogel CCS/PVA/AlCl$_3$ and 3.019 S/m for hydrogel PCS/PVA/AlCl$_3$, respectively. These results are consistent with the above bulb-lighting experiment results, and further confirm that the two hydrogels do have good electrical conductivities.

Owing to the good electrical conductivity, stretchability and adhesion performance, PCS/PVA/AlCl$_3$ and CCS/PVA/AlCl$_3$ composite conductive hydrogels are expected to be used as strain

sensors for detecting human motions. Therefore, in order to prove that CCS/PVA/AlCl$_3$ and PCS/PVA/AlCl$_3$ composite conductive hydrogels have stable sensing performance, after comprehensively considering the mechanical strengths of the composite hydrogels, 2% CCS/PVA/AlCl$_3$ and 2% PCS/PVA/AlCl$_3$ composite conductive hydrogels were selected to test the sensing performance for different human motions at room temperature.

Gauge factor (GF) is usually used to assess the strain sensitivity of conductive hydrogels, and can be calculated by the ratio of the relative resistance change to the applied strain [2,3]. So, we measured the GF values of these two hydrogels. It can be seen that the GF value of CCS/PVA/AlCl$_3$ is about 1.53 (Fig. S4), while the GF value of PCS/PVA/AlCl$_3$ is about 1.85 (Fig. S5). The latter has slightly higher GF value than the former, which is probably attributed to the difference in coordination ability (with conductive Al^{3+} ions) of catechol and pyrogallol groups in these two hydrogels.

Due to the use of polyphenols to modify CS, the hydrogel materials itself have good adhesive ability, can directly adhere to the surface of the human body, and can feed back different electrical signals through the difference in the amplitude and mode of human motions. Fig. 7 and Fig. 8 show the use of CCS/PVA/AlCl$_3$ and PCS/PVA/AlCl$_3$, respectively, composite conductive hydrogels as strain sensors for monitoring human movement.

First, the sensing test of strain sensors' own cyclic pressing and cyclic stretching was carried out. It can be seen in Fig. 7A, 7B 8A and 8B that the strain sensor reflects the rapid, uniform and regular real-time resistance change resulted from the deformation of hydrogel sensors, and the cyclic resistance change graph also reflects that the strain sensor has the performance of cyclic use. In the subsequent experiments, the two strain sensors were further used to monitor the large and small motions of the human body.
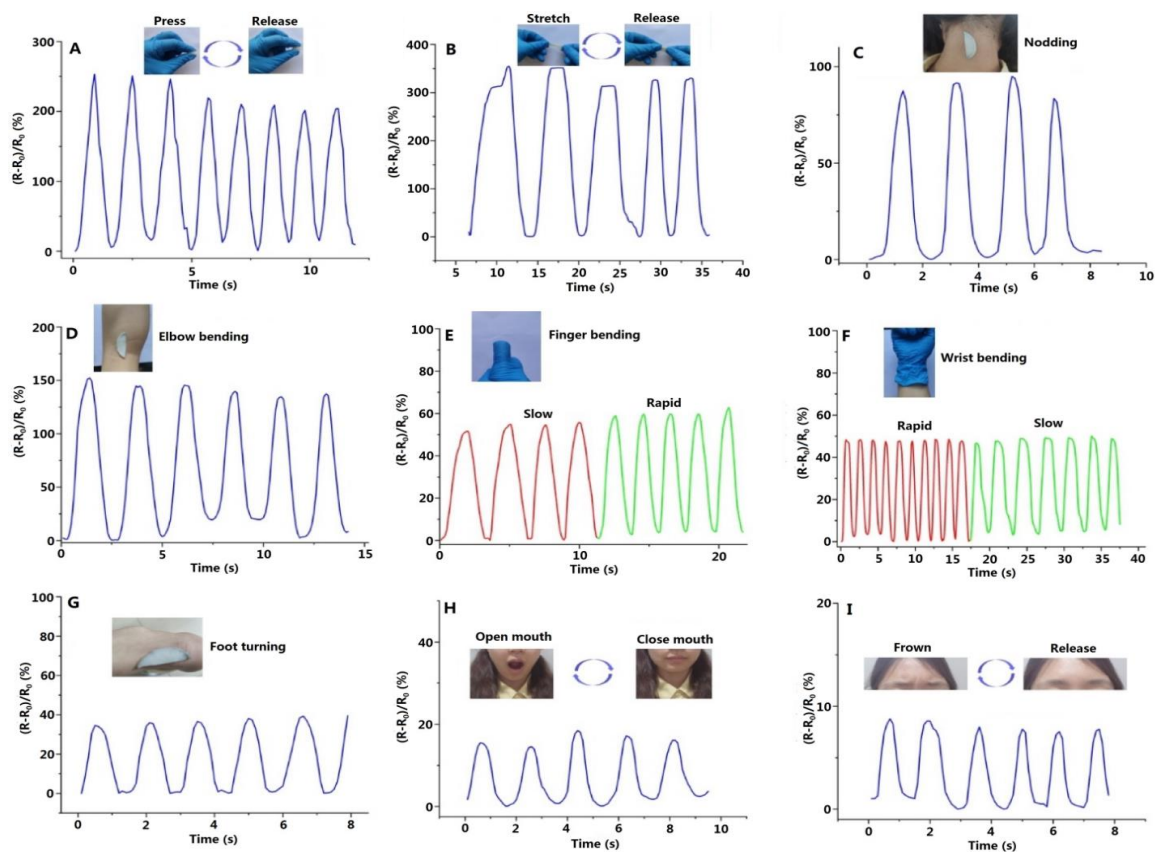

Fig. 7:   Real-time variation of the relative resistance when CCS/PVA/AlCl$_3$ hydrogel was used as sensor to monitor various human movements.

In large-scale motion monitoring, such as nodding (Fig. 7C and 8C), elbow bending (Fig. 7D and 8D), finger bending (Fig. 7E and 8E), wrist rotation (Fig. 7F and 8F) and foot rotation (Fig. 7G and 8G), both strain sensors show the rapid, real-time and specific resistance changes for these motions. For the same type of joint bending motion, the resistance change has a similar peak-shaped change curve, but for different types of motion, the obvious differences were observed in the magnitude of the relative resistance change, the frequency of the change, the peak value and the reaction time. These results show that the sensors are specific to the result feedback generated by different types of motion. In other words, the strain sensors have the function of specifically identifying exercise and giving exercise feedback, and have a wide range of application prospects in sports behavior monitoring and related sports diseases and the analysis of sports results of different groups of people.

In addition, we also used the two hydrogel sensors to monitor the small changes in the mouth-closing cycle (Fig. 7H and 8H) and the frowning face (Fig. 7I and 8I). The changes in the two types of movements are basically below 20%, which is also the result of the small-scale motion range. It can be seen that both flexible sensors show the good regular response to small changes in the human face. The monitoring of small movements can provide a corresponding practical basis for facial recognition and the expression and the analysis of human micro-emotions, and has a broad application value with the development of science and technology.
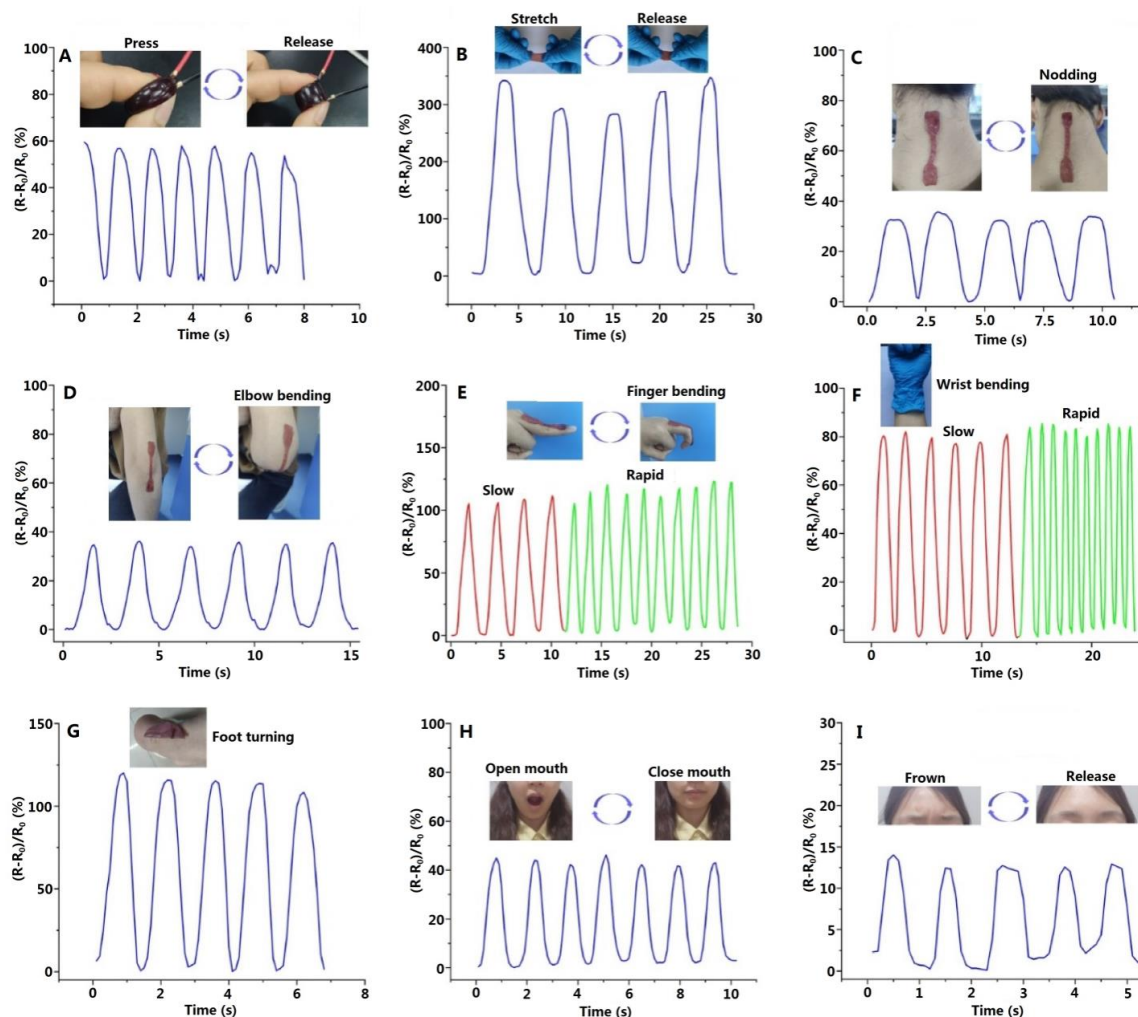

Fig. 8:   Real-time variation of the relative resistance when PCS/PVA/AlCl$_3$ hydrogel was used as sensor to monitor various human movements.

The sensing stabilities of the two hydrogel sensors were futher investigated. As shown in Fig. S6, we stretched CCS/PVA/AlCl$_3$ and PCS/PVA/AlCl$_3$ sensors about 200 cycles in 120 seconds, and their sensing curves were recorded. It can be seen that, during the process of 200-cycle stretching, the two hydrogel sensors always maintained sensitive and uniform response, and their relative resistance changes remained basically stable without excessive fluctuations. These results fully confirm their excellent sensing stabilities, which is related to their excellent mechanical properties and dense hydrogen bond structures [8,17].

In summary, using the two strain sensors, different motion types can be distinguished by the frequency, peak size, and characteristic points of the resistance change curves. The shape of the signal, loop results and peaks can reflect the actual movement of different parts of the human body, providing a theoretical basis for the diagnosis of sports diseases, People with different genders and different age groups perform the same exercise, and the results will be relatively different. Therefore, we can use the present strain sensors to collect exercise data of different people, and then build a database to sort the collected sports data for the more conveniently and more quickly locating the patient's condition and movement characteristics, etc. Feedback on small movements such as facial changes can provide specific analysis basis for facial recognition and emotion analysis. Therefore, based on the above results, the prepared CCS/PVA/AlCl$_3$ and PCS/PVA/AlCl$_3$ strain sensors have great application prospects in soft electronics fields such as motion monitoring, disease analysis and diagnosis, and facial recognition.

Conclusion

In this study, the Schiff base and NaBH$_3$CN reduction method were used to modify CS with 3,4-dihydroxybenzaldehyde and 2,3,4-trihydroxybenzaldehyde, respectively, to obtain CS derivatives CCS and PCS. Then CCS and PCS were used as the crosslinking agents of PVA to prepare the corresponding CCS/PVA and PCS/PVA hydrogels, and by taking them as the main bodies, AlCl$_3$ was introduced into the systems to prepare CCS/PVA/AlCl$_3$ and PCS/PVA/AlCl$_3$ conductive hydrogels. Finally, CCS/PVA/AlCl$_3$ and PCS/PVA/AlCl$_3$ conductive hydrogels were used as flexible strain sensors to monitor human motions. In short, we can draw the following conclusions:

1) Using the Schiff base reaction and NaBH$_3$CN reduction method, it is feasible to modify CS with 3,4-dihydroxybenzaldehyde and 2,3,4-trihydroxybenzaldehyde, and the grafting rates could reach 73% for CCS and 60% for PCS.

2) CCS and PCS can form multi-point hydrogen bonding to PVA chains to increase the crosslinking density of the hydrogel system, thereby increasing the tensile strength and elongation at break of hydrogels.

3) Due to the presence of large amount of polyphenol groups in CCS and PCS, both CCS/PVA and PCS/PVA composite hydrogels can show strong adhesion abilities to different types of substrates. The feature of being able to firmly adhere to human skin provides a practical basis for the preparation of strain sensors, and the hydrogel sensors will not fall off due to the change in the motion amplitude when monitoring various types of motion.

4) On the basis of adding AlCl$_3$ to provide ionic conductivity for the hydrogel material, both CCS/PVA/AlCl$_3$ and PCS/PVA/AlCl$_3$ hydrogels could be prepared as flexible strain sensors, which can respond quickly to human movements such as cyclic stretching, cyclic compression, finger bending, wrist rotation, elbow bending, foot rotation, and nodding, and also show satisfactory results in monitoring of small movements such as mouth-closing cycle and frowning facial expressions. It is foreseeable that both of them will have great application prospects in the fields of human motion monitoring, motion disease diagnosis, facial recognition, and micro-expression analysis in the future.

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