

Contents lists available at ScienceDirect

# Journal of Colloid and Interface Science

journal homepage: www.elsevier.com/locate/jcis

# **Regular Article**

# A highly elastic, Room-temperature repairable and recyclable conductive hydrogel for stretchable electronics



# Haifei Wang, Jiameng Lu, Huayi Huang, Senlin Fang, Muhammad Zubair, Zhengchun Peng\*

Center for Stretchable Electronics and Nanoscale Sensors, Key Laboratory of Optoelectronic Devices and Systems of Ministry of Education and Guangdong Province, College of Physics and Optoelectronic Engineering, Shenzhen University, Shenzhen 518060, PR China

# G R A P H I C A L A B S T R A C T



# ARTICLE INFO

Article history: Received 6 September 2020 Revised 11 December 2020 Accepted 12 December 2020 Available online 17 December 2020

Keywords: Stretchable electronics Conductive hydrogels Poly(vinyl alcohol) Dual-crosslinked networks Recyclable hydrogel

# ABSTRACT

Conductive hydrogels present great potential in bioelectronics, ionotronic devices, and electronic skin. However, the creeping and plastic deformation of hydrogel often lead to poor stability and low reliability in applications. Here, we report a highly elastic conductive hydrogel based on crosslinked carbon nanotubes (CNT) and poly(vinyl alcohol) (PVA). With the formation of double crosslinking interactions, i.e., strong interaction from covalent acetal bonds and weak interaction from hydrogen bonds, CNT-PVA networks exhibit good stretchability (fracture stain up to 500%), rapid recovery, zero-residual deformation, and excellent mechanical stability. As such, the electromechanical response of this dual-crosslinked conductive hydrogel is stable and repeatable for a wide range of loading rates. Benefiting from the abundant hydroxyl groups and reversible acetal linking bridges in hydrogel networks, the prepared conductive hydrogel is not only repairable at room temperature, but also recyclable.

© 2020 Elsevier Inc. All rights reserved.

# 1. Introduction

Wearable devices, with a collection of features such as light weight, high sensitivity and great flexibility, are ideal for humanmachine interaction, [1,2] body motion tracking, [3] physiological

\* Corresponding author. *E-mail address:* zcpeng@szu.edu.cn (Z. Peng). monitoring [4], and portable energy storage devices [5]. The advancement of wearable devices, particularly the stretchable ones, requires significant improvement in material properties such as mechanical flexibility, electronic characteristics and electromechanical responses [6,7]. A wide range of flexible electronic materials incorporate conductive nanofillers, such as metal nanoparticles, [8–10] liquid metals, [11,12] carbon nanotubes, [13] graphene, [14] or MXene nanosheets, [15] into nonconducting polymer elastomers to form various percolation networks. These approaches have gained unprecedented attention in the field of stretchable electronics, however, they suffer from poor reliability, low conductivity and high costs, hence limiting their performance in wearable devices.

Conductive hydrogels, composed of conductive networks and nonconducting hydrogel matrix, present superiorities including good biocompatibility, tunable mechanical performance, good stretchability and great electrical property [16–21]. As such, conductive hydrogels hold great potential in many applications ranging from bioelectronics [22] and ionotronics [23] to stretchable devices, [24] electronic skin, [25] and soft robotics [26]. As a typical hydrogel network, poly (vinyl alcohol) (PVA) is a hydrophilic polymer, containing large amount of hydroxyl groups and can be gelated by physical or chemical crosslinking. Liu and co-workers reported a high strength conductive organohydrogel, composed of physically crosslinked PVA matrix and conductive polymers (PEDOT:PSS) and prepared by using water/ethylene glycol as a medium to form combination of hydrogen bonds and crystalline domains [27]. Lee and coworkers introduced highly stretchable conductive hydrogels formed via tetrafunctional borate ion interaction with hydroxyl groups of PVA [28].

Although physically crosslinked conductive hydrogels with various interaction structures have been widely investigated, [29–32] the physically crosslinked conductive hydrogels have inevitable creep under stain conditions, hence cannot fully recover after a relatively large elongation. Therefore, the electromechanical performance of such devices is affected by the viscoelastic deformation or plastic deformation of the conductive hydrogel, resulting in poor cyclic stability and sluggish response. To overcome this challenge. researchers have been/developing elastic conductive hydrogels such as hybrid crosslinking and double networking hydrogels to eliminate the negative effects of creeping and plastic deformation [33,34]. For instance, Yu and coworkers proposed an approach to prepare highly elastic composite hydrogel by synergizing the physical interaction between graphene oxide (GO) and calcium ions and chemically crosslinked polyacrylamide (PAM) networks. As a result, the GO/PAM hydrogel exhibited good elasticity with minimum hysteresis in the mechanical cycle tests [35].

On the other hand, the increasing amount of electronic waste is a major concern of our society. The invention of recyclable electronic materials can greatly save raw source, reduce electronic waste, and help to protect the environment. Significant efforts have been put forth to develop recyclable polymer for a circular plastics economy [36–38]. To date, recyclable electronic materials have mainly relied on water-soluble polymers including PVA, [39] sodium alginate [40] and reversible cross-link polymers, which are based on dynamic covalent bonds, hydrogen bonds, coordination bonds and so on [41–44]. Moreover, it is beneficial if a recyclable electronic material is also repairable, which can extend the lifetime of a device and further reduce electronic waste.

Here, we present a highly elastic, room-temperature repairable, and recyclable conductive hydrogel based on dual-crosslinked PVA networks. In this study, CNT-PVA conductive hydrogels are formed by two types of interactions: (i) strong interaction from covalent bonds; (ii) weak interaction from hydrogen bonds. This dualcrosslinked hydrogel possesses superior features including strong elasticity, negligible hysteresis, rapid recovery and good stretchability. Besides, this conductive hydrogel exhibits rateindependent electromechanical response, which can be used for stretchable sensors such as strain sensors with large measurement range. Moreover, the prepared conductive hydrogel is repairable and recyclable. To validate these features, we demonstrate the applications of our hydrogel in recyclable wearable devices for body-motion tracking and health-indicator monitoring. Furthermore, we employ the repairability of the conductive hydrogel to assemble and reconfigurate a complex circuit framework.

# 2. Materials and method

# 2.1. Materials

Degree of hydrolysis and average degree of polymerization of poly (vinyl alcohol) (PVA), was 87.0–89.0% (mol/mol) and1750  $\pm$  50, respectively. Size of Carboxylic functional Multi-walled Carbon Nanotube (MWCNTs) was 5–12 nm in inner diameter, 30–50 nm in outer diameter and 30–50 µm in length, with purity over 90%. PVA and MWCNTs were purchased from Aladdin Reagent Co. Ltd. Glutaraldehyde (GA), concentrated hydrochloric acid (HCl) and other chemicals were analytical grade and were purchased from Sinopharm Chemical Reagent Co., Ltd.. All chemicals were used without further purification. Deionized water was used in all of the experiments.

# 2.2. Preparation of conductive hydrogel

MWCNTs were dispersed in homogeneous suspensions by the method referred to the literature [28]. PVA powder was added into MWCNTs suspensions under vigorous stirring at 90 °C for 6 h, then the homogeneous mixture was formed. The above mixture was cooled down to room temperature. 20  $\mu$ L GA was added into the mixture by following the addition of HCl under stirring, and then the mixture was degassed in the ultrasonic bath. The mixture was transferred into molds and crosslinked at 40 °C for 2 h. For investigating the effects of components on the mechanical property of conductive hydrogel, various weight percentages of PVA (5–15%) and MWCNTs (0–5%) were used. The conductive hydrogels named as CxPy, were obtained with x% CNTs (x refers to weight percentage of PVA) at fixed ratio of GA/PVA (0.05).

# 2.3. Characterizations

Scan electron microscopy images were carried on a field emission scanning electron microscope (SU-70, Hitachi). Hydrogel sample was dried by freeze-drying at -50 °C (SCIENTZ-10 N). Tensile strain tests and loading-unloading tests of the conductive hydrogels were performed using a mechanical testing apparatus (CTM 5504, MTS) with a 100 N load cell. For the tensile test, the rectangle samples with a thickness  $\approx$ 2 mm, length  $\approx$ 20–30 mm, and width  ${\approx}10~\text{mm}$  were used. All the tensile tests were carried out at room temperature and repeated three times. The stresses were calculated from formula: P = F/A, where F and A are the applied load and the starting cross-sectional area of the sample. The elastic modulus and toughness of the samples were calculated from the stress-strain curves. The electrical resistance of the conductive hydrogel was obtained using an Agilent E4980A Precision LCR meter. Variation of electrical resistance versus strain data was recorded using LCR meter under stretching with a mechanical testing apparatus at a speed of 100 mm/min. To investigate the sensor performance of conductive hydrogel for wearable sensors, the conductive hydrogels were fixed on the finger, hand and radial artery of a volunteer and the real-time R-t curves were recorded.

# 3. Results and discussions

# 3.1. Design strategy of the dual-crosslinked hydrogel networks

As shown in Fig. 1a, the dual-crosslinked conductive hydrogels were prepared by utilizing PVA as hydrogel networks, GA as a chemical crosslinker and carbon nanotubes as a conductive filler. In the hydrogel matrix, there are two types of interaction between PVA polymer chains that act as linkage bridges, i.e., weak interactions from hydrogen bonds and strong interaction from covalent bonds (Fig. 1a, iii). The hydrogen bonds are formed by the interaction of hydroxyl groups of PVA chains and act as secondary and reversible linkage bridge. According to previous reports, the weak dynamic hydrogen bond interactions can easily break in mechanical deformation, leading to energy dissipation [28]. The covalent bonds between any two PVA chains are formed by ether linkages (-C-O-C-) via acetal reaction between hydroxyl group of PVA and aldehyde group in GA [45]. Ether linkages act as main linking bridges of PVA hydrogel. Based on these structural features of hydrogel networks, strong covalent interactions help to enhance

their elasticity and mechanical strength (toughness and fracture strength), weak hydrogen interaction help to dissipate mechanical energy and to obtain high stretchability. 3D porous nanostructures of conductive hydrogels were observed from scanning electron microscopy (SEM) (Fig. 1b), revealing the formation of hydrogel networks. The conductive hydrogels have outstanding processability and can be prepared into various shapes by pre-shaped molds (Figure S1a).

# 3.2. Highly elastic conductive hydrogels

To study the stretchability and elasticity, we prepared the conductive hydrogels named as  $C_x P_y$  with x% CNTs (x refers to weight percentage of CNTs) and y% PVA (y refers to weight percentage of PVA) at a fixed weight ratio of GA/PVA of 0.05. Taking  $C_1 P_{10}$  as an example in various form factors such as string, stripe and film, it could be stretched above strain of 400% (Fig. 1c i-vi). In addition,  $C_1 P_{10}$  could be curled around glass rod, twisted and compressed (Figure S1 **b**, **c**), and even being tied to form knots (Figure S1 **d**). The prepared conductive hydrogels are not only stretchable, but



**Fig. 1.** a) Schematic illustration of the preparation of an elastic conductive hydrogel: i) a homogeneous mixture of PVA (polymer networks), CNT (conductive nanofillers) and GA (cross-linker); ii, iii) conductive hydrogel with strong interaction (covalent bonds, red square) and weak interaction (hydrogel bonds, purple square). b) SEM images of prepared conductive hydrogel revealing the three-dimensional nanostructures. c) Various formfactor of CNT-PVA conductive hydrogel under extensive stretch. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

## H. Wang, J. Lu, H. Huang et al.

can also recover to its original status with great elasticity (Supporting information videos S1).

One of the most important features of flexible electronic materials is the elastic modulus or toughness, which is an essential factor for their applications. To evaluate the mechanical properties of our conductive hydrogel, we firstly conducted tensile stress-strain test with a wide range of strain rates. Figure S2 shows that all the stress-strain curves overlapped, revealing a rate-independent mechanical behavior of the conductive hydrogel. We believe this is because the internal polymer networks of our conductive hydrogel are able to quickly establish a mechanical balance at different strain rates. The structural reformation of polymer networks is very fast and slippage between CNT bundles and PVA chains is restricted under stretching. In the following tensile tests, all the loading-unloading rates were fixed at 100 mm/min, if not specially designated.

Covalent bonds are formed through chemical cross-linking reaction between hydroxyl group of PVA and aldehyde group of GA, which are confirmed from Fourier Transform Infrared Spectroscopy [45]. As a cross-linker, GA joins two polymer chains by covalent bonds to obtain 3D polymer networks. Mechanical properties of hydrogel are related to the cross-linking density within the hydrogel matrix. The ratio of GA and PVA has large effect on the mechanical properties of prepared hydrogel (Figure S3). The cross-linker weight ratio (GA/PVA, w/w) was fixed at 0.05, as it produces good stretchability and skin-like elastic modulus. In addition, Acid reaction condition plays key role in the formation time of cross-linked polymer networks, because of acid catalyzed cross-linking reaction [46]. Therefore, the crosslinking reaction time was controlled from several minutes to hours by adjusting acid concentration (Figure S4).

Apart from the above-mentioned roles of GA and HCl, the conductive fillers (CNT) and polymer networks (PVA) also play significant roles on the mechanical properties of the hydrogel. Fig. 2**a** shows tensile stress–strain curves of CNT-PVA conductive hydrogels of  $C_0P_{10}$ ,  $C_1P_{10}$ ,  $C_3P_{10}$  and  $C_5P_{10}$ . With the increase of CNT contents, the fracture strain decreases from 500% to 300% (Fig. 2**a**1) and the young's modulus increases from 3.2 kPa to 24.6 kPa (Fig. 2**a**2). The toughness increased over 5 times from 48.5 kJ m<sup>-3</sup> at 0% CNT to 262.6 kJ m<sup>-3</sup> at 5% CNT.

The influence of PVA polymer weight percentage on the mechanical properties of the CNT-PVA hydrogel was also tested. Fig. **2b** shows tensile stress-strain curves of the CNT-PVA hydrogels of  $C_1P_5$ ,  $C_1P_{7.5}$ ,  $C_1P_{10}$ ,  $C_1P_{12.5}$  and  $C_1P_{15}$ . By increasing the weight percentage of PVA, the fracture stress of the CNT-PVA hydrogels drastically increased 34 times from 5 kPa for  $C_1P_5$  to 170 kPa for  $C_1P_5$  to 510% for  $C_1P_{15}$  (Fig. **2b1**). In addition, the elastic modulus and toughness of the hydrogel remarkably increased 37 and 44 times, respectively, from  $C_1P_5$  to  $C_1P_{15}$  (Fig. **2b2**). As the weight percentage of PVA increased to 15%, the elastic modulus and toughness reached 20.2 kPa and 368.2 kJ m<sup>-3</sup>, respectively.

As reported, mechanical strength was significantly improved for the PVA/CNT composite film [47]. The reinforcement of the conductive hydrogel was caused by synergistic interaction between PVA chains and CNTs. The enhanced strength and reduced stretchability are likely attributed to the introduction of CNT fillers [48]. As the well-dispersed CNTs are bonded to the hydrogel matrix, the intrinsically high strength of CNTs is introduced to the hydrogel. Besides, physical twines and interactions between the rigid CNTs and the soft PVA chains can also improve the mechanical strength. At the same time, the intertwining CNTs tend to restrict the movement of PVA chains, leading to the reduction in stretchability.

To investigate the elastic recovery of the CNT-PVA hydrogels from stretching to releasing states, multiple-stage cyclic tensile

loading-unloading tests were carried out. Fig. 2c shows the evolution of stress-strain curves with multiple stages of strain and relaxation:  $0 \rightarrow 50\% \rightarrow 0\% \rightarrow 100\% \rightarrow 0\% \rightarrow 200\% \rightarrow 0\% \rightarrow 300\% \rightarrow 0\% \rightarrow 400\% \rightarrow 100\% \rightarrow 10\% \rightarrow 10\% \rightarrow 100\% \rightarrow 10\% \rightarrow$ 0%. At relatively low tensile strain value (<200%), the stressstrain curve completely overlapped in the loading and unloading processes, displaying no hysteresis loops (Fig. 2c, d). The hydrogel recovered to original length with no residual strain for up to 100 loading-unloading cycles (Fig. 2e). The linear, overlapping stressstrain curves demonstrated that the CNT-PVA hydrogel is highly elastic with good mechanical stability. As the tensile strain went beyond 200%, the stress-strain curve started to display an obvious hysteresis loop. During the test, the hydrogel fractured at ~350% stain (Fig. 2c). Fig. 2f shows a possible evolution of the inner structures of the hydrogel polymer matrix under stretching. The CNT inorganic conductive fillers not only act as conductive paths, but also as the reinforcing paths [48]. With PVA molecular chains twining around CNT bundles, the interfacial stress transfer between the PVA and the CNTs can result in a mechanical reinforcement. Once stretched, the movement of PVA chains and the interaction of PVA and CNT can accumulate the elastic potential energy. Besides, dualcrosslinked PVA networks facilitate the elastic behavior at low strain state. However, under extensive elongation, the slipping and fracture of hydrogel networks can occur, leading to energy dissipation. We suppose that the energy dissipation under extensive stretch is mainly attributed to the fracture of the reversible hydrogen bonds in the cross-linked hydrogel networks. In comparison with physically crosslinked PVA networks, the CNT-PVA hydrogels, with multiple crosslinking interactions and synergized interactions between the PVA chains and CNT bundles, exhibited superior elastic behavior, excellent mechanical stability, rapid recovery, and good stretchability.

#### 3.3. Electromechanical responses

For stretchable wearable sensors, high conductivity of the sensing material plays an important role. As shown in Fig. **3a**, green light-emitting diode (LED) was lighted in a series circuit with CNT-PVA conductive hydrogel to demonstrate electronic conductivity during deformation. Powered with 5 V working voltage, the LED was well worked under stretching. As CNT-PVA hydrogels were stretched to strain at 50%, 100% and 200%, the LED brightness changed (Fig. **3 b, c**). Once the CNT-PVA hydrogel was released to its initial state, LED light brightness was fully recovered. LED showed repeatable brightness variation under cyclic stretching and releasing, indicating reliable electrical stability of CNT-PVA hydrogel (Supporting information video S2).

To investigate the electrical performance of the CNT-PVA hydrogel, the electrical resistance variations were systematically tested under varied stretching deformations. As shown in Fig. 3d, the relative electrical resistance variation ratio ( $\Delta R/R_0$ )-strain ( $\epsilon$ ) curve was recorded under stretching  $(\Delta R/R_0 = (R-R_0)/R_0$ , where R and R<sub>0</sub> are resistances under stretching and initial states, respectively). With strain enlarging, the  $\Delta R/R_0$  was raised correspondingly. The function of electrical resistance variations versus strains of the conductive hydrogel was investigated by a parabolic equation from experimental results [28] and the fitting expression is  $y = 0.478\varepsilon + 1.25 \times 10^{-3}\varepsilon^2$ , where y is the electrical resistance variations and  $\varepsilon$  is the tensile strain. It can be determined that CNT-PVA hydrogels possessed  $\Delta R/R_0$  values of 60%, 140% and 250% at strain of 100%, 200% and 300%, respectively. Such results proved that CNT-PVA hydrogel had typical electromechanical coupling feature under deformation. The feature can be explained by the relative motion of internal networks under stretching. We further investigated the effects of strain rate on stability of electrical resistance response, curves of electrical resistance variation as



**Fig. 2.** Mechanical performance of the CNT-PVA conductive hydrogel. a) Stress-strain curves, the fracture stress/fracture strain (a<sub>1</sub>) and toughness/elastic modulus (a<sub>2</sub>) of the conductive hydrogel with different weight percentages of CNT at 0%, 1%, 3% and 5%, respectively; b) Stress-strain curves, the fracture stress/fracture stress/fracture strain (b<sub>1</sub>) and toughness/ elastic modulus (b<sub>2</sub>) of the conductive hydrogel with different weight percentage of PVA at 5%, 7.5%, 10%, 12.5% and 15%, respectively; c, d) Tensile stress-strain curves of the conductive hydrogel during cyclic loading-unloading from 100% to 300% strains; d) Zoom-in of the tensile stress-strain curves from 25% to 100% strains; e) Tensile stress-strain curves with 100 loading-unloading cycles at 100% strain; f) Proposed mechanism of elastic performance of the conductive hydrogel. Tensile test at speed of 100 mm/ min.

function of time were recorded by stretching samples to tensile strain of 150% at four types of strain rates (10 mm/min, 20 mm/ min, 50 mm/min and 100 mm/min). As shown in Fig. 3e, it was found that the electrical resistance variations were same at tensile strain of 150%, irrespective of the varied strain rates. In addition, stretching tests were conducted at four varied strain rates,  $\Delta R/$  $R_0$ -strain curves fully overlapped, indicating that CNT-PVA hydrogels possessed a stable response in terms of independent strain rate. As reported, strain rate-dependent electromechanical response performance showed strong relationship with the internal kinetics of conductive paths and viscoelastic character of mechanical property [21,49]. Here, the strain rate stability of electrical resistance response mainly depended on their good mechanical elasticity and strong covalently crosslinked networks. Therefore, microscopic CNT conductive paths respond quickly to external stretching even at high loading rates, leading to strain rate-independent electrical resistance response stability.

To evaluate the stability of electrical response of the CNT-PVA hydrogels, we first stretched samples to certain tensile strain (20%, 50% and 100%) at a rate of 100 mm/min, then the tensile state was made to last for 20 s, the electrical resistance variation-time curves were recorded (Fig. **3f**). The electrical resistance variation wasn't changed when the tensile strain was kept for 20 s. When stretching to strain of 50%,  $\Delta R/R_0$  overlapped the previous electrical resistance variation-time curves within strain of 20%, then increased as continuous stretching. We also observed similar behaviors when stretching to strain of 100%. Therefore, the internal CNT conductive paths had stable microscopic interconnections under stretching and the corresponding CNT-PVA hydrogels exhibited an excellent stable electrical resistance response to



**Fig. 3.** Electromechanical response of the conductive hydrogel. a) Scheme of LED in an electric circuit with the conductive hydrogel as interconnector. b) The change of brightness in LED with various strain at 0%, 50%, 100% and 200%, respectively. c) Pristine and stretched states of the conductive hydrogel in an LED electric circuit. d) Relative electrical resistance variation ratio ((R-R<sub>0</sub>)/R<sub>0</sub>) as a function of strain. e) Electromechanical response under stretch from 0% to 100% with various tensile loading speed at 10, 20, 50 and 100 mm/min, respectively. f) Electromechanical response under stretch from 0% to 100% vitivarious tensile loading speed at 10, conductive hydrogel during five stretching-releasing cycles with different strain of 25%, 50%, and 100%, respectively. g) Variation of electrical resistance (R-R<sub>0</sub>) of the conductive hydrogel during five stretching-releasing cycles with different strain of 25%, 50%, and 100%, respectively. h) R-R<sub>0</sub> values of the conductive hydrogel under 50 repeating stretching cycles at a strain of 100%.

strain. It is demonstrated that the strong interactions between PVA chains and CNT bundles and excellent mechanical elasticity of conductive hydrogel endow itself with good electromechanical response stability. Then, the reciprocating stretching test was carried out to evaluate durability of dynamic conductive performance. The electrical resistance was measured as function of time from cyclic tensile strain-relaxation test with tensile strain of 25%, 50% and 100%, respectively. Even though different test conditions of tensile strain and loading rate were applied, as shown in Fig. 3g, electrical resistance fully recovered to initial values, indicating that CNT-PVA hydrogel had superior response stability in large range of tensile strain. In the fatigue cyclic tensile strain-relaxation test, CNT-PVA hydrogel exhibited repeatable change of electrical resistance at stretching states and  $\Delta R$  values showed unapparent change in fifty cycles (Fig. 3 h, i).

# 3.4. Demonstration on flexible strain sensors

To demonstrate its capability in tracking human motion, the CNT-PVA conductive hydrogel was fixed on a tester finger and connected with two copper wires. For finger bending test, CNT-PVA conductive hydrogel suffered tensile strain, leading to a rapid increase in electrical resistance variation. As shown in Fig. 4a, when the tester's finger was bent at angles of 25°, 50°, 75° and 90°, conductive hydrogel was stretched and corresponding resistance changed. As the tester repeatedly bent and straightened his finger, the resistance variation of sensors was recorded in real-time (Fig. 4b). The response time of resistance change is about

0.22 s both at bending and releasing process (Fig. 4c), indicating that the resistance change of conductive hydrogel reflects realtime finger motion process. Therefore, the conductive hydrogel has good capability in detection of human motion. When finger bending rate was changed (from slow bending to rapid bending), the corresponding frequency of electronic signal changed (figure S5 **a-c**), indicating that the variation of electronic signals is synchronized with finger bending. To further demonstrate their application in wearable devices (data glove), The conductive hydrogel was deposited onto cotton gloves as strain sensory channel. In this demonstration, the uncross-linked mixtures of PVA and CNT were adsorbed into the inside of textile and bonded tightly to the surface of gloves after gelation (Fig. 4d). By measuring the resistance change of each sensory channel, it can act as a data glove to monitor real-time finger motion. Fig. 4e shows the response of sensory channels for several cycles of finger bending- releasing. Apart from finger bending monitoring, the CNT-PVA hydrogel-based sensors showed capability of detecting and distinguishing hand gestures (figure S5 d-f, supporting video S2).

As an attractive application of wearable devices, monitoring of health in real-time can provide comprehensive physiological information for better understanding and diagnosis of health risks. Currently, analysis of radial artery waves is one of the most important approaches to assessment of patient's cardiovascular function. However, vibrations of radial artery are extremely weak and strains induced by pulses are very feeble. Therefore, high sensitivity and fast response time are both essential features of radial artery monitoring sensors to obtain accurate radial artery



**Fig. 4.** The sensing performance of the conductive hydrogel based wearable sensors. a) The plot of resistance variation versus time in response to finger bending at different bending angles (25°, 50°, 75° and 90°). b) The relative electrical resistance change of conductive hydrogel during cycling finger bending-releasing process. c) The response time of relative electrical resistance change in one bending-releasing process. d) Photographs of data glove involving strain sensors based on conductive hydrogels deposited on gloves. e) Electrical resistance responses of four finger motions by wearing data glove. f) Photograph of conductive hydrogel-based sensor for real-time monitoring of radial artery. g, h) Relative electrical resistance of conductive hydrogel as a wearable radial artery monitoring sensor. i-k) Wearable conductive hydrogel sensors for EMG measurement. i) the photograph of skin-tight compression sleeve with three-point conductive hydrogel electrodes. j) Conductive hydrogel with (red) and without (blue) electrolytes. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

recording. The conductive hydrogel-based sensors were placed on the wrist of an adult male to monitor real-time information of radial artery (Fig. 4f). As shown in Fig. 4g, a set of radial artery waves with stable and clearly distinguishable peaks were recorded, indicating that conductive hydrogel-based sensors are able to capture small strains induced by vibrations of radial artery. In addition, two characteristic peaks are demonstrated in precise radial artery wave (Fig. 4h), including a percussion peak (P1) caused by the incoming blood flow and a tidal peak (P2) caused by blood flow reflection. According to analysis of radial artery waves, some important parameters were obtained for diagnosis of health risks. For example, the blood pulse frequency was about 58 pules per min and the time delay between percussion wave and tidal wave was 0.26 s. Then, electromyogram (EMG) monitoring sleeve was prepared to demonstrate a potential application in biometric signal devices, [50,51] which can extract human's motion intent to control myoelectric prosthetic devices [52]. We deposited three-point conductive hydrogel electrodes onto a skin-tight

## H. Wang, J. Lu, H. Huang et al.

compression sleeve (Fig. 4i). The conductive hydrogel electrodes were bonded tightly to elastic sleeve and deformed congruously under stretching (Fig. 4j). Besides, the contractility of compression sleeve provided a stable connection between electrodes and skin during muscle motion, leading to high signal stability. As shown in Fig. 4k, EMG signals of forearm motion were extracted from commercial electrodes (black) and conductive hydrogel electrodes (red). As a result, conductive hydrogel electrode with 0.1 M NaCl as electrolytes exhibited higher EMG signals compared with traditional commercial electrodes. while, pure conductive hydrogel without electrolytes showed poor EMG signal extraction capability, because of inadequate interfacial electric signal transformation. Therefore, compared with reported literature, conductive hydrogel-based sensors demonstrated high performance with good stability and high sensitivity, leading to great application on wearable devices for real-time monitoring of physiological information.

# 3.5. Repairability and recyclability

Apart from these advantageous abilities, the conductive hydrogels also present excellent repairability and recyclability. As shown

in Fig. 5a, the detailed repairing process of CNT-PVA conductive hydrogel is illustrated. A rectangle sample was cut into two parts (Fig. 5a, i), then applying repairing solutions (a mixture of PVA, CNT and GA) at the broken site, the broken position was repaired. Taking advantage of abundant hydroxyl groups of PVA chains, the GA crosslinker in non-crosslinked repairing solutions reacted with hydroxyl groups at fracture surface of conductive hydrogels and connected two broken pieces together (Fig. 5a, ii). Fig. 5b shows the images of repaired conductive hydrogel before and after stretching, demonstrating that the repaired location (between two red dash line) possesses similar mechanical behavior with the original parts. In addition, we observed that the fracture location of the repaired sample was different from the previous cut positions, indicating satisfactory repairing effects. A mechanical tension test was carried out to evaluate the mechanical property of CNT-PVA conductive hydrogel before and after repair. As shown in Fig. 5c. the tensile stress-strain curve of repaired conductive hydrogel overlapped the curve of original sample. The elastic modulus and mechanical strength are retained, but only fracture strain slightly decreased. In comparison with conductive hydrogels based on the traditional reversible crosslinking reaction, which usually



**Fig. 5.** The repairability and recyclability of the CNT-PVA conductive hydrogel. a) Schematic drawings of the repairing process (inset: the images of conductive hydrogel before i) and after repair ii)). b) Demonstration on mechanical property of the repaired conductive hydrogel, the repairing locations were marked by red dash line and the white arrow points to the fracture position. c) The tensile stress-strain curves of conductive hydrogel before and after repair. d) Electromechanical response of relative electrical resistance variation ratio ((R-R<sub>0</sub>)/R<sub>0</sub>) versus strain for the repaired conductive hydrogel. e) Demonstration on the recycling of the conductive hydrogel, i) original sample, ii) dipped in water, iii) homogeneous mixtures after heating 24 h, iv) sample after gelation. f) The tensile stress-strain curves of the conductive hydrogel on a cotton glove i) the cotton glove after washing away conductive hydrogel ii). h) The electrical response of a strain senor using recycled conductive hydrogel as the sensing material. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

endures the degradation in mechanical performance, the CNT-PVA conductive hydrogel can fully restore their mechanical property after repairing. Moreover, the electromechanical response performance was investigated to compare the electrical properties of conductive hydrogel before and after repair. As shown in Fig. 5d, the relative electrical resistance variation ratio ( $\Delta R/R_0$ )-strain ( $\epsilon$ ) curve was recorded under stretching. The fitting function of experimental data is  $y = 0.338\varepsilon + 1.54 \times 10^{-3}\varepsilon^2$ , where y is the electrical resistance variations and  $\varepsilon$  is the tensile strain. The results indicate that the repaired conductive hydrogels possess as same electromechanical response performance as the original sample. We also demonstrated a shear-splice method to fabricate complicated structures based on the conductive hydrogel (Figure S6). Furthermore, the recyclability of the CNT-PVA conductive hydrogel is investigated. As above mentioned, the conductive hydrogel composed of dual-crosslinked polymer networks: dynamic hydrogen bonds and covalent acetal dynamic linkages. Hydrogen bonds are reversible weak interaction and can be destroyed by heating. As recently reported, acetal crosslinking networks were new type dynamic interaction, which can be recycled through dynamic exchange of acetal under hot water treatment [53]. Fig. 5e presents representative images of the recycling process. After heating the conductive hydrogel in water for 24 h, we can obtain a homogeneous mixture, which can be reused to prepared new conductive hydrogel. As shown in Fig. 5f, the mechanical tension stressstrain tests were conducted to compare their mechanical property before and after recycling in twice. The elastic modulus, tensile strength and fracture strain were retained compared with the original sample, indicating that mechanical property was not influenced in recycling process. Besides, we also demonstrated that the wearable conductive hydrogel can be washed away under hot water (Fig. 5g). Moreover, applying the 2nd recycling conductive hydrogel as sensory channel, we also successfully achieved strain sensor for finger bending monitor, which present comparable sensory capability to these original sensors (Fig. 5h).

# 4. Conclusion

In summary, a highly elastic, repairable and recyclable conductive hydrogel was developed using dual-crosslinked CNT-PVA networks. The stretchability, toughness and Young's modulus of the CNT-PVA conductive hydrogel are tunable via simple adjustment of the material composition and experimental condition. The optimized CNT-PVA conductive hydrogel exhibits high elasticity, good stretchability (up to 500% fracture strain), rapid recovery, negligible hysteresis, and rate-independent electromechanical response. Taking the advantages of this conductive hydrogel, we demonstrated its application in wearable devices for finger motion detection, pulse monitoring and electromyogram (EMG) recording. Furthermore, this conductive hydrogel possesses good repairability and recyclability, thus is an ideal electronic material in terms of reducing electronic waste. This work not only advances conductive hydrogels with much enhanced elasticity and reparability, but also for the first time realized the recyclability of a conductive hydrogel. As such, we foresee a significant increase of its application in stretchable electronics in near future.

# **CRediT authorship contribution statement**

Haifei Wang: Conceptualization, Methodology, Investigation, Writing - original draft, Writing - review & editing. Jiameng Lu: Investigation, Visualization, Data curation. Huayi Huang: Software. Senlin Fang: Visualization. Muhammad Zubair: Validation. Zhengchun Peng: Conceptualization, Supervision, Writing review & editing.

# **Declaration of Competing Interest**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

# Acknowledgements

This work was supported by the Science and Technology Innovation Commission of Shenzhen (KQTD20170810105439418, JCYJ20170818091233245), the Department of Education of Guangdong Province (2016KZDXM005) and Natural Science Foundation of Guangdong Province (2018A030310552). The authors thanks Prof. Xuechang Zhou from Shenzhen University for helpful discussions. The authors also gratefully acknowledge the help provided by Materials and Devices Testing Center, Tsinghua University Graduate School at Shenzhen on characterizing the materials. H. W. thanks Dr. Dengfeng Peng for partial financial support of this work.

# Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jcis.2020.12.035.

# References

- S. Jung, J.H. Kim, J. Kim, S. Choi, J. Lee, I. Park, T. Hyeon, D.H. Kim, Reversemicelle-induced porous pressure-sensitive rubber for wearable humanmachine interfaces, Adv. Mater. 26 (2014) 4825–4830.
- [2] J. Lee, H. Kwon, J. Seo, S. Shin, J.H. Koo, C. Pang, S. Son, J.H. Kim, Y.H. Jang, D.E. Kim, T. Lee, Conductive fiber-based ultrasensitive textile pressure sensor for wearable electronics, Adv. Mater. 27 (2015) 2433–2439.
- [3] G.S. Canon Bermudez, D.D. Karnaushenko, D. Karnaushenko, A. Lebanov, L. Bischoff, M. Kaltenbrunner, J. Fassbender, O.G. Schmidt, D. Makarov, Magnetosensitive e-skins with directional perception for augmented reality, Sci. Adv. 4 (2018) eaao2623.
- [4] J.C. Yang, J. Mun, S.Y. Kwon, S. Park, Z. Bao, S. Park, Electronic skin: Recent progress and future prospects for skin-attachable devices for health monitoring, robotics, and prosthetics, Adv. Mater. 31 (2019) 1904765.
- [5] Z. Li, D. Lou, K. Chen, W. Jiang, G.S. Han, Recent advances in flexible/stretchable supercapacitors for wearable electronics, Small 14 (2018) 1702829.
- [6] B. Wang, A. Facchetti, Mechanically flexible conductors for stretchable and wearable e-skin and e-textile devices, Adv. Mater. 31 (2019) 1901408.
- [7] H.R. Lim, H.S. Kim, R. Qazi, Y.T. Kwon, J.W. Jeong, W.H. Yeo, Advanced soft materials, sensor integrations, and applications of wearable flexible hybrid electronics in healthcare, energy, and environment, Adv. Mater. 32 (2020) 1901924.
- [8] Y. Tang, S. Gong, Y. Chen, L.W. Yap, W. Cheng, Manufacturable conducting rubber ambers and stretchable conductors from copper nanowire aerogel monoliths, ACS Nano 8 (2014) 5707–5714.
- [9] A. Hirsch, H.O. Michaud, A.P. Gerratt, S. de Mulatier, S.P. Lacour, Intrinsically stretchable biphasic (solid-liquid) thin metal films, Adv. Mater. 28 (2016) 4507–4512.
- [10] N. Matsuhisa, D. Inoue, P. Zalar, H. Jin, Y. Matsuba, A. Itoh, T. Yokota, D. Hashizume, T. Someya, Printable elastic conductors by in situ formation of silver nanoparticles from silver flakes, Nat. Mater. 16 (2017) 834–840.
- [11] M.D. Dickey, Stretchable and soft electronics using liquid metals, Adv. Mater. 29 (2017) 1606425.
- [12] A. Fassler, C. Majidi, Liquid-phase metal inclusions for a conductive polymer composite, Adv. Mater. 27 (2015) 1928–1932.
- [13] K.Y. Chun, Y. Oh, J. Rho, J.H. Ahn, Y.J. Kim, H.R. Choi, S. Baik, Highly conductive, printable and stretchable composite films of carbon nanotubes and silver, Nat. Nanotechnol. 5 (2010) 853–857.
- [14] Y. Pang, K. Zhang, Z. Yang, S. Jiang, Z. Ju, Y. Li, X. Wang, D. Wang, M. Jian, Y. Zhang, R. Liang, H. Tian, Y. Yang, T.L. Ren, Epidermis microstructure inspired graphene pressure sensor with random distributed spinosum for high sensitivity and large linearity, ACS Nano 12 (2018) 2346–2354.
- [15] Y. Cai, J. Shen, G. Ge, Y. Zhang, W. Jin, W. Huang, J. Shao, J. Yang, X. Dong, Stretchable Ti<sub>3</sub>C<sub>2</sub>T<sub>x</sub> MXene/Carbon nanotube composite based strain sensor with ultrahigh sensitivity and tunable sensing range, ACS Nano 12 (2018) 56– 62.
- [16] L. Pan, G. Yu, D. Zhai, H.R. Lee, W. Zhao, N. Liu, H. Wang, B.C. Tee, Y. Shi, Y. Cui, Z. Bao, Hierarchical nanostructured conducting polymer hydrogel with high electrochemical activity, Proc. Natl. Acad. Sci. U. S. A. 109 (2012) 9287–9292.
- [17] F. Zhao, Y. Shi, L. Pan, G. Yu, Multifunctional nanostructured conductive polymer gels: Synthesis, properties, and applications, Acc. Chem. Res. 50 (2017) 1734–1743.

#### H. Wang, J. Lu, H. Huang et al.

- [18] Q. Rong, W. Lei, M. Liu, Conductive hydrogels as smart materials for flexible electronic devices, Chem. - Eur. J. 24 (2018) 16930–16943.
- [19] L. Han, K.Z. Liu, M.H. Wang, K.F. Wang, L.M. Fang, H.T. Chen, J. Zhou, X. Lu, Mussel-inspired adhesive and conductive hydrogel with long-lasting moisture and extreme temperature tolerance, Adv. Funct. Mater. 28 (2018) 1704195.
- [20] P. Song, H. Qin, H.L. Gao, H.P. Cong, S.H. Yu, Self-healing and superstretchable conductors from hierarchical nanowire assemblies, Nat. Commun. 9 (2018) 2786.
- [21] Y.Z. Zhang, K.H. Lee, D.H. Anjum, R. Sougrat, Q. Jiang, H. Kim, H.N. Alshareef, MXenes stretch hydrogel sensor performance to new limits, Sci. Adv. 4 (2018) eaat0098.
- [22] H. Yuk, B. Lu, X. Zhao, Hydrogel bioelectronics, Chem. Soc. Rev. 48 (2019) 1642–1667.
- [23] C.H. Yang, Z.G. Suo, Hydrogel ionotronics, Nat Rev Mater 3 (2018) 125–142.
- [24] H.R. Lee, C.C. Kim, J.Y. Sun, Stretchable ionics a promising candidate for upcoming wearable devices, Adv. Mater. 30 (2018) 1704403.
- [25] H. Wang, Z. Wang, J. Yang, C. Xu, Q. Zhang, Z. Peng, Ionic gels and their applications in stretchable electronics, Macromol. Rapid Commun. 39 (2018) 1800246.
- [26] H.L. Park, Y. Lee, N. Kim, D.G. Seo, G.T. Go, T.W. Lee, Flexible neuromorphic electronics for computing, soft robotics, and neuroprosthetics, Adv. Mater. 32 (2020) 1903558.
- [27] Q. Rong, W. Lei, L. Chen, Y. Yin, J. Zhou, M. Liu, Anti-freezing, conductive selfhealing organohydrogels with stable strain-sensitivity at subzero temperatures, Angew. Chem., Int. Ed. Engl. 56 (2017) 14159–14163.
- [28] G. Cai, J. Wang, K. Qian, J. Chen, S. Li, P.S. Lee, Extremely stretchable strain sensors based on conductive self-healing dynamic cross-links hydrogels for human-motion detection, Adv. Sci. 4 (2017) 1600190.
- [29] W. Li, F. Gao, X. Wang, N. Zhang, M. Ma, Strong and robust polyaniline-based supramolecular hydrogels for flexible supercapacitors, Angew. Chem., Int. Ed. Engl. 55 (2016) 9196–9201.
- [30] H. Liao, X.L. Guo, P.B. Wan, G.H. Yu, Conductive MXene nanocomposite organohydrogel for flexible, healable, low-temperature tolerant strain sensors, Adv. Funct. Mater. 29 (2019) 1904507.
- [31] M.H. Liao, P.B. Wan, J.R. Wen, M. Gong, X.X. Wu, Y.G. Wang, R. Shi, L.Q. Zhang, Wearable, healable, and adhesive epidermal sensors assembled from musselinspired conductive hybrid hydrogel framework, Adv. Funct. Mater. 27 (2017) 1703852.
- [32] Q. Wang, X. Pan, C. Lin, X. Ma, S. Cao, Y. Ni, Ultrafast gelling using sulfonated lignin-Fe<sup>3+</sup> chelates to produce dynamic crosslinked hydrogel/coating with charming stretchable, conductive, self-healing, and ultraviolet-blocking properties, Chem. Eng. J. 396 (2020) 125341.
- [33] X. Zhao, Multi-scale multi-mechanism design of tough hydrogels: Building dissipation into stretchy networks, Soft Matter 10 (2014) 672–687.
- [34] Z. Wang, C. Xiang, X. Yao, P. Le Floch, J. Mendez, Z. Suo, Stretchable materials of high toughness and low hysteresis, Proc. Natl. Acad. Sci. U. S. A. 116 (2019) 5967–5972.
- [35] H.P. Cong, P. Wang, S.H. Yu, Highly elastic and superstretchable graphene oxide/polyacrylamide hydrogels, Small 10 (2014) 448–453.
- [36] P.R. Christensen, A.M. Scheuermann, K.E. Loeffler, B.A. Helms, Closed-loop recycling of plastics enabled by dynamic covalent diketoenamine bonds, Nat. Chem. 11 (2019) 442–448.
- [37] J.M. García, G.O. Jones, K. Virwani, B.D. McCloskey, D.J. Boday, G.M. ter Huurne, H.W. Horn, D.J. Coady, A.M. Bintaleb, A.M.S. Alabdulrahman, F. Alsewailem, H.

A.A. Almegren, J.L. Hedrick, Recyclable, strong thermosets and organogels via paraformaldehyde condensation with diamines, Science 344 (2014) 732–735.

- [38] J.-B. Zhu, E.M. Watson, J. Tang, E.Y.-X. Chen, A synthetic polymer system with repeatable chemical recyclability, Science 360 (2018) 398–403.
- [39] L. Teng, S.C. Ye, S. Handschuh-Wang, X.H. Zhou, T.S. Gan, X.C. Zhou, Liquid metal-based transient circuits for flexible and recyclable electronics, Adv. Funct. Mater. 29 (2019) 1808739.
- [40] Q. Liang, Q. Zhang, X. Yan, X. Liao, L. Han, F. Yi, M. Ma, Y. Zhang, Recyclable and green triboelectric nanogenerator, Adv. Mater. 29 (2017) 1604961.
- [41] C. Dang, M. Wang, J. Yu, Y. Chen, S. Zhou, X. Feng, D. Liu, H. Qi, Transparent, highly stretchable, rehealable, sensing, and fully recyclable ionic conductors fabricated by one-step polymerization based on a small biological molecule, Adv. Funct. Mater. 29 (2019) 1902467.
- [42] H.G. Liao, S.L. Liao, X.L. Tao, C. Liu, Y.P. Wang, Intrinsically recyclable and selfhealable conductive supramolecular polymers for customizable electronic sensors, J. Mater. Chem. C 6 (2018) 12992–12999.
- [43] Z. Zou, C. Zhu, Y. Li, X. Lei, W. Zhang, J. Xiao, Rehealable, fully recyclable, and malleable electronic skin enabled by dynamic covalent thermoset nanocomposite, Sci. Adv. 4 (2018) eaaq0508.
- [44] Z. Guo, H. Gu, Y. He, Y. Zhang, W. Xu, J. Zhang, Y. Liu, L. Xiong, A. Chen, Y. Feng, Dual dynamic bonds enable biocompatible and tough hydrogels with fast selfrecoverable, self-healable and injectable properties, Chem. Eng. J. 388 (2020) 124282.
- [45] H.S. Mansur, C.M. Sadahira, A.N. Souza, A.A.P. Mansur, FTIR spectroscopy characterization of poly (vinyl alcohol) hydrogel with different hydrolysis degree and chemically crosslinked with glutaraldehyde, Mater. Sci. Eng., C 28 (2008) 539–548.
- [46] R. Rudra, V. Kumar, P.P. Kundu, Acid catalysed cross-linking of poly vinyl alcohol (PVA) by glutaraldehyde: effect of crosslink density on the characteristics of PVA membranes used in single chambered microbial fuel cells, RSC Adv. 5 (2015) 83436–83447.
- [47] X.F. Zhang, T. Liu, T.V. Sreekumar, S. Kumar, V.C. Moore, R.H. Hauge, R.E. Smalley, Poly(vinyl alcohol)/SWNT composite film, Nano Lett. 3 (2003) 1285– 1288.
- [48] X. Tong, J.G. Zheng, Y.C. Lu, Z.F. Zhang, H.M. Cheng, Swelling and mechanical behaviors of carbon nanotube/poly (vinyl alcohol) hybrid hydrogels, Mater Lett 61 (2007) 1704–1706.
- [49] F. Zhu, J. Lin, Z.L. Wu, S. Qu, J. Yin, J. Qian, Q. Zheng, Tough and conductive hybrid hydrogels enabling facile patterning, ACS Appl. Mater. Interfaces 10 (2018) 13685–13692.
- [50] L. Han, X. Lu, M. Wang, D. Gan, W. Deng, K. Wang, L. Fang, K. Liu, C.W. Chan, Y. Tang, L.T. Weng, H. Yuan, A mussel-inspired conductive, self-adhesive, and self-healable tough hydrogel as cell stimulators and implantable bioelectronics, Small 13 (2017) 1601916.
- [51] H. Jin, N. Matsuhisa, S. Lee, M. Abbas, T. Yokota, T. Someya, Enhancing the performance of stretchable conductors for e-textiles by controlled ink permeation, Adv. Mater. 29 (2017) 1605848.
- [52] A. Furui, S. Eto, K. Nakagaki, K. Shimada, G. Nakamura, A. Masuda, T. Chin, T. Tsuji, A myoelectric prosthetic hand with muscle synergy-based motion determination and impedance model-based biomimetic control, Sci. Robot. 4 (2019) eaaw6339.
- [53] Q. Li, S.Q. Ma, S. Wang, W.C. Yuan, X.W. Xu, B.B. Wang, K.F. Huang, J. Zhu, Facile catalyst-free synthesis, exchanging, and hydrolysis of an acetal motif for dynamic covalent networks, J. Mater. Chem. A 7 (2019) 18039–18049.