# Facile preparation of eco-friendly, flexible starch-based materials with ionic conductivity and strain-responsiveness

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**ABSTRACT**: This work demonstrates a facile and "green" method to prepare eco-friendly, flexible, transparent, and ionically conductive starch-based materials, which are highly potential in personal health monitoring applications such as disposable electrodes. This method relies on the use of $CaCl_2$ solution and enables both the efficient disorganization and amorphization of high-amylose starch granules with low energy consumption and the reinforcement of the starch chain network by starch–metal cation complexation. Specifically, the method involves a simple mixing of a high-amylose starch with $CaCl_2$ solution followed by heating the mixture at 80 °C for 5 min. The whole process is completely environmentally benign, without any waste liquid or bioproducts generated. These resulting materials displayed tunable mechanical strength (500–1300 kPa), elongation at break (15–32%), Young's modulus (4–9 MPa), and toughness (0.05–0.26 $MJ/m^3$), and suitable electrical resistivity (3.7–9.2 $\Omega \cdot m$). Moreover, the developed materials were responsive to external stimuli such as strain and liquids, satisfying the requirements for wearable sensor applications. Besides, composed of only starch, $CaCl_2$, and water, the materials are much cheaper and eco-friendly (can be consumed by fish) compared with other polymer-based conductive hydrogels.

*KEYWORDS*: *Starch-based ionically conductive materials; Green biopolymer engineering; Eco-friendly materials; Wearable sensors; Strain-responsiveness; Liquid-responsiveness*

**INTRODUCTION**

Polymer-based hydrogels represent one of the most promising types of substrate, which are usually biocompatible, soft, stretchable, and transparent. These hydrogels are composed of flexible polymer networks containing significant amounts of water. The polymer network makes them solid-like, while the aqueous phase enables them to be biocompatible and able to diffuse electric charge carriers, which generates electrical signals.[1] In order to absorb and hold a high content of water, polymer substrates for hydrogels should have plenty of hydrophilic groups (e.g. ─COC─, ─OH, ─COOH, ─COO, or ─CONH$_2$) such as polyvinyl alcohol (PVA),[2-4] polydopamine,[5] polyamide,[4] polyacrylamide,[6] polypyrrole.[7] The crosslinked network structures formed impart hydrogels with desirable attributes for wearable sensors, drug delivery, medical dressings, and tissue engineering. However, the applications of polymer hydrogels are highly limited by their high prices, especially for application as disposable items, particularly due to the chemical synthesis routes. Besides, with the rapid growth of electronic waste, there has been a focus on the development of environmentally friendly polymer materials for disposable electronics applications. In this regard, the use of natural polymers sourced from biomass for fabricating cheap, biodegradable hydrogels and the development of "green" and facile fabrication processes are highly demanded.[8]

Natural polymers (biopolymers) such as cellulose, starch, chitosan, alginate, and protein are not only renewable, cheap, biodegradable, and biocompatible, but also contain abundant hydrophilic groups for forming hydrogels.[9-11] Among them, starch is a polysaccharide found in plants such as maize, potato, cassava, wheat, and rice and has been widely focused for both food and non-food applications. Native starch has a supramolecular, semicrystalline granule structure based on two major types of biomacromolecule, amylose (a linear chain composed of α-(1–4)-linked D-glucose

units with limited branches) and amylopectin (a highly branched chain composed of an α-(1–4)-linked D-glucose backbone and about 5% α-(1–6)-linked branches) and involving strong intermolecular hydrogen bonding.[12] For the utilization of starch, it is important to use a solvent such as ionic liquid (IL), usually along with heat treatment, to disorganize the supramolecular granule structure of native starch to form a homogenous material.[13-19] As a result, starch can be processed into functional materials such as ionically conductive materials. Wang et al.[20] showed that the maximum electrical conductivity of starch/montmorillonite nanocomposites plasticized by 1-allyl-3-methylimidazolium chloride ([Amim]Cl) was 0.5 S/cm. Xie et al.[21] prepared starch-based electrically conductive films plasticized by 1-ethyl-3-methylimidazolium acetate ([$C_2$mim][OAc]). While such films showed Young's modulus nearly 800 MPa, their electrical conductivity was below $10^{-5}$ S/cm. According to Zhang et al.[22], starch films containing a higher content of [$C_2$mim][OAc] had enhanced electrical conductivity up to $10^{-3}$ S/cm, whereas its Young's modulus was only about 4 MPa. Hou et al.[23] reported an amylopectin/water/salt hydrogel being electrically conductive with multiple desirable features. Although this hydrogel displayed electrical conductivity as high as 36 S/cm, it was clay- or plasticine-like and cannot be used as an elastic sensor. Domene-López et al.[24] prepared starch/multi-walled carbon nanotubes (MWCNTs) films with [$C_2$mim][OAc] as a plasticizer. The films had high electrical conductivity, 56 S/m, based on the combination of MWCNT and [$C_2$mim][OAc].

Despite the huge efforts to develop ionically conductive materials based on biopolymer such as starch, it is still highly challenging for starch hydrogels to achieve both high mechanical flexibility and high ionic conductivity, which severely restricts their applications.[3] Specifically, for starch-based materials, a tight network is favorable for good mechanical properties but causes low ionic conductivity due to the limited water content. Contrarily, while increasing the water content is

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favorable for the movement of ions, this will weaken the interaction between starch chains, leading to poor mechanical properties. Moreover, it is extremely challenging to prepare starch-based materials or hydrogels with adequate mechanical properties cost-effectively because of the significant energy required for the phase transition of starch from native hierarchically structured semicrystalline granules into a disordered state, and the necessity of chemical reactions to form a crosslinked network.[25] Therefore, it is highly interesting to develop simple and cost-effective approaches to fabricate starch-based bio-electrodes with high mechanical strength and flexibility as well as high ionic conductivity for better meeting legislative requirements and application demands. This forms the intention of this current work, which demonstrates that by only using starch and a salt, materials with excellent flexibility, strain-sensitivity, and eco-friendliness can be prepared via a facile and "green" method (without any chemical reactions). This efficacy of this method was tested on a high-amylose starch, which, generally, is much more resistant to processing than amylopectin-rich starches[26-27] because of its more compact granule structure and higher thermal transition temperature.[28-29] While interactions and entanglements between amylopectin chains are weak due to the highly branched short-chain structure, those between long, linear, flexible amylose chains are much stronger,[26, 30] leading to better mechanical properties and less water-sensitivity.[26, 31-32] Thus, our method to cost-effectively prepare high-amylose starch-based materials could be highly meaningful practically.

**EXPERIMENTAL SECTION**

**Materials.** Gelose 80 maize starch (G80) was supplied by National Starch Pty Ltd (Lane Cove, NSW 2066, Australia), which has about 80% amylose content (provided by the manufacturer). The original moisture (MC) of the starch was 12.6±0.4% (detected at 120 °C for 5 min by a rapid moisture analyzer (QL-720B, Scientific Instrument Co., Ltd, China). Anhydrous calcium chloride

(CaCl$_2$, chemically pure) was purchased from Aladdin Reagent (Shanghai) Co., Ltd (China). All solutions are prepared with distilled water.

**Sample preparation.** A CaCl$_2$ solution of 38.5% (w/w) concentration was prepared by first adding anhydrous CaCl$_2$ into distilled water. After that, the starch was mixed with the solution at dry starch/anhydrous CaCl$_2$ mass ratios of 2.5/2.0, 2.5/2.2, 2.5/2.5, 2.5/2.8, and 2.5/3.1. The mixtures were heated in a water bath at 80 °C for 5 min, which allowed the mixtures to transform into transparent hydrocolloids fully. The cooling of the hydrocolloids to room temperature (RT) resulted in starch/CaCl$_2$ composite materials. Before characterization, the materials were stored in different relative humidity (RH) environments (33%, 57%, and 85%, achieved by saturated MgCl$_2$, NaBr and KCl salt solutions, respectively) for 48 h. The final MCs of the materials were measured under 120 °C for 10 min by the rapid moisture analyzer. Before moisture analysis, the materials were cut into tiny pieces (about 3 mm in diameter).

**Resistivity measurements.** After moisture equilibration, the materials were cut into a rectangle shape of 4×75×0.5 mm, and their electrical resistivity was detected by an electrochemical workstation (CHI 650, CH Instruments, Inc., USA).

**Stimulus-responsiveness measurements.** The 2.5/2.5 (w/w) starch/CaCl$_2$ material after conditioned at 57% RH was chosen for stimulus-responsiveness measurements. The materials were cut into a rectangle shape of 4×75×0.5 mm for stretching and 25×10×3 mm for compression. Then, the rectangle samples were fixed at the clamp of the mechanical testing machine (GC-WD-50, Dongguan Guangce Instrument and Equipment Co., Ltd, China). When they were stretched or compressed, the electric current was recorded by the electrochemical workstation. During the measurements, the samples were covered with kitchen cling film (polyethylene) to avoid moisture loss.

**Tensile testing.** Tensile testing of materials was conducted using a TA.XTplusC Texture Analyzer (Stable Micro Systems Ltd, UK) with 10 kg load cell at RT. The shape of the samples was followed by Chinese National Standard GB/T 528-2009, 75×4 mm. The extension rate was kept at 5 mm/s and tensile strength, toughness, elongation at break, and Young's modulus were evaluated by the software of the instrument. For each sample, at least five tests (based on five specimens) were performed.

**Structural characterization.** X-ray diffraction (XRD) analysis of the samples was carried out using an Xpert PRO diffractometer (PANalytical B.V., Netherlands) operated at 40 mA and 40 kV with Cu Kα radiation (wavelength 0.1542 nm). The scanning was performed from 5° to 50° $2\theta$ at a speed of 10°/min and a step size of 0.033°.

For Fourier-transform Infrared (FTIR) spectroscopy, a Tensor 27 FTIR spectrometer (Bruker, Germany) equipped with a diamond attenuated total reflectance (ATR) accessory was used. Before measurement, the materials were cut into pieces in the size of 20×20 mm. For each spectrum, 64 scans were recorded over a range of 4000–400 $cm^{-1}$ at RT with a resolution of 4 $cm^{-1}$, co-added, and Fourier-transformed. The background spectrum was recorded in air and subtracted from the sample spectra.

For scanning electron microscopy (SEM), the samples were freeze-dried for 12 h and then were fractured in liquid nitrogen to obtain cross-sections. Some areas of the cross-sections were wiped by wet cotton swabs with distilled water for three times, followed by further wiping using dry cotton swabs and blowing with RT air using an air blower for one minute to dry totally. Morphologies of the original and treated cross-sections were imaged by a scanning electron microscope (JEOL JSM-7001F, Tokyo, Japan) with an accelerating voltage of 10 kV and a spot size of 6 nm. Meanwhile, energy-dispersive X-ray spectroscopy (EDS) for Ca and Cl elements

was performed. Before examination, samples were coated with platinum using an Eiko sputter coater.

The calcium contents in starch-based materials were detected by atomic absorption spectrometry (AAS, Thermo Scientific iCE 3500). The samples included the original cross-sections and the treated ones, which were soaked and stirred in distilled water for 48 hours. The sample preparation was followed by Chinese National Standard GB 5009.92-2016. Specifically, 10 mL of hydrogen nitrate solution (69 wt%) and 0.5 mL of perchloric acid solution (70 wt%) were added to 5 g of the material, and the obtained solution was heated to 220 °C for 2 h. After cooling, the volume of the solution was adjusted to 50 mL by distilled water, and the cation can be detected using the AAS facility.

**Statistical analysis.** Microsoft Excel software was used to fitting linear regression and obtain correlation coefficients ($R^2$). Data analysis followed one-way analysis of variance (ANOVA) and Duncan's test for a statistical significance $p \leq 0.05$ using the SPSS Statistics v19.0.

## RESULTS AND DISCUSSION

**Material design and processing.** Although starch can be made into a gel form easily, it is technically challenging to realize starch-based materials with both excellent mechanical strength and ionic conductivity without chemical crosslinking. Simple gelatinization of starch in water will only form a diluted polymer system, where interactions (manly hydrogen bonding) and entanglements between starch chains are weak, leading to poor mechanical properties and low water-holding capability. Although a more condensed chain network (resulting from a higher starch content in the material) can improve starch chain interaction to some extent, it also decreases the amounts of ions that can move freely, leading to reduced ionic conductivity.

Recently, we and other researchers have found that some salt ions (e.g. $Zn^{2+}$ and $Ca^{2+}$) can not only disorganize and amorphize starch granules effectively but also reinforce the starch chain network by forming amylose–metal cation inclusion complexes.[33-36] Since these salt ions are hygroscopic and can combine with water to form hydrates easily, polymer materials containing them could have improved water-holding capacity.[3] Moreover, these salt ions can impart the materials with electrical conductivity. In this work, we chose $CaCl_2$ solution, which enabled the facile preparation of starch-based materials by heating in an 80 °C water bath for only 5 min (see **Fig. 1**). The MC of the starch-based materials equilibrated in 33%, 57%, and 85% RH environments are 35.9±1.6%, 42.1±1.4% and 55.2±2.6%, respectively (see **Table S1** in the Supporting Information), which are higher than those of common starch-based materials.[26]

This sample preparation process is completely environmentally benign, without any waste liquid or bioproducts generated. Moreover, compared with traditional ways of processing starch-based materials through extrusion or compression, which requires much more mechanical and thermal energy input, the phase transition of G80 starch granules in this process is easy and complete at a lower temperature (with lower energy input) with the assistance of salt ions. Therefore, this method can be considered to be facile and "green".
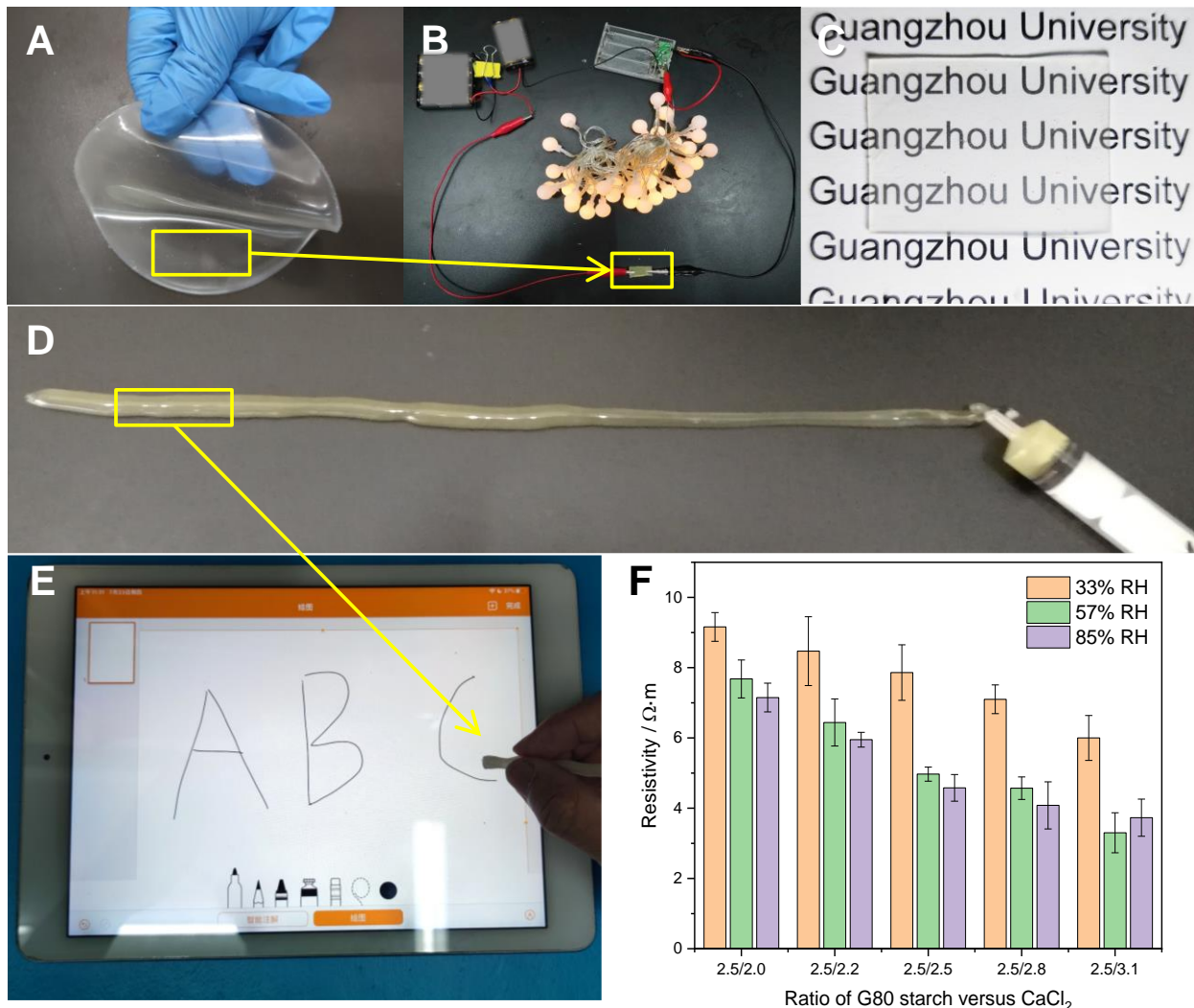
**Fig. 1** Preparation of starch/CaCl$_2$ composite materials and their electrical conductivity. A) A film with a starch/CaCl$_2$ dry mass ratio of 2.5/2.5 conditioned at 57% RH; B) The film was connected in a battery-powered circuit, making LED bulbs lit; C) The film with 1 mm thickness on top of word-printed paper, showing its transparency; D) An extruded stick with a starch/CaCl$_2$ dry mass ratio of 2.5/2.5; E) The stick was used as a capacitive stylus pen for the touchscreen of an electronic device; F) The electrical resistivity of starch/CaCl$_2$ composite materials with different starch/CaCl$_2$ dry mass ratio conditioned at different RH.

For preparing starch-based materials, we also tested $ZnCl_2$ and $MgCl_2$ solutions, which can also disorganize G80 starch granules.[33] However, $MgCl_2$ solution could not destruct G80 starch granules totally and the resulting network was weak. Accordingly, the starch/$MgCl_2$ composite materials were easy to break and not transparent (see **Figure S1** in the Supporting Information). $ZnCl_2$ solution is also not suitable as its strong acidity can cause severe hydrolysis of starch chains; as a result, only the sticky starch paste could be formed (see **Figure S1** in the Supporting Information).

**Electrical conductivity of starch/$CaCl_2$ composite materials.** The starch-based ionically conductive film consisting of only G80 starch and $CaCl_2$ solution (starch/$CaCl_2$ dry mass ratio: 2.5/2.5; conditioned at 57% RH) is shown in **Fig. 1A.** This film was prepared by solution casting and was highly flexible and transparent (see **Fig. 1C**), which is contributed by the full phase transition of starch from original semicrystalline granules into a disordered, amorphous state. Besides, a stick-like material was also prepared by extrusion using a syringe, as shown in **Fig. 1D**. This flexible and transparent film is potential to be used for disposable wearable sensors for personal health monitoring, while the extruded sticks demonstrate the possibility of the formulation for 3D-printing for various shapes and architecture requirements.

The high concentration of $CaCl_2$ solution is essential for the preparation of such a starch material. The lowest salt concentration to disorganize G80 starch granules is 31%.[33] If the concentration is lower than that, a transparent mixture cannot be formed and even a film cannot be formed. Besides, the mass of water also influences the state of mixture strongly. If the starch/$CaCl_2$ dry mass ratio was higher than 2.5/2.0, the starch/water mass ratio is higher than 2.5/3.2 under the constant salt concentration of 38.5%. In this case, an adequate phase transition of starch cannot be achieved and the mixture contains loose white powder balls that are not saturated by the liquid. If the

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starch/CaCl$_2$ dry mass ratio was lower than 2.5/3.1, the starch/water mass ratio is lower than 2.5/5.0, which means there is too much water to form a free-standing material.

The dimension of the starch-based material could be adjusted by varying the mold size and starch and CaCl$_2$ concentrations. In **Fig. 1A**, the film thickness could vary from 0.08 mm to 1.0 mm; and in **Fig. 1D**, the stick diameter could range from 0.5 mm to 5 mm. Both of them were electrically conductive, which can be shown by the light of LED bulbs in a battery-powered circuit (**Fig. 1B**) and the capacitive stylus pen for the touchscreen of an electronic device (**Fig. 1E**). Specifically, in **Fig. 1B**, the electric current provided by series-circuited six batteries with a total voltage of 9 volts could transit through a rectangular shape (20×7×0.5 mm) of the starch-based film (also shown in **Video Clip S1** in the Supporting Information). In **Fig. 1E**, the letters can be written on a capacitive touchscreen with the starch-based stick (diameter: 5 mm) due to the electrical conductivity of the stick (also shown in **Video Clip S2** in the Supporting Information).

**Fig. 1F** shows that the electrical resistivity of starch/CaCl$_2$ composite materials was in the range of 3.7–9.2 Ω·m, which is similar to those of ionically conductive hydrogels[1, 7, 37] and synthetic polymer-based hydrogels[3] reported. These values are only about 1% of starch-based electrically conductive films containing IL as a conductively active substance.[20-21, 24] Furthermore, the electric resistivity decreased with increasing CaCl$_2$ mass ratio and RH. This is as expected as CaCl$_2$ offers free ions in the materials and the high RH imparts the materials with high moisture content and pathways for the movement of ions.

**Stimulus-responsiveness of starch/CaCl$_2$ composite materials.** The electrical conductivity of starch/CaCl$_2$ composite materials is based on the mobility of free ions (ionic conductivity) through the aqueous phase that is dispersed among the starch chain network. In this sense, any changes of the material shape or the starch chain network may vary the electric resistivity, which can be

considered as electrical responsiveness to stimuli[38-39] (**Fig. 2**). The material for stimulus-responsiveness testing had a starch/CaCl$_2$ dry mass ratio of 2.5/2.5 and was conditioned at 57% RH.

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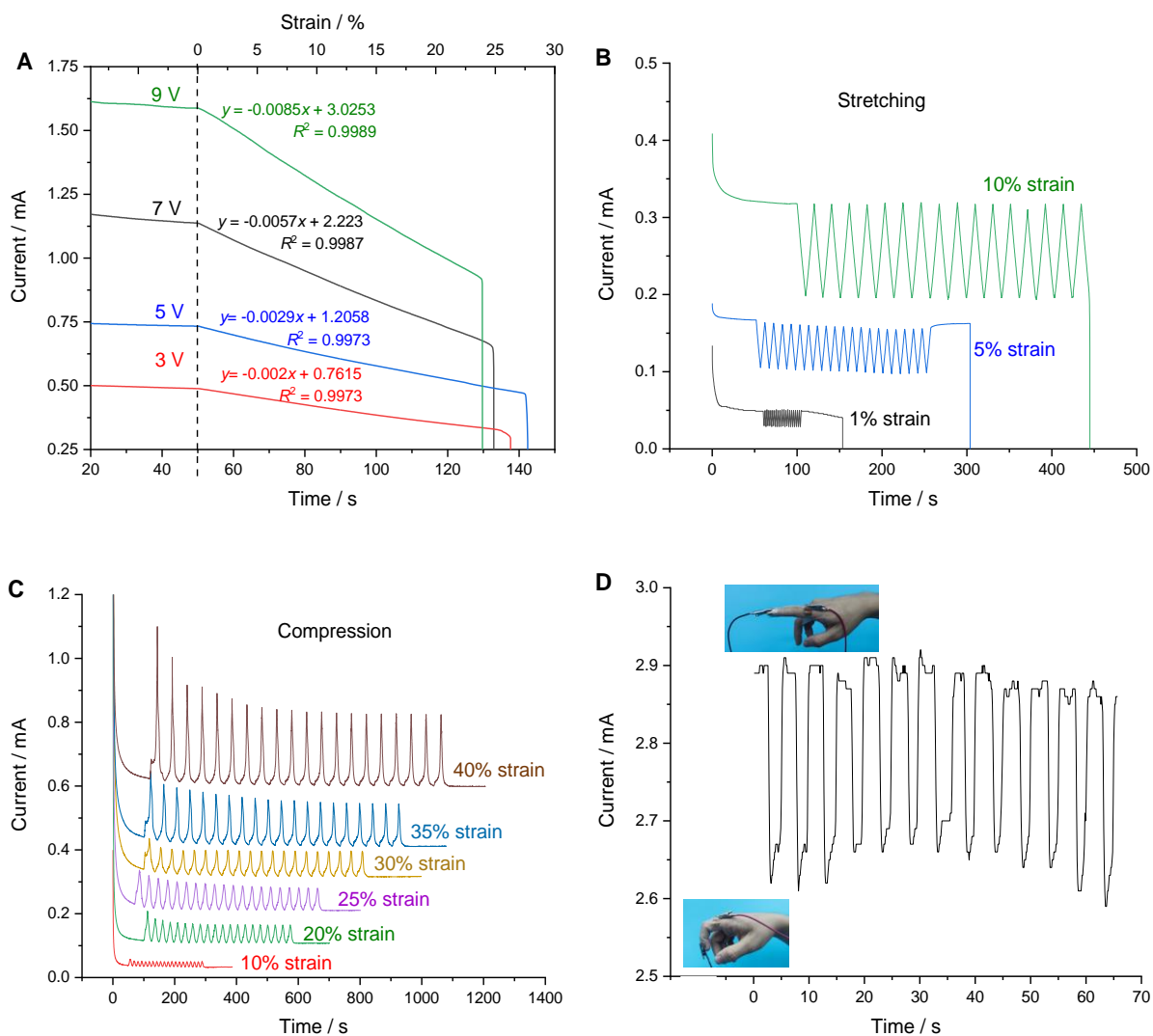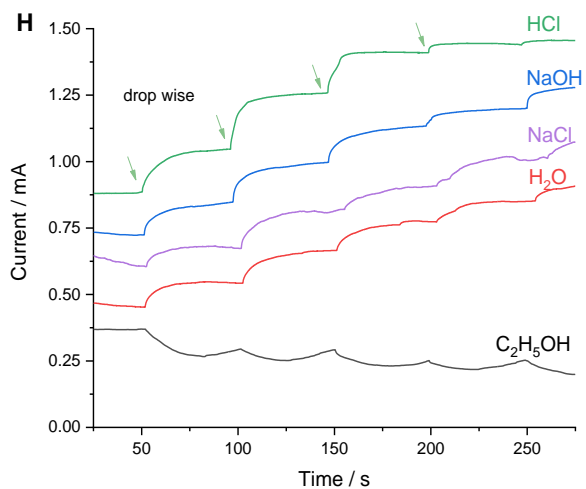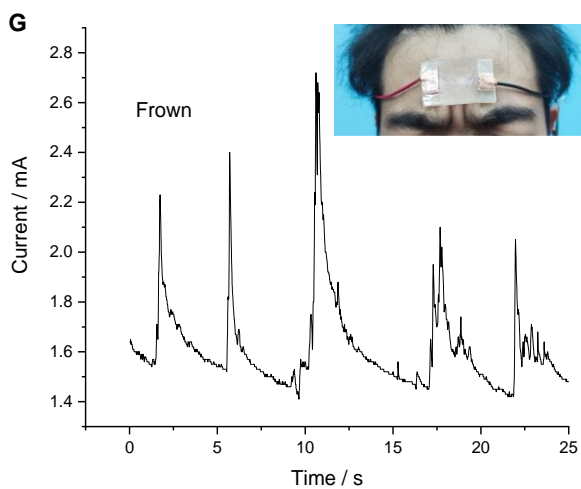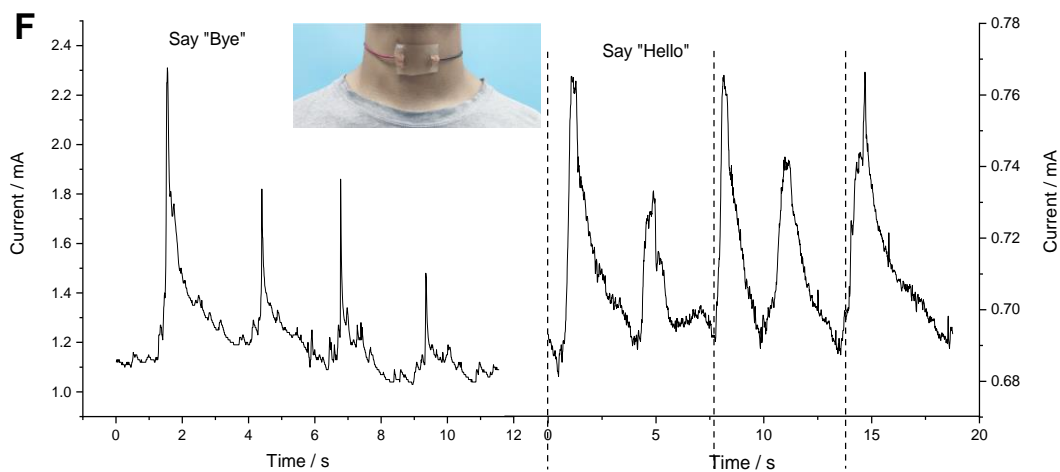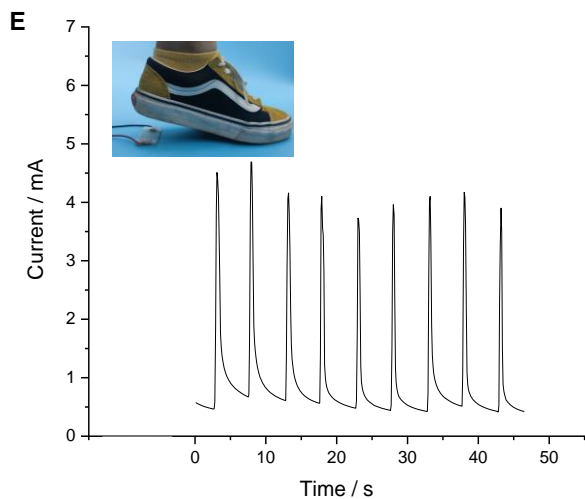
**Fig. 2** Stimulus-responsiveness (electrical conductivity change) of a starch/CaCl$_2$ composite material (starch/CaCl$_2$ dry mass ratio: 2.5/2.5; conditioned at 57% RH) subjected to A) strain, B) stretching cycles, C) compression cycles, D) finger bending, E) foot stepping cycles, F) the vibration of throat, G) face expression changes, and H) liquid (10 μL) contact.

In **Fig. 2A**, the strain-induced electrical conductivity change of the starch/CaCl$_2$ composite material (size: 4×75×0.5 mm) was evaluated under different voltage (3–9 V). The tension began at 50 s, and the strain rate was 0.2 mm/s. A linear relationship between the electric current and the time (strain) can be seen with correlation coefficients higher than 0.997, demonstrating the electric signal can accurately reflect the extent of deformation of the material. The maximum strain of the material was 21–24%, after which point the material would break and the current went back to 0 mA. Moreover, the slope (ignoring negative values) of the regression line for the electric current vs. time (strain) relationship increased with increasing voltage. This is as expected as voltage is the driving force for ion mobility, and a higher voltage can lead to greater sensitivity of ion mobility to strain.

In **Fig. 2B**, continuous stretching cycles were applied to the same starch/CaCl$_2$ composite material with a size of 4×50×0.5 mm. Both the stretching and recovering rate was 0.5 mm/s. Upon stretching, the distance for ion movement alongside the stretching direction increased, leading to higher electric resistivity and thus lower electric current. Even when the strain was only 1%, the responsiveness to deformation as shown by the change in electric current can be observed clearly. The response of circular current vs. strain was instant (with no time lag). Moreover, the material was fatigue-resistance, which means it could sustain for at least 20 cycles without apparent

permanent dimensional changes under 10% strain. However, if the strain was 15%, the material could only remain unbroken for up to 5 cycles.

The changes in electric current for the same material subjected to compression cycles were shown in **Fig. 2C**. The size of the material was 25×10×3 mm. Both the compression and recovering rates were 0.05 mm/s. Upon compression, the distance for ion mobility shortened, resulting in lower electric resistivity and higher electric current. The material fatigue-resistance against compression was better than against stretching. Even under 40% strain, at least 20 times of compression did not cause any apparent permanent dimensional changes. Therefore, the materials could be better used in compression situations.

Based on the strain-sensitive conductivity, the starch/CaCl$_2$ composite materials can be applied for wearable monitors. In **Fig. 2D**, the material was attached to a finger, and the bending movements of the finger could be recorded as fluctuated electric current signals (also shown in **Video Clip S3** in the Supporting Information). In **Fig. 2E**, the material was placed under a shoe, and the number of steps could be detected by electric current signals. In **Fig. 2F**, the material was attached to the throat of a person. Since the sound is accompanied by the vibration of the throat, the different words spoken can be recorded in the form of different electric current signals. This is exampled by a double-syllable word "Hello" and a high-frequency word "Bye". Moreover, in **Fig. 2G**, since human mood can be reflected by facial expressions, such as frown, when the material was attached to one's forehead, the mood could be recorded in the form of electric current.

The above results indicate that while the stretchability and fatigue-resistance of starch/CaCl$_2$ composite material do not surpass those of synthetic polymer materials reported elsewhere,[7] their strain-sensitivity could well satisfy the requirements for personal wearable monitors. Besides, considering the facile and "green" fabrication process and the low price of starch, which is only

1/4 to ½ of the price of the synthetic polymers for hydrogels, starch/CaCl$_2$ composite materials could be highly potential for cheap and disposable personal wearable monitoring devices, especially in the medical field. Moreover, starch, due to its abundant hydroxyl groups and thus chemical versatility, could be easily modified to achieve additional crosslinking or functionality. Therefore, the starch/CaCl$_2$ materials demonstrated in this paper can provide insights into the development of similar biopolymer-based materials with tailored properties and wider applications.

We further tested how the material could be responsive to different liquids. In **Fig. 2H**, different liquid drops were placed onto the material surface. NaCl, NaOH and HCl solutions of 0.01 mol/L concentration were used, along with pure water and ethanol. Each drop was 10 μL in volume. Except for ethanol, all drops caused cumulative increments in electric current. This is as expected as the material is hydrophilic and can absorb water to increase ion mobility. Moreover, the change ratio of electric current ($\Delta I/I_0$) was about 8% for the first drop of water or NaCl solution, which demonstrates that high sensitivity of the material to liquid contact. Besides, the $\Delta I/I_0$ value was 16% for HCl and 11% for NaOH, which means the material is more sensitive for an acid solution than for alkaline and neutral solutions. This also demonstrates the material is pH-sensitive, which may be caused by the influence of H$^+$ or OH$^-$ on ion mobility. On the other hand, when a drop of ethanol was placed on the material, the electric current decreased, which is reverse to the cases of other liquids tested. The reason can be attributed to the strong water-binding ability of ethanol, which hinders the mobility of ions through the aqueous phase.

**Environmentally friendliness of starch/CaCl$_2$ composite materials.** Starch-based materials are readily degradable in the natural environment. In particular, starch/CaCl$_2$ composites are completely benign in water and marine environments. **Figure S2A** and **Figure S2B** in the

Supporting Information show that small pieces of the starch-based material (starch/$CaCl_2$ dry mass ratio: 2.5/2.5; conditioned at 57% RH) can all be quickly eaten by goldfish without any obvious negative effects to the animal (also shown in **Video Clip S4** in the Supporting Information), demonstrating the eco-friendliness of the material. **Figure S2C** and **Figure S2D** in the Supporting Information show that large pieces of the material can be disintegrated into tiny pieces, especially upon stirring for 48 hours, which can be safely consumed by planktons or aquatic plants. This shows that starch/$CaCl_2$ composite materials will not cause issues to wildlife.

**Mechanical properties of starch/$CaCl_2$ composite materials. Fig. 3** shows that the mechanical properties of starch/$CaCl_2$ composite materials can be largely varied by starch/$CaCl_2$ dry mass ratio and RH, Young's modulus 4–9 MPa, elongation at break 16–32%, tensile strength 500–1300 kPa, and toughness 0.05–0.26 MJ/m$^3$. These results are similar to those of solution-cast starch-based materials reported previously.[40] Besides, all the mechanical parameters (including elongation at break) decreased with increasing RH. In this regard, high RH resulted in high MC, which could probably weaken the starch chain network in the materials. Moreover, starch/$CaCl_2$ composite materials were flexible, having similar mechanical properties as nanocomposites of silver nanowires (AgNW) and polydimethylsiloxane (PDMS) elastomer with a sandwich structure.[41]
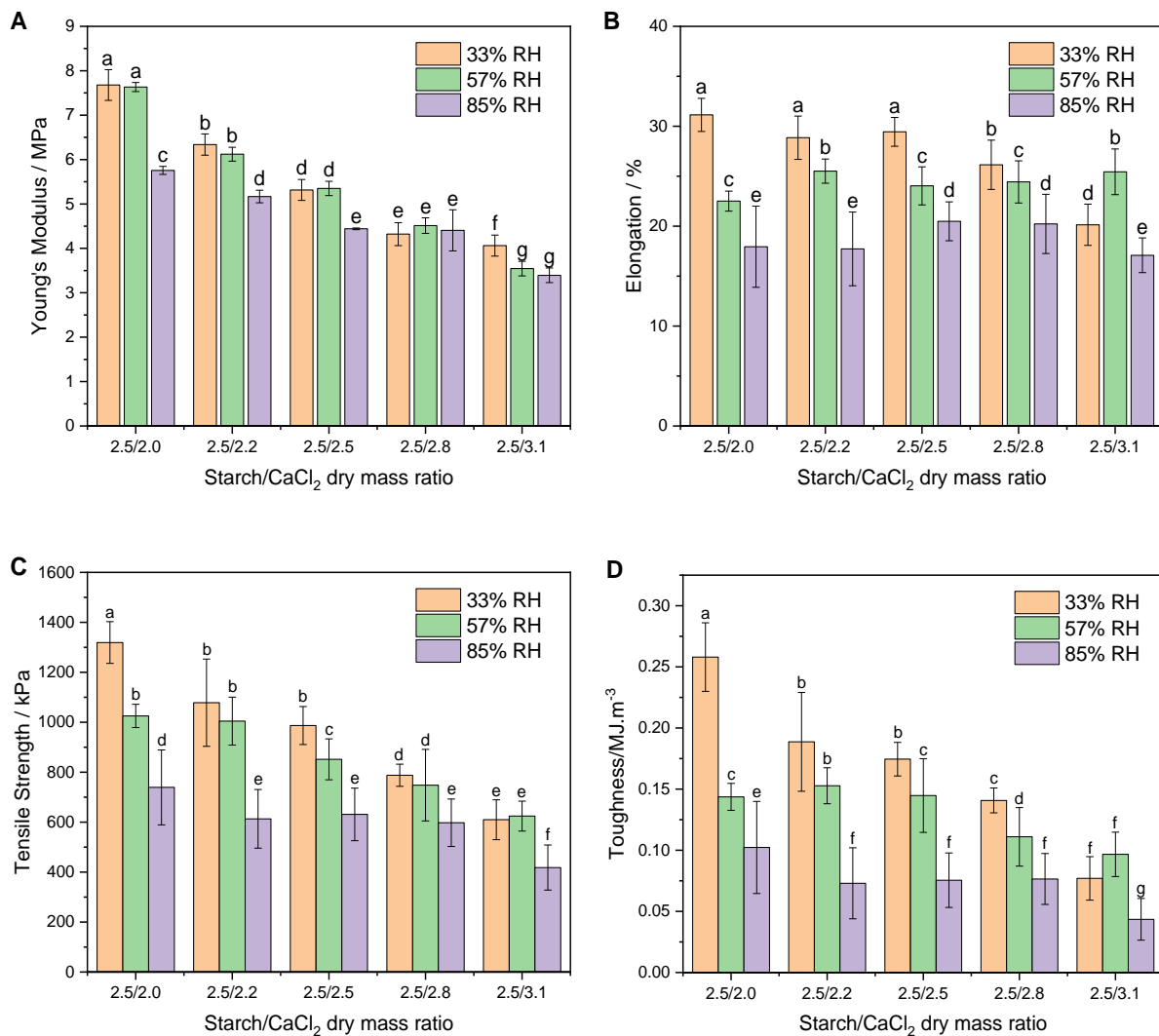
**Fig. 3** Mechanical properties (A, Young's modulus; B, elongation at break; C, tensile strength; D, toughness) of starch/CaCl$_2$ composite materials.

**Structures of Starch/CaCl$_2$ composite materials**. XRD curves (**Fig. 4A**) show that, compared with native G80 starch, starch/CaCl$_2$ composite materials were predominantly amorphous. This indicates that CaCl$_2$ solution could not only disorganize and amorphize G80 starch granules totally within 5 min, but also hinder subsequent starch recrystallization. The amorphous structure also

suggests that salt ions were dispersed homogeneously in the materials without the formation of salt crystals.
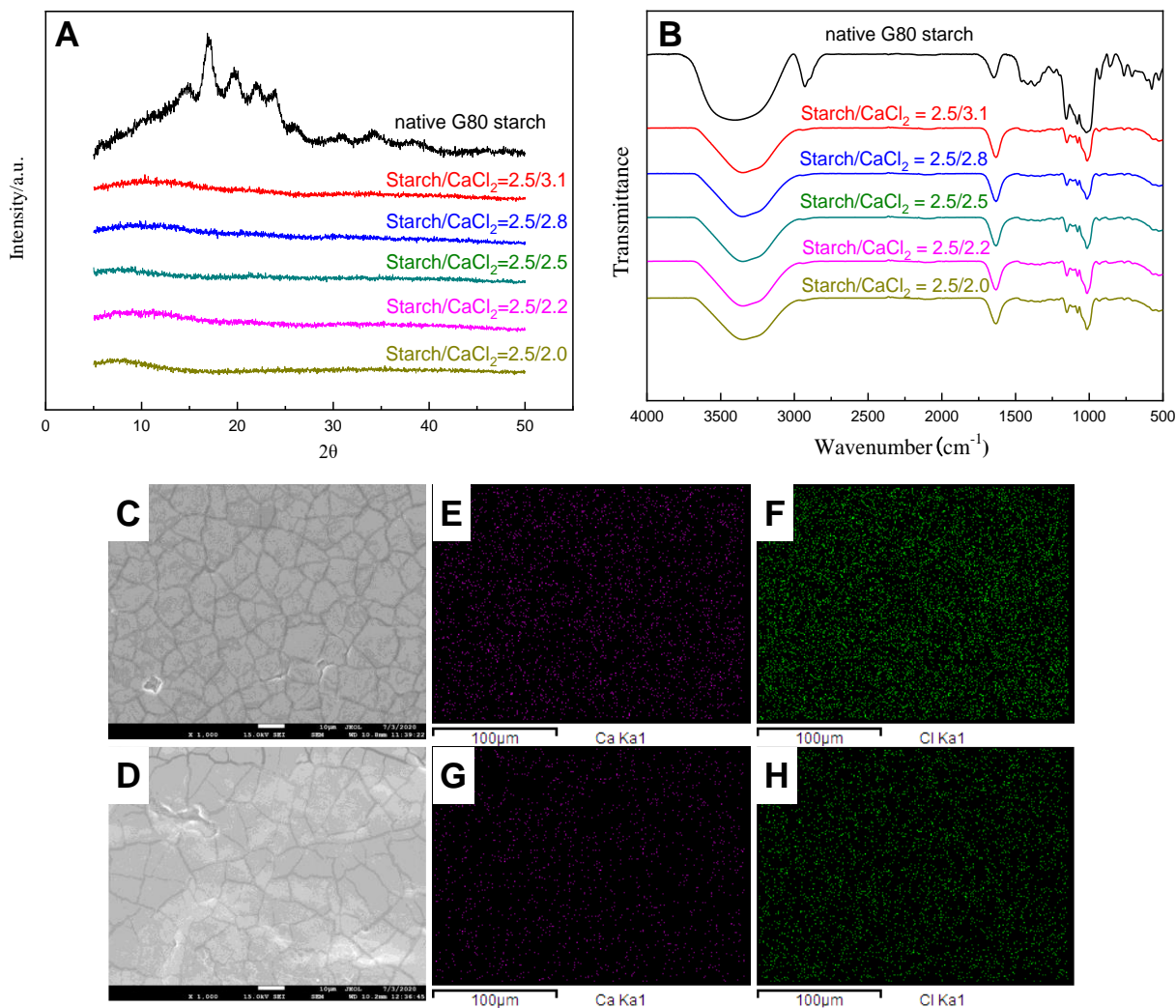


**Fig. 4** Structural analysis results for starch/$CaCl_2$ composite materials (starch/anhydrous $CaCl_2$ dry mass ratio is 2.5/2.5 and conditioned at 57% RH). A) XRD curves and B) FTIR spectra for native G80 starch and starch/$CaCl_2$ composite materials with different starch/$CaCl_2$ dry mass ratio and conditioned at 57% RH; C) and D) Scanning electron microscopy (SEM) images of the cross-sectional surfaces of the starch/$CaCl_2$ composite material (starch/anhydrous $CaCl_2$ dry mass ratio: 2.5/2.5; conditioned at 57% RH) before and after wiping, respectively; E) and F)

EDS images for Ca element (in violet) and Cl element (in green) of the sample in C, respectively; G) and H) EDS images for Ca element (in violet) and Cl element (in green) of the sample in D, respectively.

FTIR spectroscopic analysis (**Fig. 4B**) indicates that, after processing, some characteristic peaks for native G80 starch vanished, including 2930 cm$^{-1}$, 1420 cm$^{-1}$, 1380 cm$^{-1}$, 863 cm$^{-1}$, and 763 cm$^{-1}$. The peak at 2930 cm$^{-1}$ corresponds to the asymmetric stretching vibration of —CH$_2$;[42-43] the peaks at 1420 cm$^{-1}$ and 1380 cm$^{-1}$ are associated with the bending vibration of —CH;[44] the peak at 863 cm$^{-1}$ is indicative of the bending vibration of —CH or —CH$_2$;[45] and the peak at 763 cm$^{-1}$ represents the rocking vibration of —CH$_2$.[46] The changes of these peaks indicate the variations to the methylene (—CH$_2$—) of starch chains. Since methylene only emerges in C6 among the glucoside, it can be deduced that there was strong interaction of the hydroxyl group of C6 with a salt ion, leading to reduced attractive forces to the two hydrogen atoms of methylene.[42, 47] Moreover, it was previously suggested that coordinated complexation can be formed between Ca$^{2+}$ and the oxygen atoms on the C6 hydroxyl group.[48] Here, we consider it should be this starch-Ca$^{2+}$ complex that caused the variation to the FTIR spectra.

While our previous study[33] indicated no differences in the FTIR spectra between starch–Ca complex and native starch, here in this current work, starch/CaCl$_2$ composite materials showed obviously different FTIR patterns from that of native G80 starch. In this regard, we consider that due to the high salt contents in the materials, all C6 hydroxyl groups bound with Ca$^{2+}$ ions. Therefore, there could be a threshold for the mobility of ions, at which point all C6 hydroxyl groups are coordinated with Ca$^{2+}$. This explains the situation that when the starch/CaCl$_2$ dry mass ratio was less than 2.5/2 (w/w), the electrical conductivity of the material dropped sharply.

**Fig. 4C** and **Fig. 4D** show the cross-sectional morphologies of a representative starch/$CaCl_2$ composite material (starch/$CaCl_2$ dry mass ratio: 2.5/2.5; conditioned at 57% RH) before and after wiping respectively. Both morphologies were full of cracks, likely to be caused by dehydration. Before wiping, the substrate among cracks was smooth and homogeneous. Nonetheless, after wiping, many micron-scale pores can be observed on the substrate, which might be caused by the release of free ions by water. To confirm this, **Fig. 4E** and **Fig. 4F** show the EDS results for Ca and Cl elements respectively before wiping, which indicate homogenous dispersion of Ca and Cl elements in the material. The amount of Cl element seems to be higher than that of Ca element, corresponding to the proportions of these elements in $CaCl_2$. After wiping (**Fig. 4G** and **Fig. 4H**), the intensities of Ca and Cl elements reduced significantly, suggesting large amounts of these elements were removed. This analysis confirms the origin of micron-scale pores. With free salt ions mostly removed, there were still ions remaining and homogeneously dispersed in the material, due to the complexation between starch and $Ca^{2+}$.

Furthermore, the free $Ca^{2+}$ content in the starch/$CaCl_2$ composite material (starch/$CaCl_2$ dry mass ratio: 2.5/3.1; MC: 41.6±2.3%) was measured by atomic absorption spectrometry. Specifically, in the original materials, the $Ca^{2+}$ content was 111.9±4.6 mg/g, which is close to the theoretical value 116.5 mg/g. After soaking and stirring in water for 48 hours, the material turned into tiny pieces (see **Figure S2D** in the Supporting Information), and the residual $Ca^{2+}$ content was only 0.88±0.08 mg/g. Therefore, nearly all $Ca^{2+}$ were free ions and can migrate out of the starch network. Similar results can be seen for other starch/$CaCl_2$ composite materials, from 94.1±5.3 mg/g to 0.77±0.04 mg/g (starch/$CaCl_2$ dry mass ratio: 2.5/2.5; MC: 41.7±1.0%) and from 80.2±1.8 mg/g to 0.75±0.04 mg/g (starch/$CaCl_2$ dry mass ratio: 2.5/2.0; MC: 43.1±0.6%).

Based on the above discussion, a schematic of the starch/CaCl$_2$ composite material structure is shown in **Fig. 5**. We propose that the entanglement and interaction between helical amylose chains provide the foundation of the material network. Water molecules bind with hydroxyl groups of starch chains and salt ions and disperse evenly among the network. The different aqueous phase regions are not isolated but are connected by channels. Under electric voltage, free ions (e.g. Ca$^{2+}$, Cl$^{-}$, H$^{+}$, and OH$^{-}$) in aqueous phase regions can move through the channels, acting as electric charge carriers. The densities of free ions and aqueous channels are influenced by the starch network, determining the material electric resistivity. More specifically, the deformation of the material can impact the availability of channels between aqueous phase regions, as shown by the strain-sensitivity. When water or other ions are absorbed by materials, the density or mobility of free ions changes, as reflected by the sensitivity of the material to moisture or pH.
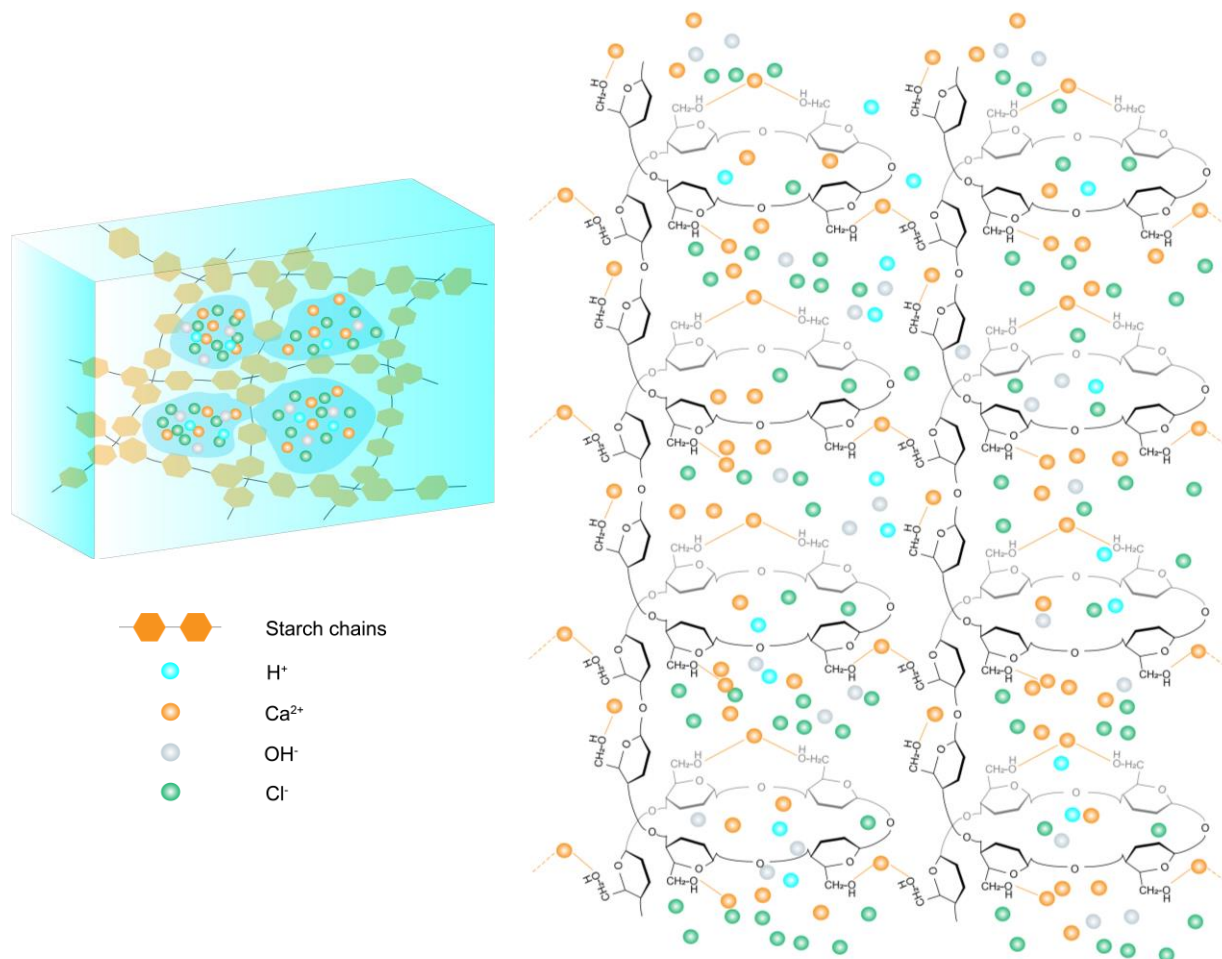
**Fig. 5** Schematic representation of starch/CaCl$_2$ composite material structure.

## CONCLUSIONS

In this paper, flexible, transparent and eco-friendly starch-based ionically conductive materials were successfully prepared by a facile and "green" method. The method involves only the mixing of a high-amylose starch with CaCl$_2$ solution followed by heating the mixture at 80 °C for 5 min. During this whole process, no waste liquid or bioproducts were generated. Suitable starch/CaCl$_2$ mass ratios are from 2.5/2.0 to 2.5/3.1. The electric resistivity of the materials was 3.7–9.2 Ω·m,

which is similar to those of other synthetic polymer-based hydrogels and much lower than IL-plasticized starch-based films in the literature. The materials had tensile strength from 500 kPa to 1300 kPa, elongation at break from 16% to 32%, Young's modulus from 4 MPa to 9 MPa, and toughness from 0.05 to 0.26 $MJ/m^3$. Besides being biodegradable, the materials could be quickly and totally eaten by fish without causing any issues, demonstrating their eco-friendliness. Moreover, the materials were highly sensitive to strain and liquids as shown by the changes in electric current, demonstrating their potential to be applied as wearable sensors. Considering the low price and the renewability, starch/$CaCl_2$ composite materials are especially useful as disposable electrodes in personal health monitoring.

ASSOCIATED CONTENT

**Supporting Information (SI)** is available free of charge on the ACS Publications website at DOI: xxx. See SI for supplementary Tables and Figure.

- Pictures of a starch/$MgCl_2$ composite material (starch/$MgCl_2$/water mass ratio: 4/2/4; conditioned at 57% relative humidity for 48 h) and a mixture of starch/$ZnCl_2$/water (mass ratio: 3/3.3/3) (**Figure S1**); Pictures of a starch/$MgCl_2$ composite material (starch/$CaCl_2$ dry mass ratio: 2.5/2.5; conditioned at 57% RH) in water eaten by goldfish and subject to stirring (**Figure S2**); and the moisture contents of starch/$CaCl_2$ composite materials (**Table S1**).

- Video showing that a starch/$CaCl_2$ composite material (starch/$CaCl_2$ dry mass ratio: 2.5/2.5; conditioned at 57% RH) was used to connect an electric circuit (**Video Clip S1**); that a starch/$CaCl_2$ composite material (starch/$CaCl_2$ dry mass ratio: 2.5/2.5) was used to write on a capacitive touchscreen (**Video Clip S2**); that a starch/$CaCl_2$ composite

material (starch/CaCl$_2$ dry mass ratio: 2.5/2.5; conditioned at 57% RH) attached to a finger could allow the bending movements of the finger to be recorded as fluctuated electric current signals (**Video Clip S3**); and that small pieces of a starch/CaCl$_2$ composite material (starch/CaCl2 dry mass ratio: 2.5/2.5; conditioned at 57% RH) was eaten by goldfish (**Video Clip S4**).

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### Author Contributions

All authors have given approval to the final version of the manuscript.

### Notes

The authors declare no competing financial interest.

**ABBREVIATIONS**

IL, ionic liquid; [C$_2$mim][OAc], 1-ethyl-3-methylimidazolium acetate; G80, Gelose 80 corn starch; MC, moisture content; RH, relative humidity;

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Starch chains

H⁺

Ca²⁺

OH⁻

Cl⁻
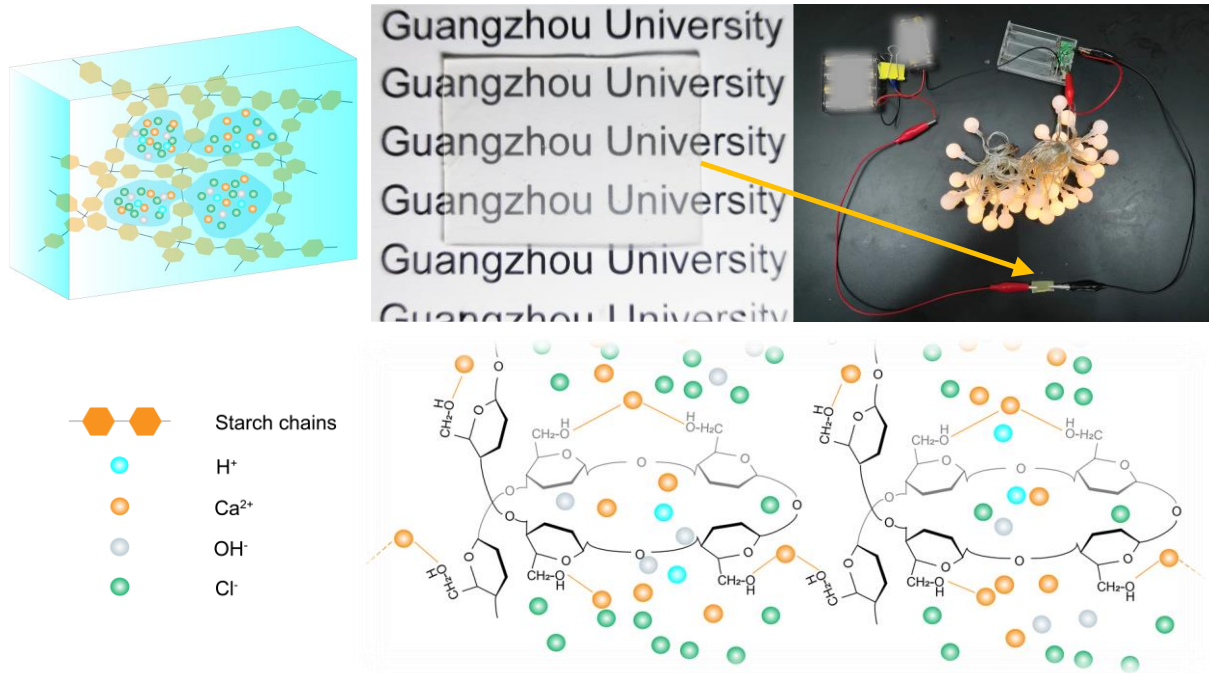
## SYNOPSIS

$CaCl_2$ solution enables the facile preparation of flexible and ionically conductive starch-based materials without waste generation, potential for disposal electronics.

# § Supporting Information §

# Facile preparation of eco-friendly, flexible starch-based materials with ionic conductivity and strain-responsiveness

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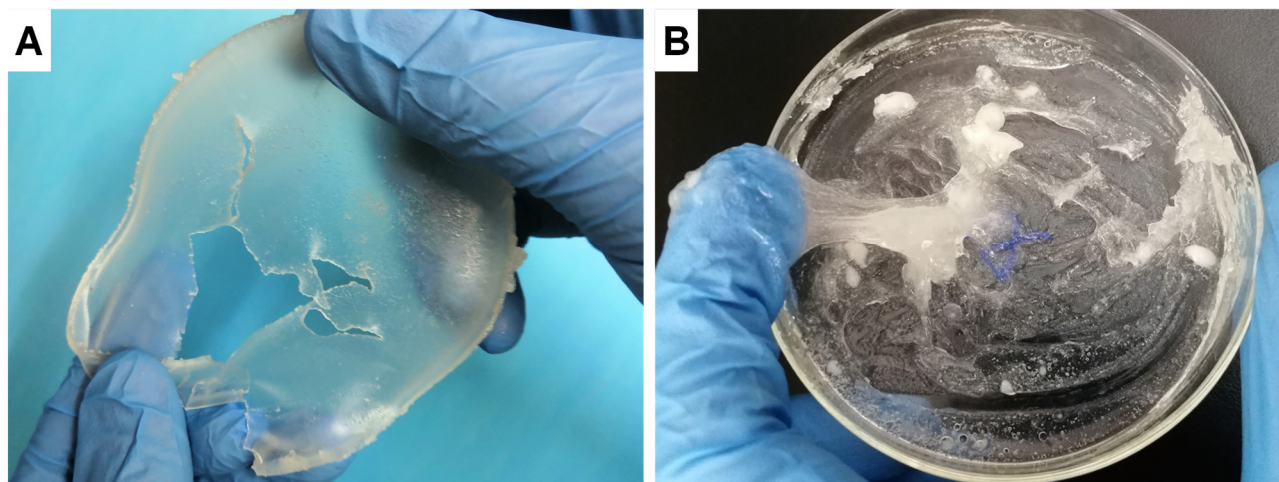
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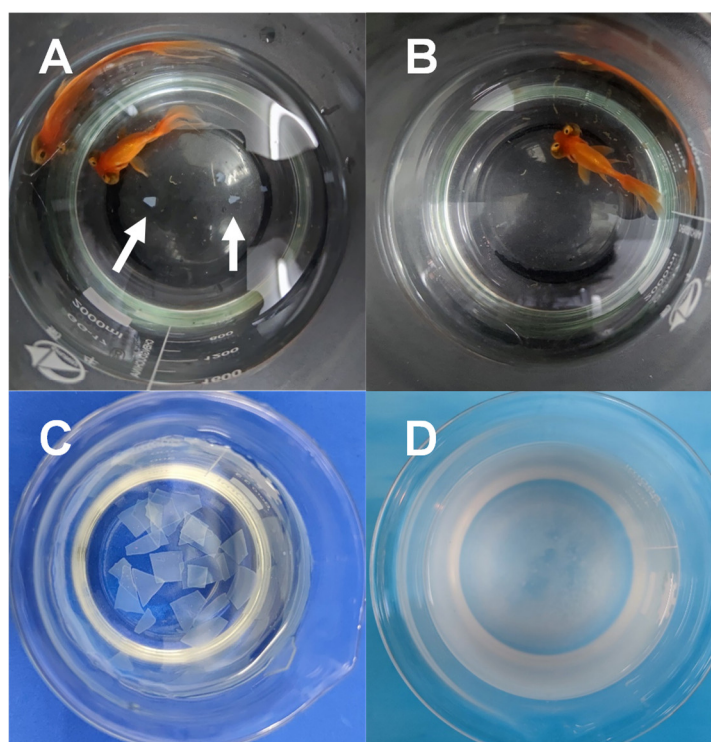**Number of Figures: 2**

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## Table of Content

# 1 Figures



**Figure S1.** A) Starch/MgCl$_2$ composite material (starch/MgCl$_2$/water mass ratio: 4/2/4; conditioned at 57% relative humidity for 48 h); and B) a mixture of starch/ZnCl$_2$/water (mass ratio: 3/3.3/3).



**Figure S2.** A) Starch/CaCl$_2$ composite material (starch/CaCl$_2$ dry mass ratio: 2.5/2.5; conditioned at 57% RH) (labelled by arrows) in water before eaten by goldfish; B) after eaten by the fish; C) The same material in water before stirring; and D) after stirring for 48 h.

# 2 Tables

**Table S1** Moisture contents of starch/CaCl$_2$ composite materials.

| RH | Mass ratio of starch/CaCl$_2$ (%) | | |
|---|---|---|---|
| | 2.5:2.0 | 2.5:2.5 | 2.5:3.1 |
| 33% | 34.4±1.7[f] | 35.9±1.2[e] | 37.3±0.4[e] |
| 57% | 43.1±0.6[d] | 41.7±1.0[d] | 41.6±2.3[d] |
| 85% | 52.5±0.8[c] | 55.3±1.7[b] | 58.0±0.4[a] |

Data are represented in the form of average ± standard deviation; superscripts with different letters in the table indicate significant differences ($p \leq 0.05$).