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Stable, Strain-Sensitivity Conductive Hydrogel with Anti-freezing Capable, Remoldability and Reusability

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Abstract:

Conductive hydrogels have important potential in biosensors, bioactuators and health recording electrodes, but they are often troubled by sensitivity, operating temperature range and whether they can be recycled or not. In this paper, conductive hydrogels polyvinyl alcohol/glycerol/polyaniline (PGA) were prepared by organic combination of low-cost polyvinyl alcohol (PVA), polyaniline (PANi） and glycerin. First, the effects of PVA, glycerol, aniline/phytic acid solution concentration on the mechanical properties, electrical properties and frost resistance of the PGA gel were discussed. Second, the interaction energies of PVA, PANi, phytic acid, glycerol and water molecules were analyzed by Materials Studio. Then, a simple biosensor fabricated using the PGA gel realized the detection of the conventional motion signal of the human body. The conductive gel has high sensitivity (GF=2.14), fast response time (230ms) and can be circulated several times (~540 cycles). Furthermore, the PGA conductive gel can maintain good electrical conductivity (0.32S/m) and mechanical properties even at -20°C. Also, the gel can be recovered by heating injection, cooling and cyclic freeze-thaw three-step method. It is believed that the PGA conductive gel

would be used as a novel multifunctional material at subzero temperatures in various fields, such as flexible electrode, sensors, and wearable devices.

Keywords:

Polyaniline Antifreeze hydrogel Conductive hydrogel Biosensor PVA Remodeling

1. Introduction

Hydrogels are three-dimensional (3D) microstructures polymeric networks that have a high level of hydration, flexibility, good mechanical strength and resilience. In recent years conductive hydrogel has been used to prepare biosensors[1], bioactuators and health recording electrodes with high sensitivity, short response time and multiple recycling applications[2]. To date, a large number of literature have reported the many kinds of biosensors based on conductive hydrogels[1-3], such as piezoresistive, triboelectric, capacitive and piezoelectric biosensors[4-5]. In biosensors, the conductive hydrogel deforms with the organs or body motion, and the electrical conductivity of the gel changes positively or negatively, meanwhile biological signals can be converted and recorded in real time[5]. According to existing literature many kinds of the conductive matrix of conducting polymers (such as polyaniline[6], polypyrrole[7], poly(3,4-ethylene dioxythiophene)[8] and poly(styrene sulfonate) (PEDOT:PSS)[9]), or inorganic conductor (carbon based[10] and metallic based nanomaterials) have been used to fabricate conductive hydrogel[11-12]. Normally conductive hydrogels based on a hydrated matrix of conducting polymers have poor strength/flexibility due to their rigid chain. Nanomaterials are easy to aggregate in the hydrogel, which weakens the

conductivity and mechanical properties of the hydrogels. Additionally, conventional conductive hydrogels cannot be used at subzero temperatures and also have not long-term stability because inevitably freeze. Hence, a big challenge remains to synthesize conductivity hydrogels that incorporate long-time stability, anti-freezing property, mechanical strength and electrical conductivity simultaneously.

Among the common conductive polymers, PANi has been widely used to prepare conductive composite materials due to its facile and lose cost manufacturing process. However, both aniline and polyaniline exhibit strong hydrophobicity and are difficult to combine with hydrophilic hydrogels. Zhenan Bao[13] et al. prepared PANi hydrogels through phytic acid doped aniline, obtaining a gel with the conductivity of 0.11s • cm^{-1} and realizing the preparation of supercapacitors. The method of doping aniline with protonic acid coordination can improve the solubility of aniline in water and increase the conductivity of polyaniline, which provides good experience for the preparation of polyaniline composite hydrogels. While because of the rigid molecular chain of PANi, the mechanical properties of PANi hydrogel are poor and fragile, which makes it limited in application and recycling. Consequently, there is still an unresolved problem concerning the preparation of PANi conductive hydrogels with good mechanical properties and recycling performance.

The PVA hydrogels obtained by cyclic freezing and thawing are traditional physical gels with high mechanical strength and good ductility. It has been reported that the conductive polymer-based hydrogels based on PANi and PVA were made by either physical blending of PANi particles and PVA solution with subsequent

crosslinking[14, 15], impregnation of aniline into preformed PVA hydrogel with subsequent polymerization of aniline[14-15] or dynamic boronate bond. Particularly the PANi-PVA hydrogel crosslinked by the dynamic boronate bond showed remarkable tensile strength (5.3 MPa) and electrochemical capacitance (928 F g^{-1}) [16].

In addition, organisms will live in some extremely low temperature environments, and hydrogel - based biosensors will be severely restricted by freezing in sub-zero environments. Recently, some freezing tolerance conductive hydrogels have been developed by introducing anti-freezing agent such as glycerol and ethylene glycol (EG) into hydrogels[17-21]. Liu et al.[18] reported stable flexibility and strain-sensitivity in the temperature range from -55.0 to 44.6 °C, which prepared using the H_2O/ EG solution as the dispersion medium, PVA as a soft hydrophilic polymer and poly (3,4-ethylene dioxythiophene): polystyrene sulfonate (PEDOT:PSS) solution as a conductive polymer. Lu et al.[17] also reported conductive hydrogel which was obtained in glycerol-water binary solvent system, Polydopamine (PDA)-decorated carbon nanotubes (CNTs) as conducting nanofillers, acrylamide (AM) and acrylic acid (AA) monomers copolymer as hydrophilic polymer. This conductive hydrogel can maintain all the hydrogel properties under extreme wide temperature spectrum (-20 or 60 °C) and stored for a long term.

Based on these results, we hypothesized that the combination of an anti-freezing agent (glycerol) with a strong and robust conductive polymer-based hydrogels (PVA/PANi) through proper supramolecular interactions would yield a new anti-freezing conductive hydrogel. In this paper, we successfully prepared a

glycerol-water conductive PGA gel with PANi as the conductive polymer, which simultaneously possesses anti-freezing performance, good conductivity, long-term stability, good mechanical properties, remoldability and reusability. The conductive PGA gel has good electrical conductivity (0.335 S/m), fracture strain (472%) and fracture stress (94KPa). Impressively it can be used to prepare a biosensor with high sensitivity (GF=2.14), short response time (230 ms) and recycled many times without a significant loss. Even at -20 °C the PGA gel maintains good electrical conductivity (0.320 S/m) and flexibility. Also, the gel can be remolded and reused by three steps of heating, cooling, and cyclic freezing-thawing method. Furthermore, the conductive PGA gel can be prepared on a large scale with low-cost materials. This is of great significance in practical production and application.

2. Results and discussion

2.1 Preparation of Samples

We prepared pure PVA hydrogels (PxG_0A_0 gel), PVA/glycerol hydrogels ($PxGyA_0$ gel) and a series of PVA/glycerol/PANi hydrogels (PxGyAz gel) respectively, where x represents the ratio of the mass of PVA to the volume of the water (w/v %), y represents the volume ratio of glycerol and water (v/v %) and z represents the ratio of aniline/phytic acid solution to glycerin/water solution (v/v %). The preparation process of the gel can be divided into three simple steps: Solution mixing, low-temperature polymerization and cyclic freezing and thawing (Figure S1). Polyaniline was synthesized by a simple chemical method. Aniline monomer is

oxidized and polymerized by ammonium persulfate in the acidic environment provided by phytic acid. Phytic acid protonated amine and imine groups on polyaniline molecular chain to realize conductivity and crosslinking of polyaniline. On the other hand, because phytic acid contains a large number of phosphorus groups, polyaniline is hydrophilic and can be uniformly distributed in PVA[13]. Figure 1a shows the macroscopic morphology of the three gels prepared. PVA hydrogel is white and opaque, PVA/glycerol hydrogel is white and transparent, while the PGA gel is dark green. In addition, the 30× 30 cm× 0.17 cm PGA hydrogel film has been prepared easily in the laboratory (Figure 1.b). It suggests that the PGA gel could realize large-scale industrial production.

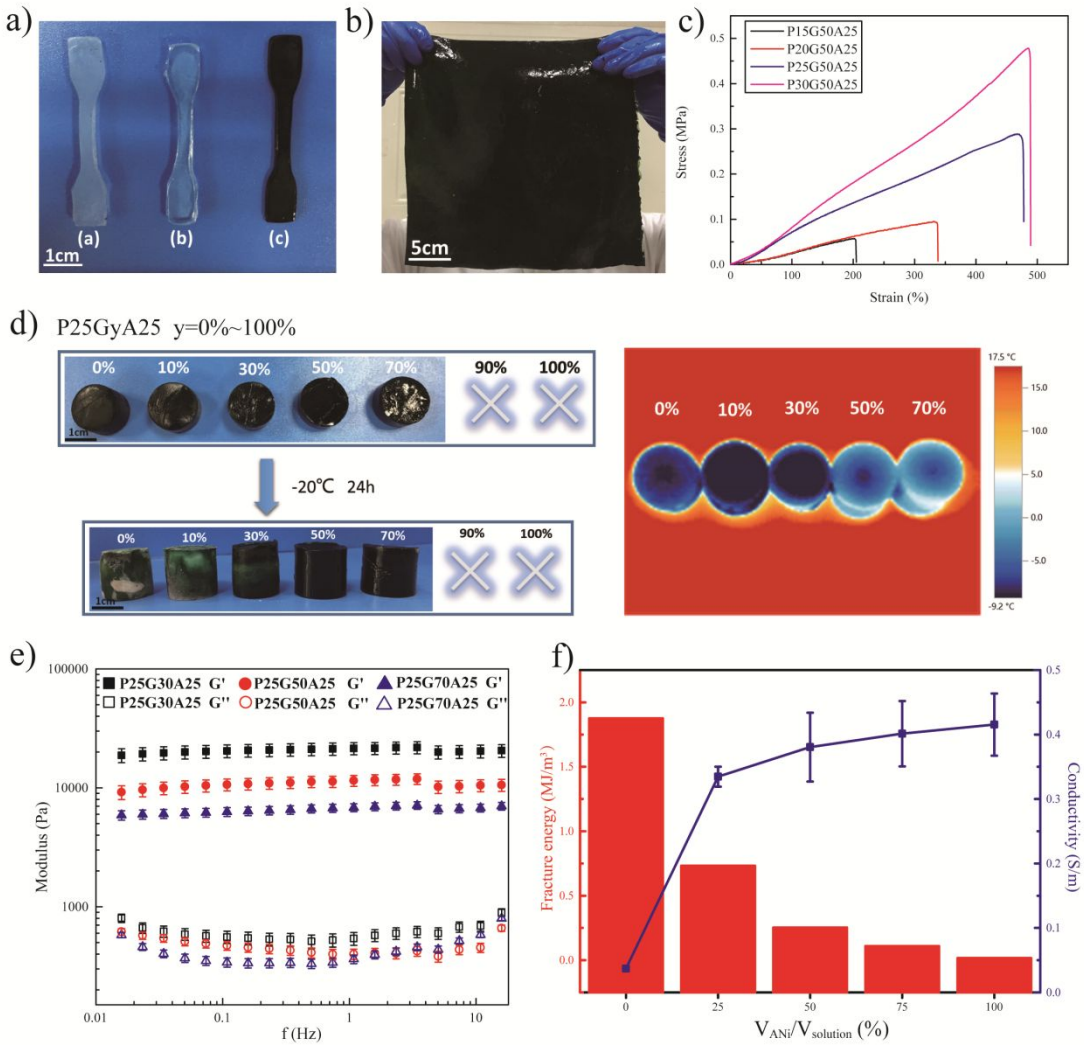

Figure 1. a) Photographs of three gels, corresponding to $P_{25}G_0A_0$, $P_{25}G_{50}A_0$, and $P_{25}G_{50}A_{25}$ gels from left to right. b) Photo of $P_{25}G_{50}A_{25}$ gel with a size of 30 cm × 30 cm × 0.17 cm. c) Stress-strain curves of $P_xG_{50}A_{25}$ gels (x=15%, 20%, 25% and 30%). d) Photographs of $P_{25}G_yA_{25}$ gels before and after freezing at −20 °C for 24 hours and Infrared image of $P_{25}G_yA_{25}$ gels after freezing (y=0%~100%). e) Storage modulus (G') and loss modulus (G'') of $P_{25}G_yA_{25}$ (y=30 %, 50 % and 70 %) gels were measured by dynamic rheological test under constant deformation. f) Fracture energy and conductivity of $P_{25}G_{50}A_z$ gels (z=0 %~100 %).

The effects of PVA, glycerol and aniline/phytic acid concentrations on the mechanical strength, frost resistance and electrical conductivity of PGA gel have been discussed respectively. First, the mechanical properties of $P_xG_{50}A_{25}$ gels with different PVA content have been tested (Figure 1.c and Table S2). It was found that as the

amount of PVA increased from 10% to 30%, the fracture stress of $P_xG_{50}A_{25}$ gel increases from 56 Kpa to 477 Kpa. That's because the number of PVA molecular chains increase to bear more loading force during the stretching. However, more PVA can also lead to the excessive viscosity and more bubbles of the solution, which results increasing the difficulty of preparation and further use of the gel. Therefore, PVA content of PGA gel was used with a mass fraction of 25 % (Fracture stress=280 KPa, fracture strain=472 %) in this paper.

Then the frost resistance and mechanical strength of the $P_{25}G_yA_{25}$ gels with different glycerol content (0%~70%) have been investigated. When the volume ratio of glycerol is more than 70%, the PVA cannot dissolve in the water/glycerin binary solution. Therefore the glycerol content of PGA gels is discussed from 0% to 70%. In frost resistance test, the PGA gel samples were placed at -20°C for 48 h, and then took it out for observation by eyes and infrared imager (Figure 1.d). It was found that the antifreeze ability of $P_{25}G_yA_{25}$ gels increased with the volume ratio of glycerol (0%-70%). As shown in Figure 1.d, when the glycerol concentration in the gel is 10-30%, there are obvious white ice crystals on the gel surface. The result of corresponding infrared thermography shows that the temperature of the gel surface is around -9.2°C, which also indicates the gel is icing. However, when the glycerol concentration is 50%-70%, there is no ice crystal and the infrared image shows that the temperature is about 0~5°C. It indicates that the PGA gel will not freeze even under - 20°C for a long time (48 h).

To contrast, the anti-freezing ability of different volume ratio glycerin/water

binary solution has also been explored. It can be found that when the glycerin/water volume is 50%~70%, and the freezing point of the solution can reach about -29.3~-42.9°C (Table S4, Figure S2 and Figure S3) indicating the best antifreeze ability. This result is consistent with the antifreeze effect of PGA gel.

Also, the influence of glycerol concentration on the gel strength was further discussed. $P_{25}G_{30}A_{25}$, $P_{25}G_{50}A_{25}$, and $P_{25}G_{70}A_{25}$ gels with glycerol volume ratios of 30%, 50%, and 70% were prepared and subjected to constant temperature rheological tests. As shown in Figure 1.e, the storage modulus (G') of the PGA gels decrease from 20.2KPa to 6.49 KPa with glycerol concentration increasing from 30 % to 70 %. According to their storage modulus platforms, the effective cross-linking point density of gel was calculated (Table S5). Obviously, it can be seen that the density of effective crosslinking points decreased from 37.0 to 16.1 mol/m^3 with glycerol concentration increasing from 30 % to 70 %. This indicated that the glycerol destroyed some hydrogen bond cross-linked microdomains, resulting in the mechanical properties of the PGA gel decline. This also explains why the previously mentioned PVA/glycerol gel is transparent. Therefore, to balance the mechanical strength and frost resistance of PGA gel, the optimal glycerin/water volume ratio of the PGA gel is 50%.

The dosage of monomer Aniline/Phytic acid solution also affects the mechanical properties and conductivity of PGA gels. It can be observed in Figure 1.f and Figure S4 that as the Aniline/Phytic acid solution increases from 0% to 100%, the conductivity of PGA gel increases from 0.037 to 0.415 S/m, whereas the fracture

energy of gel decreases from 1.88 to 0.02 MJ/m^3. The more dosage of monomer Aniline/Phytic acid solution results in more PANi which provides more channels for electrons to pass through, so the conductivity increases. At the same time, the Young's modulus of the PGA gel increases from 30.2 KPa to 34.5 KPa (Figure S5) due to the rigid PANi chain, resulting in more brittle of the PGA gel and the obvious decrease of fracture strain (from 617 % to 85 %) and fracture energy (from 1.88 to 0.0168 MJ/m^3) (Table S3). Considering the effect of dosage of monomer Aniline/Phytic acid solution, in order to obtain a strong and robust conductive polymer-based hydrogels, the optimal dosage of Aniline/Phytic acid solution is finally determined to be 25%. Therefore, the PGA gels herein refer to $P_{25}G_{50}A_{25}$ gel unless otherwise stated, which has a moderate anti-freezing effect, mechanical strength and electrical conductivity.

2.2 Characterization of Samples

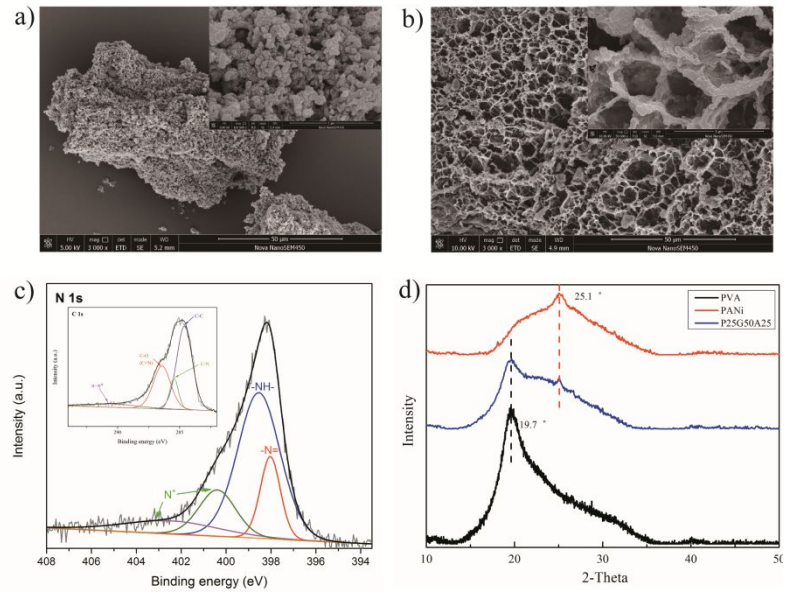

Figure 2. a) and b) are SEM photos of PANi powder and dry $P_{25}G_{50}A_{25}$ hydrogel, respectively. Illustration is an enlarged view. c) XPS N 1s and C 1s (Illustration) spectrum of PGA gel. d) X-ray diffraction pattern of PANi, PVA and PGA gel.

FTIR spectra of PVA, PGA gel and PANi powder show that PANi can be

successfully obtained by solution polymerization at low temperature, and PGA gel can be successfully fabricated by PVA and PANi (Figure S6). Scanning electron microscopy image (SEM) of PANi powder (Figure 2a) shows a porous structure, formed by piling up spherical particles. And the SEM image of PGA (Figure 2b) shows that the PANi particles are evenly and neatly distributed on the walls of the PVA. In addition, the amount of Aniline/Phytic acid also affects the accumulation of PANi (Figure S7). X-ray photoelectron spectroscopy scans (XPS) of PVA gels and PGA gels are shown in Figure S8. In Figure 2c, the N 1s spectrum of PGA gel can be deconvoluted into four bonding states located at 398.2, 399.5, 400.6, and 402.3 eV, which correspond to quinoid imine (-N=), benzenoid amine (-NH-), positively charged imine (N+) in the bipolaron state and protonated amine in the polaron state[22-23], indicating phytic acid successfully protonated the nitrogen element in PANi molecular chain. Similarly, the peaks of PANi (C-N 285.4 eV) and PVA (C-O 286.2 eV) can be obtained by fitting the peaks of C1s peaks[24-25]. It is further illustrated that the PGA gel is successfully compounded by PVA and PANi. In addition, the π–π* satellite in aromatic is observed at 290.4 eV, indicating that the conjugation of benzene rings existed among the PANi chains[26]. Therefore, the porous structure obtained by accumulation of PANi spherical particles is through π -π stacking of benzene rings and phytic acid doping[13]. Furthermore, X-ray diffraction (XRD) of PVA, PANi and PGA gel were tested. As shown in Figure 2d, in the X-ray diffraction curve of PGA gel, the crystalline peaks appear at 2 θ=25.1 ° and 19.7 °, corresponding to periodicity paralleling of the PANi chains (π-π stacking)[13, 27] and the (101) plane of

the PVA crystal[28], respectively. And compared with the pure sample, the crystallization peak has no obvious shift, which indicates that PVA crystal and PANi crystal have no mutual influence.

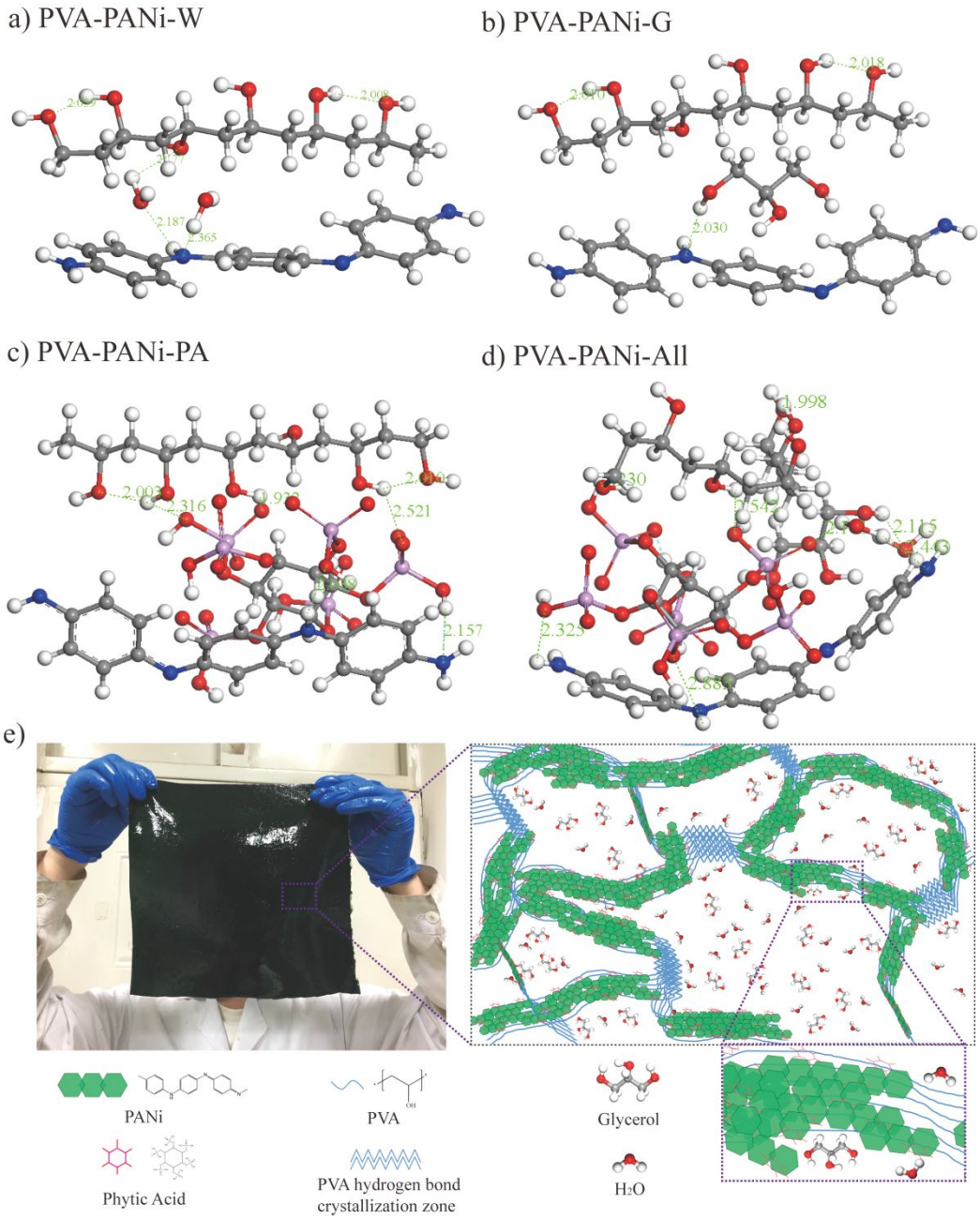

Figure 3. The interaction of PVA-PANi-W a), PVA-PANi-G b), PVA-PANi-PA c) and PVA-PANi-All d). e) Schematic diagram of PGA gel.

In order to gain further insight into the role of PANi, glycerol and phytic acid in the hydrogel, Materials Studio has been used to simulate the molecular structure and

calculate the interaction energy by the density functional theory (DFT) program DMol3. The interaction energies of the following three cases were calculated respectively: 1) water molecules and glycerol molecules; 2) PVA molecules coexist with water molecules and glycerol molecules; 3) PVA molecules and PANi molecules coexist with water molecules, glycerol molecules and phytic acid molecules.

Firstly, we find out the stability of water molecules and glycerol molecules coexisting is stronger than that of water molecules alone or glycerol molecules alone due to the strong hydrogen bonding between glycerol and water molecules[17] (Figure S9 and Table S6). Consequently, it is precisely the hydrogen bonding between glycerol and water molecules, and the protective effect of glycerol backbone molecules inhibits the growth of ice crystals in water and achieves the antifreeze effect of glycerol/water solution[29].

Secondly, when glycerol and water molecules coexist, the interaction energy with PVA molecular chains is higher than that of glycerol or water molecules alone (Figure S10 and Table S7). It is demonstrated that more hydrogen bonds have been formed between glycerol/water molecules and the PVA molecular chain, while some hydrogen bonds between the PVA molecular chains in crystal microdomains have been broken. Therefore, the gel becomes transparent and the crosslinking density and storage modulus (Fig. 1e) are significantly reduced.

Finally, the structure of PVA/PANi and water molecules (Figure 3.a), glycerol molecules (Figure 3.b), phytic acid molecule (Figure 3.c) and all of the above molecules (Figure 3.d) were optimized and corresponding interaction energies were

calculated (Table 1). The results demonstrated that water, glycerol and phytic acid could stabilize the PANi/PVA molecular chain by hydrogen bonding and protonation. The strong interaction energies of PVA-PANi, PVA-PANi-W (PVA/PANi and water molecules), PVA-PANi-G (PVA/PANi and glycerol molecules), PVA-PANi-PA (PVA/PANi and phytic acid molecules) and PVA-PANi-All (PVA/PANi and all molecules) were -0.216 Ha, -0.261 Ha and -0.406 Ha respectively, higher than the combination of PVA and PANi molecular chains alone (-0.039 Ha). Moreover, the interaction can reach -1.55Ha if all "stabilizers" (water, glycerin, phytic acid) work together, also demonstrated that water, glycerol and phytic acid interacted intensively with the PANi/PVA molecular chain to form multiple hydrogen bonds.

Form	Interaction energy (Ha)
PVA-PANi	-0.039±0. 001
PVA-PANi-W	-0.216±0. 002
PVA-PANi-G	-0.261±0. 001
PVA-PANi-PA	-0.406±0. 001
PVA-PANi-All	-1.55±0. 01

Table 1. The calculated interaction energy in PVA-PANi, PVA-PANi-W, PVA-PANi-G, PVA-PANi-PA and PVA-PANi-All. All simulations were repeated three times.

Base on the DFT analysis, we can draw a schematic diagram of the PGA gel structure (Figure 3.e). The PVA molecular chains can be formed hydrogen bond crystal microdomains by cyclic freeze-thaw. However, the crystal microdomains are partially destroyed by introducing glycerol. The boundary between water and crystal phase becomes blurring, hence the PVA/glycerol gel is colorless and transparent.

Simultaneously, the strong hydrogen bonding of the glycerol/water molecules

and the protection of the glycerol backbone prevent the ice crystals from growing in the water/glycerol solution, endowing the PVA/glycerol anti-freezing properties. The porous spherical particles of PANi have obtained by low-temperature polymerization of aniline in phytic acid, PVA, and water/glycerol solution. The one effect of phytic acid is protonated cross-linked and doped PANi, another effect of phytic acid is forming multiple hydrogen bonds with PVA, water and glycerol. It is the multiple synergistic effects of phytic acid, water and glycerol that allows the PANi particles to be uniformly adsorbed on the walls of the PVA. The PANi particles doped and crosslinked by phytic acid are uniformly distributed and in contact with each other, providing a pathway for electron transfer, giving the gel good electrical conductivity.

2.3 Conductive properties of the PGA gel

It is known that PANi particles adsorbed on the PVA chain form a conductive path by physical contact, so that under the external deformation the PANi particles come out of contact with each other, resulting in a decrease in electrical conductivity. To investigate the strain-resistance response of the PGA gel, a tensile loading-unloading test in the electric circuit was carried. As shown in Figure 4.a, the relative resistance variation $((R-R_0)/R_0)$ of the $P_{25}G_{50}A_{25}$ gel stepwise increased to different levels with the strain from 0 to 100 % respectively. After releasing the external strain, it quickly returned to the initial value and can be cycled for several times ($\approx$ 5 times). We took the relative resistance variation corresponding to deformation in Figure 4.a to obtain Figure 4.b and carried out linear fitting to obtain

gauge factor (GF=2.14), which is superior to previously reported level 0.48~0.63[30-31].

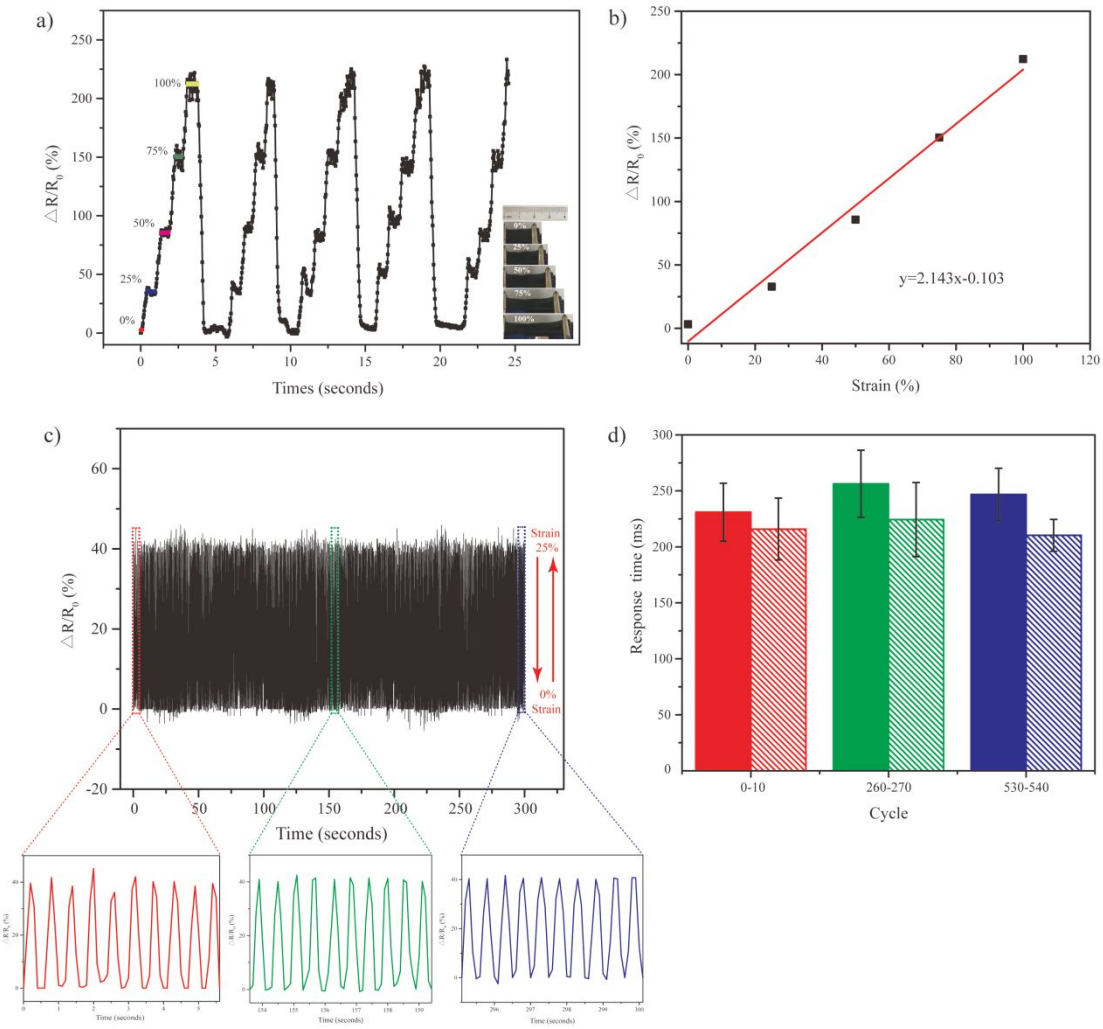

Figure 4. a) Relative resistance variation ((R − R_0)/R_0) of PGA gel stretched to 0 %, 25 %, 50 %, 75 % and 100 % in five cycles. b) Relative resistance variation of PGA gel under different strains. c) Relative resistance variation of the PGA gel under continuous Stretch and release from 0 to 25% strains for 300 s (~540 cycles). d) Average response time for stretching and release in 0~10, 260~270, and 530~540 cycles, respectively

In addition, the gel can normally work at a tensile strength of 0-71.3KPa (deformation 0 to 100%) and maintain a stable GF factor. Usually, the pressure strength of human body movements is in the range of 0-100 KPa[4-5], hence the gel can be expected to measure most human movements. More important, the gel was further subjected to cyclic stretching and release about 540 cycles, and the change range of stretching deformation was 0%-25% (Figure.4.c), demonstrating that the relative

resistance-deformation relationship remained stable as the number of cycles increased. Take the initial (0~10), middle (260~270), and end (530~540) three stages of the cyclic test, all with good repeatability and stability, which shows the PGA gel had no obvious strain residual and stress loss under slight deformation. Therefore, it can be used prepare biosensor for long-term and multiple uses. Furthermore, as shown in Figure 4.d, the response times of the three ten-cycles (Figure 4.c) of the stretching and release process were separately counted. Although the response time of the stretching process was slightly longer than that of the release process, the total time is approximately 230 ms, indicating the fast-responding PGA gels can detect high-speed motion. These results demonstrate that sensitive hydrogel with relative resistance as a function of deformation can be used to prepare biosensors for detecting the human movement.

2.4 Biosensor based on PGA gel

The capabilities of the PGA gel biosensors for practical applications of human activity monitoring are investigated. Simple biosensors made of PGA gel, commercial adhesive tape and copper wire can detect and record the movement signals of different parts of the human body in real time. As shown in Figure 5, the swallowing action of the throat (Figure 5a) and the bending actions of the fingers (Figure 5b), the action of the elbow (Figure 5c) and the knees (Figure 5d) are recorded. All test curves have clear and obvious transition points with good repeatability and stability, even the slight jitter of the throat during swallowing can also be recorded in real time,

reflecting the high sensitivity of the sensor. Additionally, bending motions at different rates can also be recorded when bending fingers (Movie S1), knees slowly and rapidly, without significant delay. These results demonstrate that the PGA gel biosensors can recognize gentle motion (i.e. throat knot vibration) and large body motions (including finger bending, elbow bending and knee bending), which may be useful in diagnosis and physical therapy (such as gait training to help stroke patients recover).

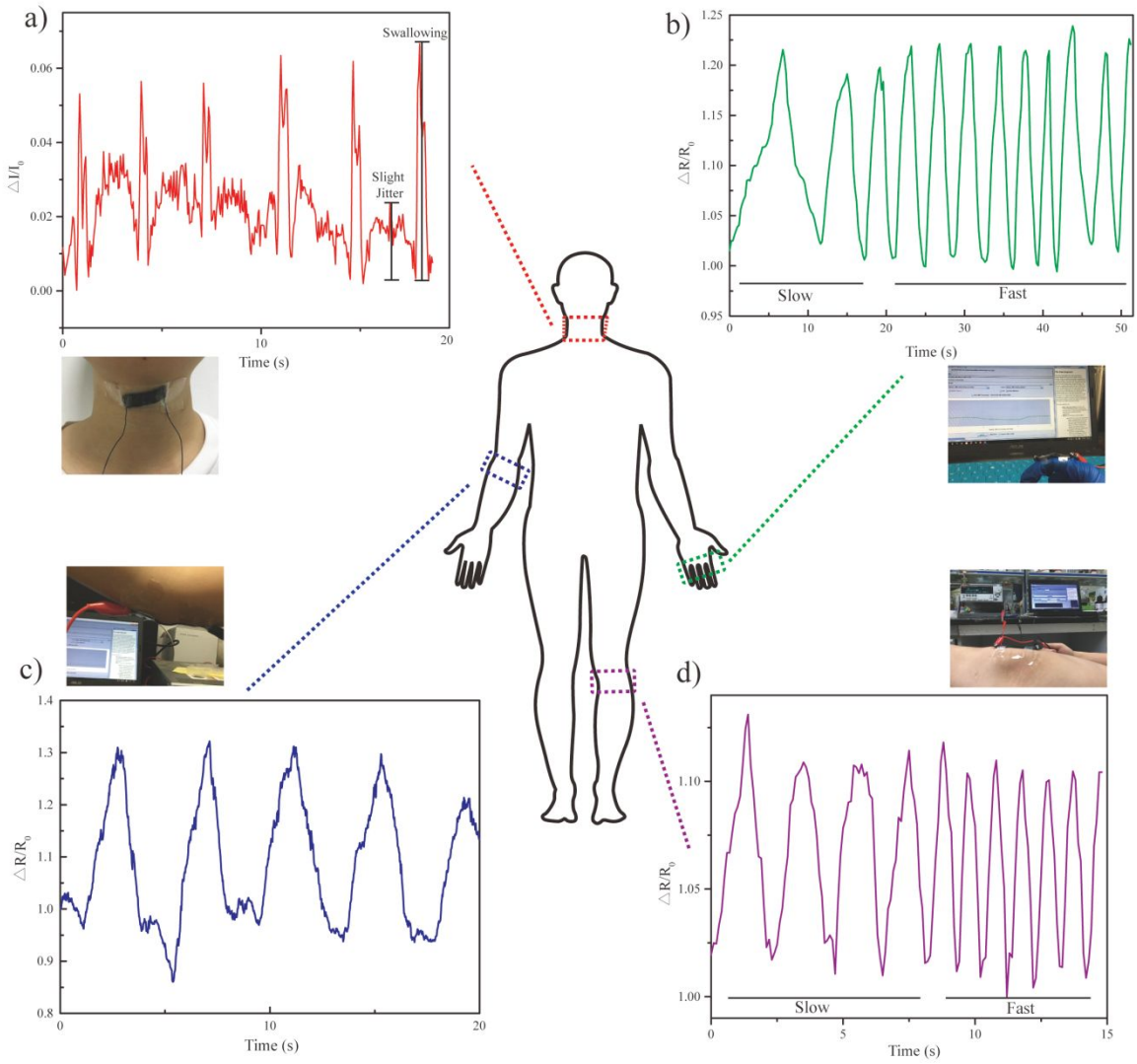

Figure 5. a) Relative current variations of the sensor attached to the throat induced by drinking water. Relative resistance variations of the sensor attached on the index finger b) the elbow c) and the knee d) induced by bending.

2.5 Anti-freeze properties of PGA gel

As mentioned above, glycerin prevents the gel from freezing. Hence the PGA gels can be endowed with good anti-freezing capability. To investigate the performance of the PGA gels after undergoing subzero temperatures, the hydrogels were placed in a freezer with low temperature (- 20 °C) for 24 h, then the mechanical properties and conductivity of these samples were tested immediately after taken out. For comparison, the PGA gel was soaked in deionized water for 3 days to sufficiently remove glycerin and designated as PGA-R gel. It was found that the PGA gels had

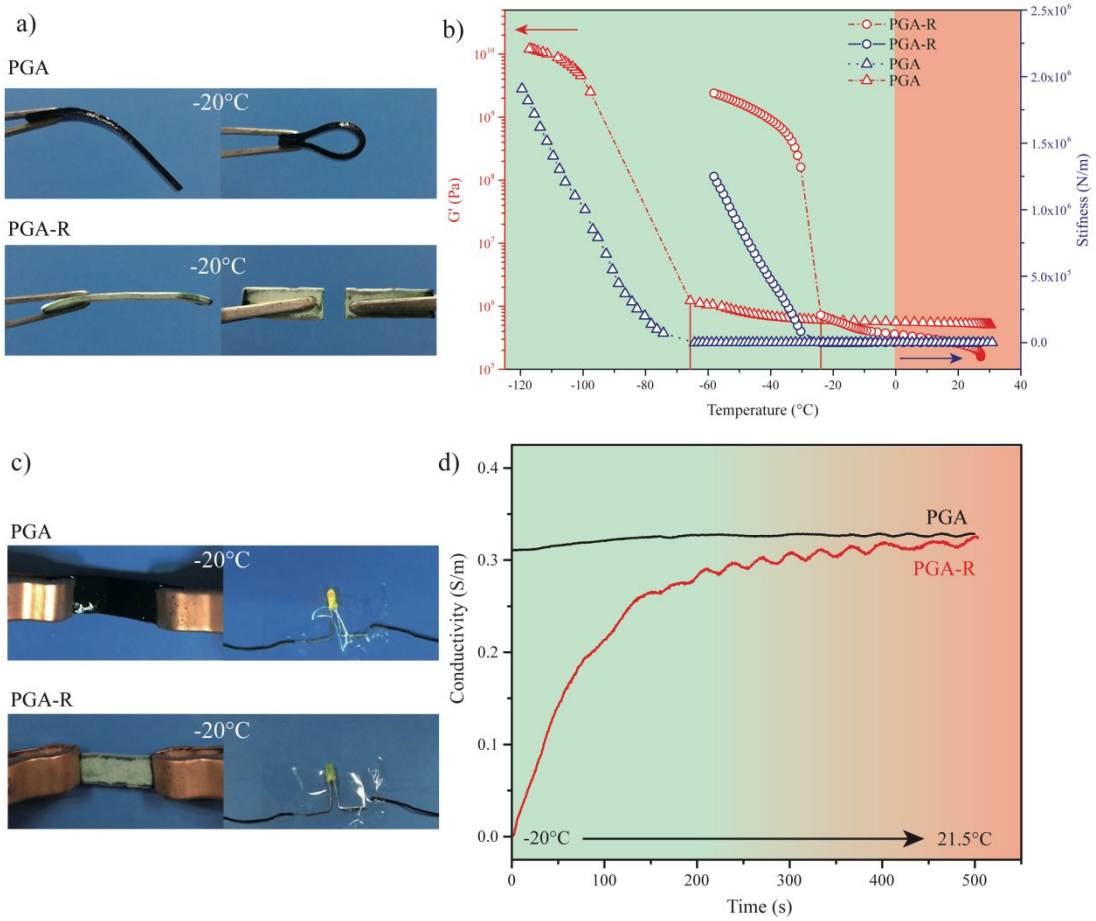

Figure 6 a) Bending PGA gel and PGA-R gel at -20 °C. b) Detecting the storage modulus and stiffness of PGA gel from 25 °C to -120 °C and PGA-R gel from 25 °C to -60 °C, respectively (○ Represents PGA-R, Δ Represents PGA). c) The PGA gel or PGA-R gel, LED lamp and 3V power supply are connected at -20 °C. d) Conductivity as a function of time after transferring PGA gel and PGA-R gel from -20 °C refrigerator to a 25.6 °C environment.

significant anti-freeze effect compared with the PGA-R gel. As shown in Figure 6a

the PGA gel exhibited high flexibility to bend at will, and had high resilience to quickly recover from deformed shapes at -20 °C (Figure S12). In contrast, the PGA-R gel was hard and brittle, and brittle fracture easily occurs when bending (Figure 6.c). The storage modulus and stiffness of PGA-R and PGA gels were tested by dynamic mechanical analysis from 25 °C to -60 °C or -120 °C. The stiffness of PGA-R gel began to increase at about -24 °C, and the storage modulus also increased rapidly, indicating that the growth of ice crystals made the macro PGA-R gel hard and brittle (Figure 6b). However, the stiffness and storage modulus of PGA gel began to increase at about -66 °C, indicating that the PGA gel has a freezing point temperature of about 42 °C lower than that of the PGA-R gel due to the presence of glycerol, which is also same with the freezing point temperature of glycerin/water (G_{vol}=60 %) solution mentioned above. Furthermore, the conductivity of PGA-R and PGA gels was investigated as a function of temperature (Figure 6.d). The gel was frozen at -20 °C for 24 hours, then taken out and placed in a room temperature environment (25.6 °C) to naturally heat up. It was found that the conductivity of PGA gel increased slightly and remained at about 0.32 S/m overall, while the conductivity of PGA-R gel was seriously affected by temperature. The conductivity of PGA-R gel was close to 0 S/m (at -20 °C), then increased to about 0.3 S/m (at 21.5 °C) gradually with the temperature increase. In Figure 6.c, the PGA gel illuminates the LED lamp even at -20 °C, while the PGA-R gel does not. In summary, the PGA gel containing glycerin maintains good conductivity (0.32 S/m) at subzero temperatures, demonstrating the glycerin endow conductivity hydrogel outstanding anti-freezing feature. Further, we

tested the deformation sensitivity of the sensor at -20°C (Movie S2 and Figure S13). We can find that PGA gel still has good deformation responsiveness even at -20°C.

2.6 Remolding property of PGA gel

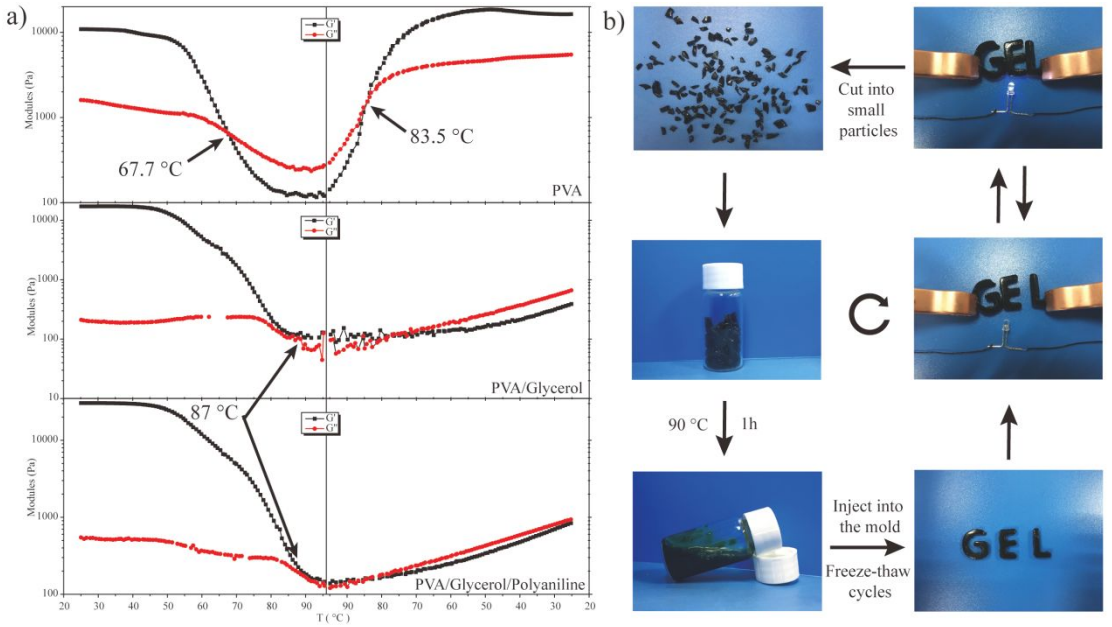

Figure 7 a). From top to bottom, the storage modulus (G') and loss modulus (G") of PVA gel, PVA/glycerin gel and PGA gel were measured by dynamic rheological test with the temperature range was 25℃ to 95℃ and 95℃ to 25℃. b) PGA gel can be recycled through three steps: heating and dissolving, re-injection molding and cyclic freeze–thaw.

It is well known that the remoldability and reusability are important and intriguing features of the gels. In order to change their permanent shape as required, the gels need to be appropriate thermoplastic rheological properties. The physical crosslinks of hydrogen bonding and crystalline domains endowed the anti-freezing conductive PGA hydrogels thermoplastic properties. Therefore the PGA hydrogels can be remolded and reused by heating. In this work small deformation (1%) oscillatory measurement was applied to characterize the dynamic rheological properties of PVA, PVA/glycerol and PGA gels respectively. The samples were tested at a constant strain of 1% and a frequency of 7.5Hz, the temperature first increased from 25°C to 95°C at a rate of 3°C/min and then reduced from 95°C to 25°C at the

same rate. Figure 7.a illustrates the temperature dependence of the storage modulus G′ and loss modulus G″ for PVA, PVA/glycerol and PGA gels respectively. It was found that G′ was always much higher than G″ and appeared as a plateau over the 25°C to 45°C temperature range for PVA, PVA/glycerol and PGA gels, which indicates the crosslinked network structure of the gels are stable from 25°C to 45°C. As temperature increase, there was a gel-sol transition at 67.7°C for the PVA hydrogel, the gel turned into a viscous solution. As the temperature dropped from 95 to 83.5 °C the PVA viscous solution appeared a sol-gel transition and turned into a gel again, which corresponded to the destruction and reconstruction of the hydrogen bonding in microregions of the PVA. However, the G′ and G″ of the PVA/glycerol and PGA gel obviously decreased with the temperature increased and were close at about 87°C. During cooling, there was no significant sol-gel transition, and the G′ and G″ were kept basically same, the samples exhibit a liquid state. These results suggest the PVA/glycerol and PGA gel can be softened and became a sol state by heating, and maintained liquid state when cooled at room temperature. However, they can transform the gel state again after cyclic freezing and thawing. This special rheological property can be used to recover and reshape gels. In order to further confirm this property, the PGA gel which cut into small pieces was heated to 90°C, then cooled to 50°C and injected into molds with different shapes. Finally, new shapes formed after repeated freezing and thawing (Figure 7.b). More importantly, the PGA gel reshaped in this way can still maintain its original softness and conductive ability, which can make LED lights.

3. Conclusion

In this paper, a composite conductive hydrogel (PGA gel) was successfully prepared. The effects of PVA, glycerol and aniline/phytic acid solution dosage on the mechanical properties, electrical properties and frost resistance of PGA gel were discussed. It was found that the multiple synergistic effects of glycerol, water molecules and phytic acid can stabilize PVA and PANi molecular chains. The PGA gels can maintain good mechanical and conductive even at subzero temperatures (-20°C). PVA molecular chain in PGA gel provides gel flexibility, PANi provides the conductive path, glycerol prevents ice crystals from growing in the gels. Therefore the conductive PGA gel with good mechanical properties, high sensitivity and the anti-freezing feature can be obtained. Thereafter, a biosensor fabricated with the PGA conductive gel was used to measure the human body's normal motion signal with high sensitivity, short response time and multiple use cycles. In addition, the non-covalent crosslinks endow the conductive PGA gel with intriguing remoldability and reusability, which are important for practical applications. After heating more than 87°C, the PGA gels can be melted and reshaped via injection molding and cyclic freeze-thaw. Impressively in combination with all the properties above, it is believed that this conductive PGA gel will be a promising material for applications at subzero temperatures in various fields, such as the flexible electrode, sensors, and wearable devices.

Conflicts of interest

There are no conflicts of interest to declare.

Acknowledgement

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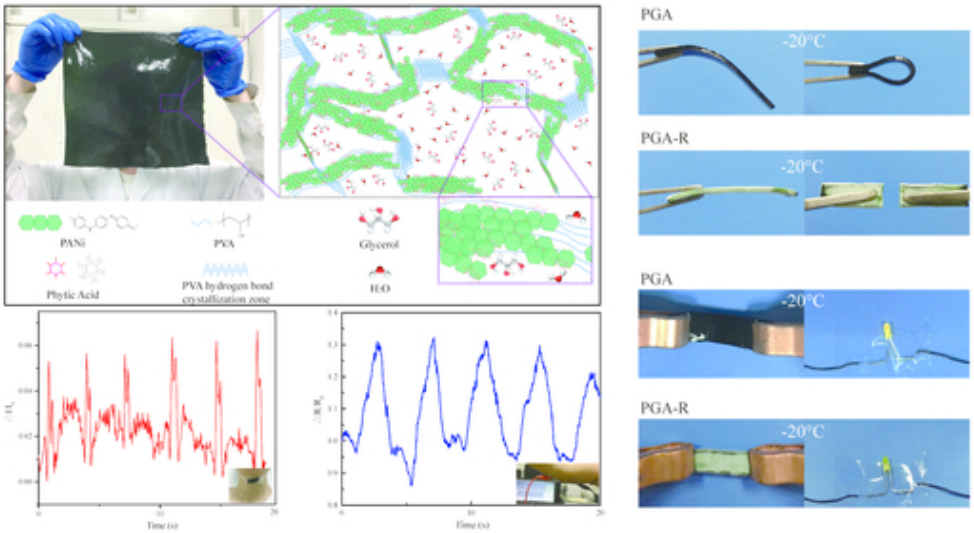

Abstract Graphic

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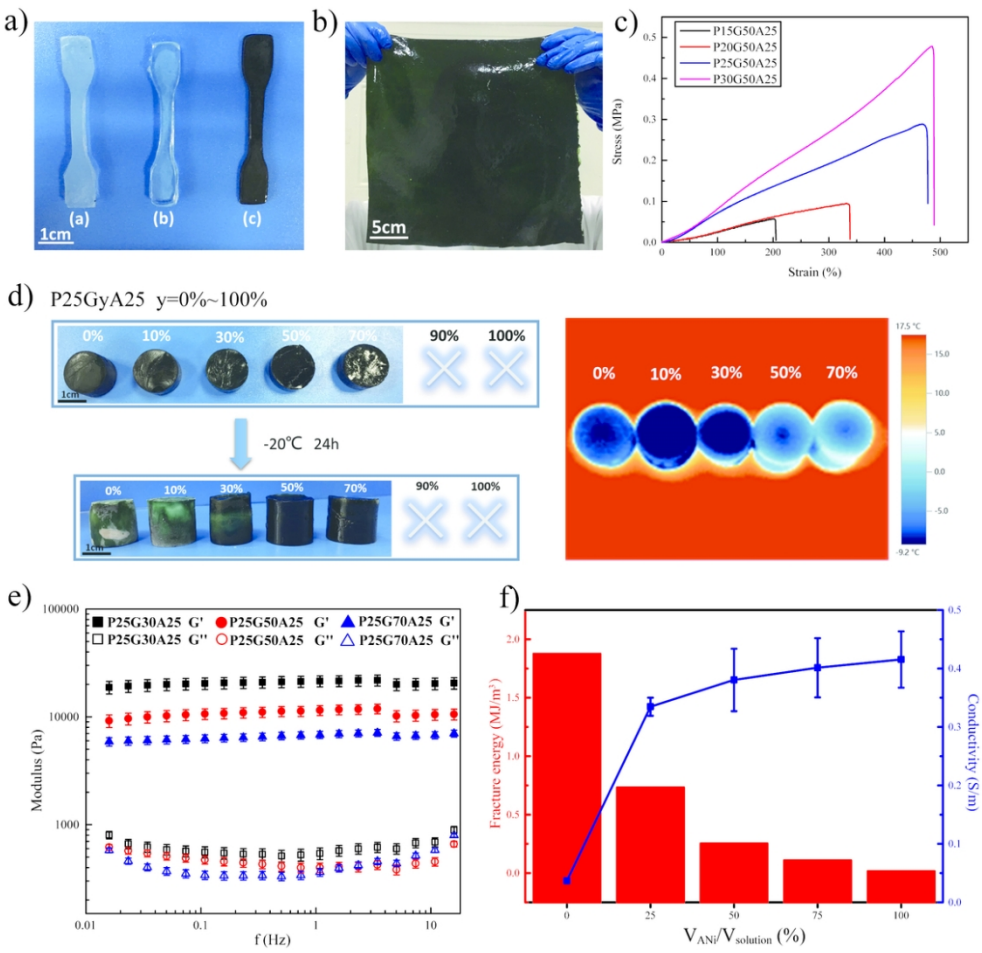

Figure1

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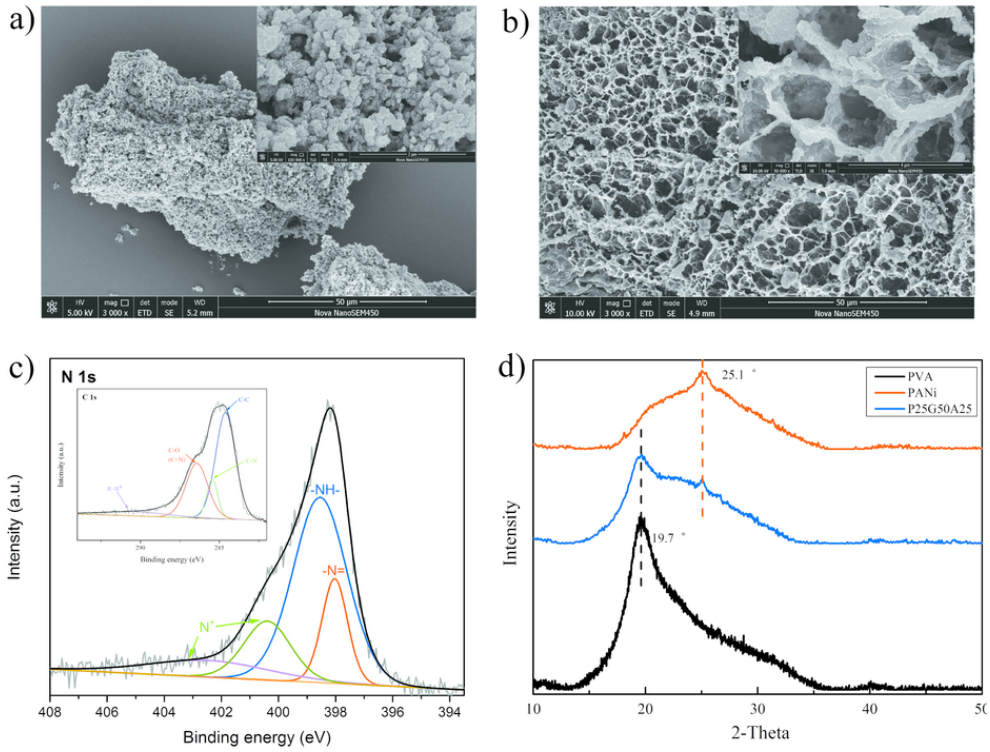

Figure 2

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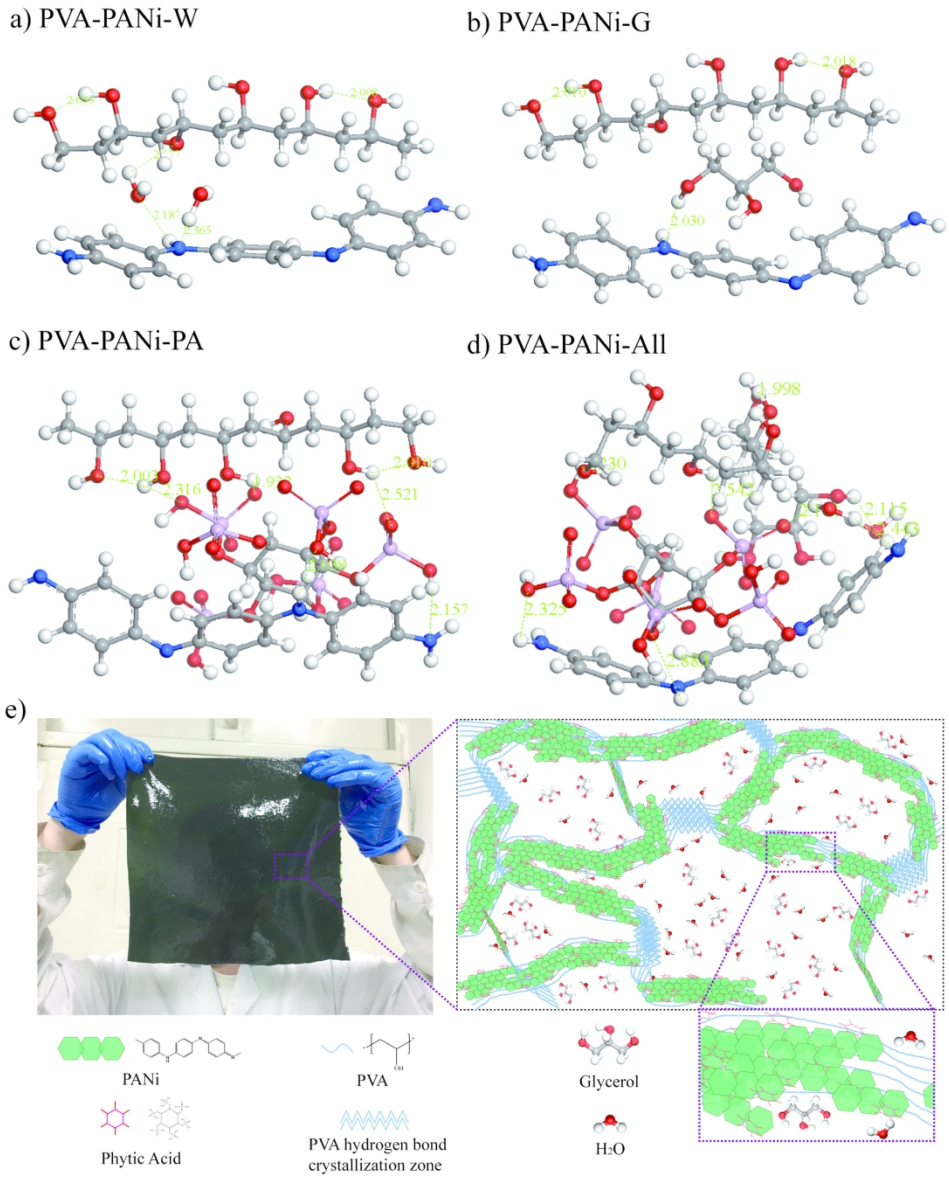

Figure 3

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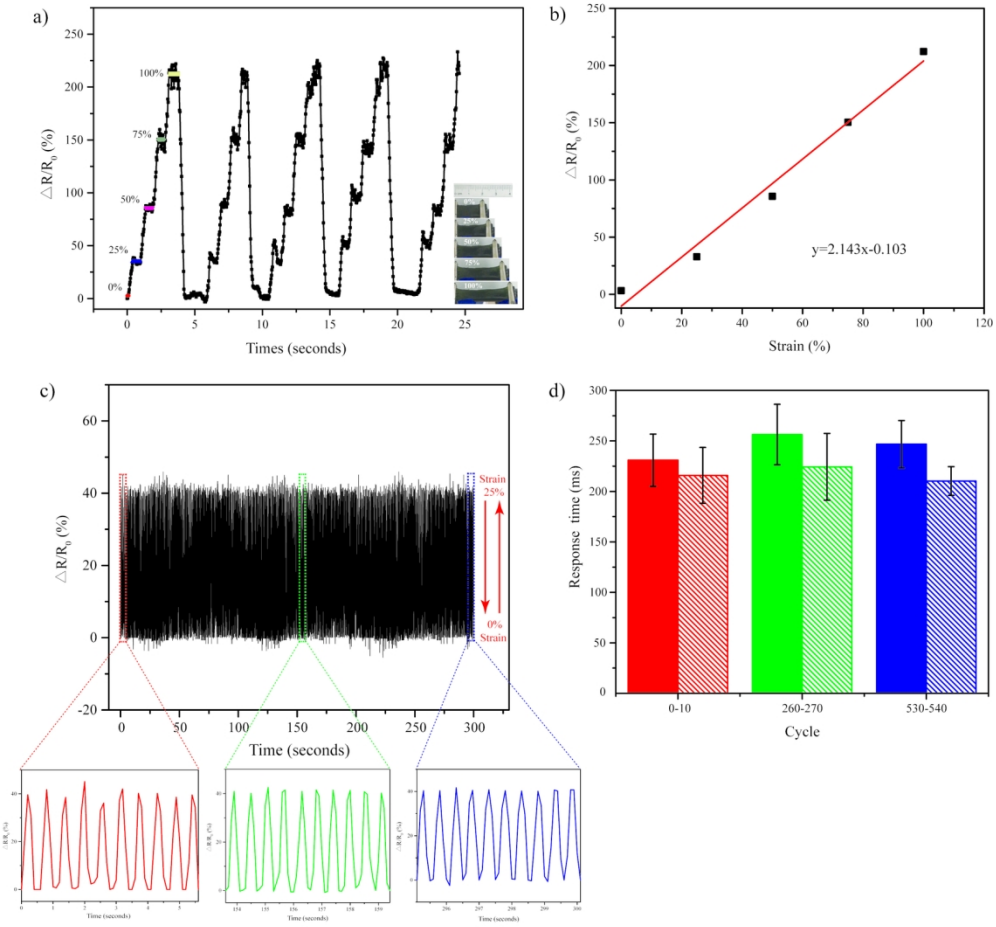

Figure 4

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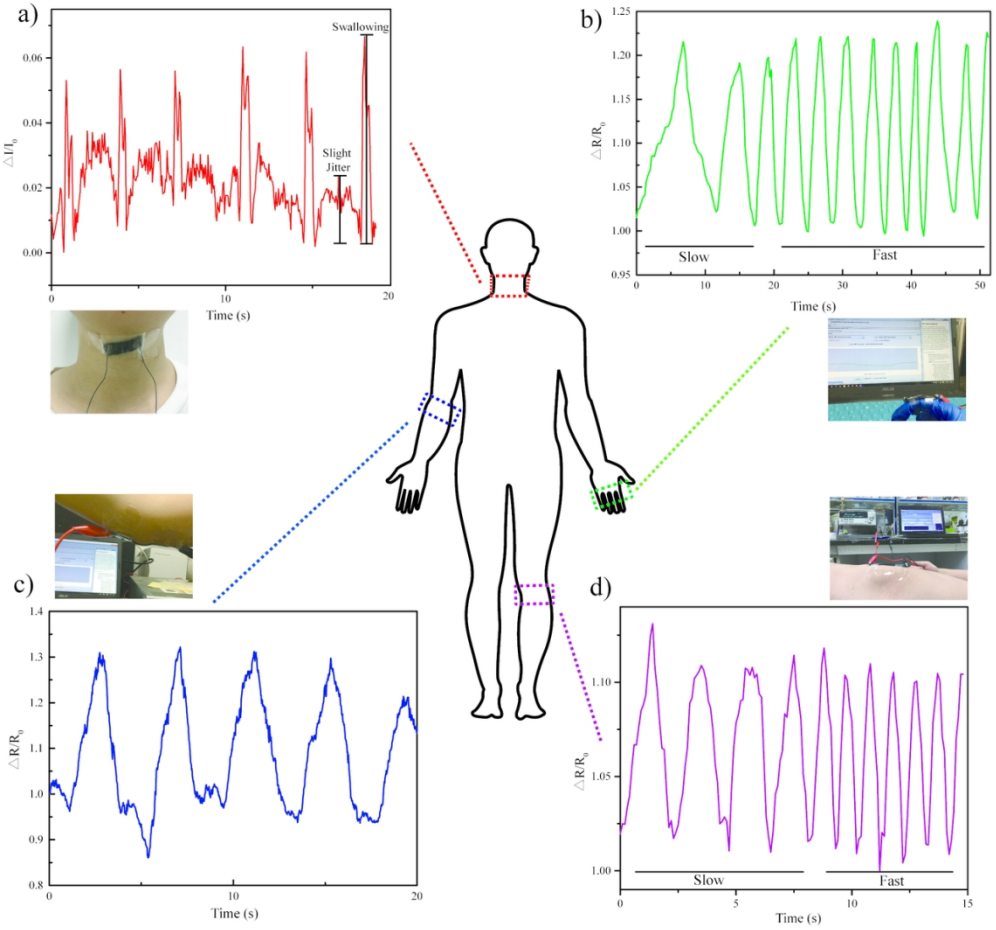

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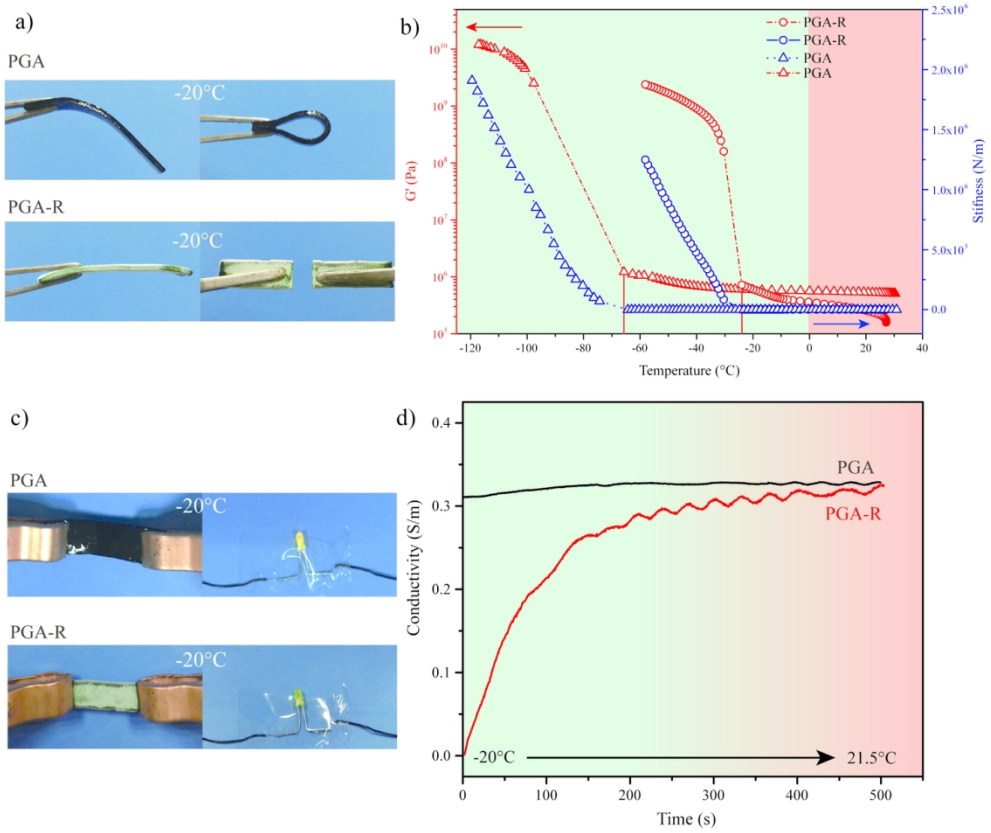

Figure 6

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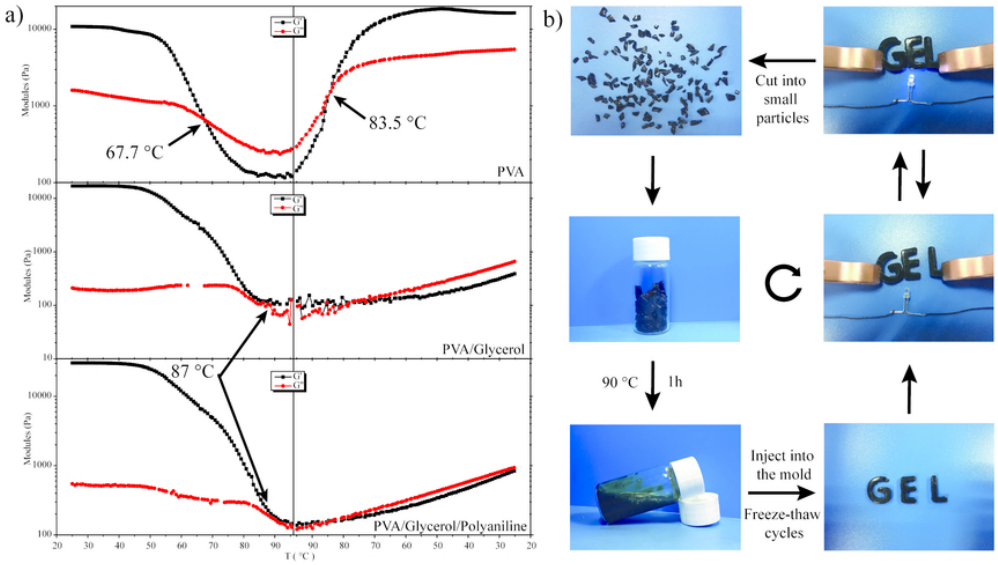

Figure 7

73x41mm (300 x 300 DPI)