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Highly Stretchable, Compressible, Adhesive, Conductive Self-healing Composite Hydrogels with Sensor Capacity

Ji-Jun Wang, Qiang Zhang, Xing-Xiang Ji, and Li-Bin Liu*

State Key Laboratory of Biobased Material and Green Papermaking, School of Chemistry and Pharmaceutical Engineering, Qilu University of Technology (Shandong Academy of Sciences), Jinan 250353, China

Electronic Supplementary Information

Abstract The design and fabrication of conductive hydrogels with high stretchability, compressibility, self-healing properties and good adhesion remains a significant challenge. We have fabricated composite hydrogels by random polymerization of acrylic acid (AA) and dopamine (DA) in the presence of multi-walled carbon nanotubes (MWCNTs). The π-π interaction between DA and MWCNTs makes MWCNTs stably and homogenously dispersed in water. The fabricated PAA-PDA/CNT composite hydrogels possess relatively high mechanical strength (maximum Young's modulus: 800 kPa) and can be stretched to 1280% strain and compressed to 80% strain. The multiple hydrogen bonding formed between functional groups of PAA-PDA and MWCNTs can effectively dissipate energy and quickly achieve self-healing. The composite hydrogels also show good adhesion and can easily adhere to various inorganic or organic surfaces. In addition, the hydrogel reveals stable strain sensitivity and can be used as skin sensors.

Keywords Hydrogels; Self-healing; Conductivity; Sensor

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INTRODUCTION

Sensors with stretchability, wearability, flexibility have attracted great research interest because they can be applied to intelligent robots,[1–5] bioelectrodes,[6,7] wearable electronic skins[8–14] and other fields. The wearable smart sensors transfer physical signals such as temperature[15] and strain,[16–18] into electrical signals for transmission and recording, and thus detect various physiological changes or movement changes. In recent years, research on smart sensors has shown a significant increase. Graphene,[19,20] carbon nanotubes,[16,21] conductive polymers[17,22] and other materials have been doped or embedded into the polymer matrix to make smart sensors. Despite their flexibility, many of the sensors are not stretchable or compressible, whereas these properties are important for sensors applied in some special environment. In addition, wearable sensors used in human joint motion detection will inevitably be subject to mechanical damage caused by continuous bending and stretching, so it is necessary to have rapid self-healing and fatigue resistance. Because there is no self-adhesion, many smart sensors require additional fixing devices such as tape to help with adhesion. Therefore, design and fabrication of smart sensors with the above-mentioned properties such as stretchability, compressibility, and self-healing ability, as well as good adhesion, are greatly demanded.

Conductive hydrogel materials combining the stretchability, flexibility, and conductivity are excellent candidates for wearable smart sensors. For example, Yang *et al.*[7] used agar, polyacrylamide and lithium ions to prepare a transparent, injectable dual network hydrogel by a simple one-pot method. The hydrogel has an extremely wide strain window and a high strain coefficient, which can accurately detect changes in human joint motion, but it does not have self-healing performance, and cannot repair mechanical damage suffered during use, which seriously affects the actual situation applications. Wearable self-healing sensors will inevitably be subject to physical damage caused by continuous stretching and bending during the detection of human movements. Therefore, fast self-healing performance is an important factor for practical applications. Self-healing performance generally depends on the actions of repair agents,[23,24] dynamic covalent bonds,[25,26] and non-covalent bonds.[26,27] Compared with the self-healing effect of the repairing agent released on the crack at the time of damage, and the self-healing of dynamic covalent bonds requiring external stimulation, non-covalent bonding (electronic interaction,[28,29] hydrogen bonding,[30] host-guest interaction,[31] metal coordination[32]) is more attractive and can be self-healing multiple times. Bao and coworker[33] reported that a composite material sensor composed of

* Corresponding author, E-mail: lbliu@qlu.edu.cn

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supramolecular organic polymer with embedded nickel nanostructured particles exhibits excellent mechanical and electrical self-healing properties under environmental conditions, and has improved its service life. However, in actual use, the sensor cannot be directly adhered to human skin, and the assistance of tapes and straps is required, which complicates the operation process. Therefore, it is still a great challenge to prepare a wearable sensor with self-healing, adhesion, and wide detection range.

Because dopamine (DA) and mussel adhesion proteins have similar catechol groups, they can easily adhere to a variety of inorganic and organic materials, which provides a new inspiration for electronic skin that does not require additional adhesives. Here we designed a novel hydrogel based on dopamine-modified multi-walled carbon nanotubes (MWCNTs). The π-π interaction between MWCNT and dopamine makes MWCNTs homogenous dispersion in water.[34] The conductive composite PAA-PDA/CNT hydrogels were obtained by random copolymerization of acrylic acid (AA) and DA in the presence of MWCNT. *N,N'*-methylenebisacrylamide was used as cross-linker. The hydrogels not only possess good stretchability and compressibility, but also possess good self-healing ability due to the multiple hydrogen bonds between the functional group of PAA-PDA and MWCNTs (Fig. 1). In addition, the conductive composite hydrogel exhibits a wide strain range and high sensitivity and excellent adhesion to rubber, plastic, metal, and skin, showing great potential for application in wearable smart sensors.

EXPERIMENTAL

Materials

Carboxylic multi-walled carbon nanotubes (purity: 98%) were purchased from Zhongke Times Nano Co., Ltd. Acrylic acid (AA) and *N,N'*-methylenebisacrylamide (MBA) were supplied by Aladdin. Dopamine hydrochloride (DA) was provided from Macklin Reagent Co., Ltd. Ammonium persulfate (APS) was purchased from Sinopharm Chemical Reagent Co., Ltd.

Preparation of the PAA-PDA/CNT Conductive Hydrogel

A certain amount of dopamine hydrochloride (0, 0.02, 0.04, or 0.06 g) and 10 mL of sodium hydroxide solution with a pH value of 11 were added to the round bottom flask of 25 mL, and a certain amount of MWCNT (accounting for 0 wt%, 2.5 wt%, 5 wt%, 7.5 wt%, or 10 wt% of the quality of polymer monomer) was added. After stirring and ultrasound for about 2 h, a certain amount of acrylic acid (3 g) and MBA (0, 0.003, 0.006, 0.009, or 0.012 g) were added into the above mixture with stirring for 30 min. Then APS (2 wt%) was added. The precursor solution was transferred to glass tube with inner diameter of 5.5 mm. After ultrasonication to remove bubbles, polymerization was performed in an oven at 35 °C for about 12 h. After polymerization, the hydrogel was removed from the glass tubes and placed in Petri dish to dehydrate in air at room temperature for about 20 h. The resulting hydrogel containing about 30 wt% water was obtained. In this work, the hydrogels are abbreviated as $A_3D_xC_y$, where A, D, C represent AA, DA, and CNT, respectively; *x*, *y* refer to the amount of DA (0, 0.02, 0.04, 0.06 g) and the amount of CNT (0 wt%, 2.5 wt%, 5 wt%, 7.5 wt%, 10 wt%), respectively.

Self-healing Process of Conductive Hydrogel

The hydrogel was cut into two sections. Since the cut surface of the hydrogel has certain stickiness, the two sections will be joined together when just put together. A drop of water was dripped on the damaged interface. No external force was required for self-healing and the connected hydrogels were allowed to stand in the air with different time for self-healing.

Mechanical Testing

The tensile test was carried out using a microcomputer-controlled electronic universal testing machine (Hensgrand, WDW-02, China). The prepared hydrogel samples were measured at 25 °C using a tensile speed of 100 mm·min^{-1}. The formula for calculating the tensile stress is $\sigma = F/\pi R^2$, where *F* is

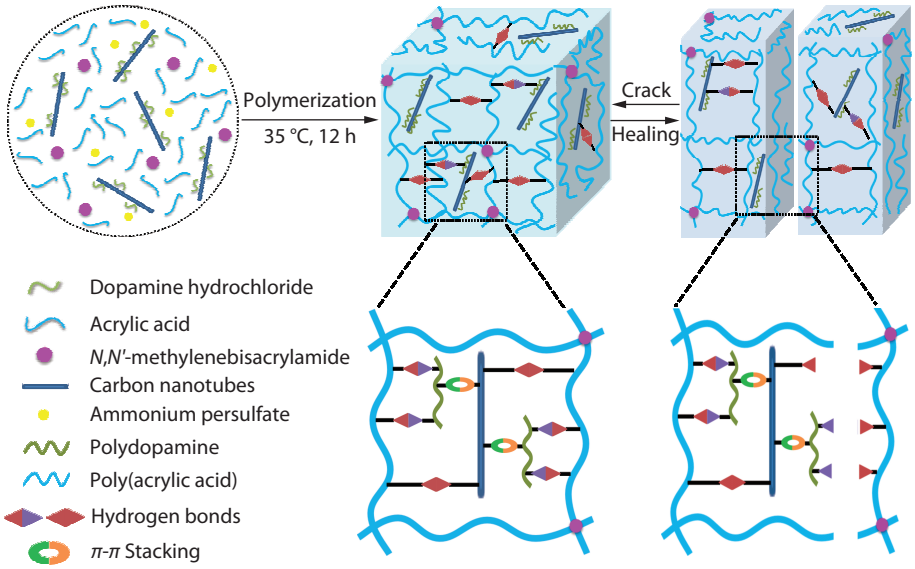

Fig. 1 Schematic diagram of the fabrication of conductive self-healing hydrogel.

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the tensile force and πR^2 is the cross-sectional area. The tensile strain $\varepsilon = (l - l_0)/l_0 \times 100\%$, l_0 is the original length, l is the length after stretching. Fracture toughness was characterized by the fracture energy (U, MJ·m^{-3}), and calculated by the area enclosed by the integrated stress-strain curve: $U = \int \sigma d\varepsilon$. Young's modulus was calculated in the initial linear range from the stress-strain curves. The tensile cycle test was measured by using a hydrogel sample at the same tensile speed and the same gauge length of 3 mm diameter with a maximum strain of 400%.

The compression cycle was tested by using a cylindrical hydrogel sample with a diameter of 6 mm and a length of 10 mm. The measurement was performed at a compression speed of 10 mm·min^{-1} with a maximum strain of 80%. The dissipated energy for each cycle is defined as the area of the hysteresis loop included in the load-unload curve: $\Delta U = \int_{\text{loading}} \sigma d\varepsilon - \int_{\text{unloading}} \sigma d\varepsilon$.

Adhesion Test

The T peeling test was applied to PAA-PDA/CNT composite hydrogel containing 5% MWCNT to different substrates (aluminum, copper, poly(vinyl chloride), polytetrafluoroethylene) with a length of 30 mm and a width of 10 mm. The two sides were attached to each other, and a microcomputer-controlled electronic universal testing machine was used to perform the T peeling test.

Sensing Test of Conductive Hydrogel

The hydrogel sensor was attached to a finger joint, which was connected to a universal source meter (Tektronix, 2450A, USA). Based on changes in sensor resistance, the sensing performance of the hydrogel was analyzed during stretching and various motions.

Characterizations

X-ray diffraction (XRD) measurements were tested using a D-8 ADVANCE X-ray diffractometer (Bruker-AXS, Germany). The voltage is 40 kV and the current is 40 mA. The scanning angle is in the range of 5° to 80°.

RESULTS AND DISCUSSION

Before polymerization, the steady dispersion of MWCNTs is a key point to obtain a uniform conductive hydrogels. Usually, MWCNTs are not easily dispersed in water, and are inclined to aggregate due to strong π-π interaction.[15] In our case, dopamine was used to improve the dispersion of MWCNTs. As shown in Fig. S1(a) (in the electronic supplementary information, ESI), MWCNTs without dopamine will aggregate and precipitate after 5 min standing. In contrast, addition of dopamine makes MWCNTs homogenous dispersion and stable in air without precipitation after one day of standing. This indicates that dopamine has successfully adhered to the surface of MWCNTs by π-π interaction between MWCNTs and dopamine and made a uniform and stable dispersion.[35]

The phase structure of the conductive hydrogel was characterized by X-ray diffraction (XRD) measurement as shown in Fig. S1(b) (in ESI). For MWCNTs, a peak around at about 25.9° can be observed, which represents the structure of the graphite (002). The pattern of the PAA-PDA polymer without adding MWCNTs shows no sharp peaks, indicating that the polymer is homogeneously amorphous. After the addition of MWCNTs, the pattern of PAA-PDA/MWCNTs shows no diffraction peak of MWCNTs similar to that of PAA-PDA, indicating the uniform dispersion of MWCNTs into the hydrogel.

The self-healing ability of the hydrogel was first measured. During the self-healing process, a drop of water was dripped onto the damaged interface, causing part of the hydrogel at the interface to swell with water and promote the movement of the polymer chain. Multiple hydrogen bonds among the polymer chain, CNT, and PDA will make polymer chain move from one side to the other and entangle to form a new polymer network, completing self-healing process. In order to obtain high mechanical composite hydrogels with high self-healing ability, the content of MBA was first studied. MBA as the cross-linker can adjust the cross-linking density of hydrogels. By changing the content of MBA, the composite hydrogels with different mechanical properties were obtained. Fig. 2(a) shows the stress-strain curves of PAA-PDA/CNT hydrogels with different MBA contents and the stress-strain curves after self-healing. It can be seen that as the MBA content increases from 0.003 g to 0.012 g, the stress of the composite hydrogels is increased from about 0.15 MPa to 0.6 MPa, and the elongation at break is reduced from 880% to ~450%. In order to ensure the self-healing efficiency, the effect of self-healing time on self-healing efficiency was first evaluated (Fig. S2 in ESI). It can be seen that the stress and elongation at break of $A_3D_{0.04}C_5$ hydrogel after self-healing increased significantly with the increase of self-healing time. After 8 h of self-healing, its self-healing efficiency can reach 50%, while after 24 h of self-healing, the stress and elongation at break of the sample are very close to those of the original sample, and the self-healing efficiency reached 98%. Therefore, the study of the effect of different monomer content on the self-healing performance was carried out for the 24 h healing time. Thus, for the hydrogels with different amounts of MBA, the self-healing ability of the hydrogel gradually decreases from nearly 100% self-healing efficiency to 50% with the increase in MBA content. This is because the addition of MBA forms multi-crosslinking points that increase the rigidity of the hydrogel and reduce the toughness. Correspondingly, the increase in the crosslinking density inhibits the movement of polymer chains, weakening the self-healing ability of hydrogels. Considering the mechanical strength and self-healing ability, PAA-PDA/CNT hydrogels with MBA content of 0.006 g were selected in the following work. After the self-healing process of the hydrogels with such low MBA content, the new intertwined multiple hydrogen bond network can almost make up for the mechanical performance damage caused by the covalent network fracture.

The content of dopamine also affects the mechanical strength and self-healing ability. As shown in Fig. 2(b), with the increase of dopamine content, the stress of PAA-PDA/CNT hydrogels decreases from 0.6 MPa to 0.2 MPa, while the elongation at break increases from 400% to 1180%. Meanwhile, with the gradual increase of dopamine content, the self-healing ability of hydrogels is also gradually enhanced and the self-healing efficiency is gradually improved from

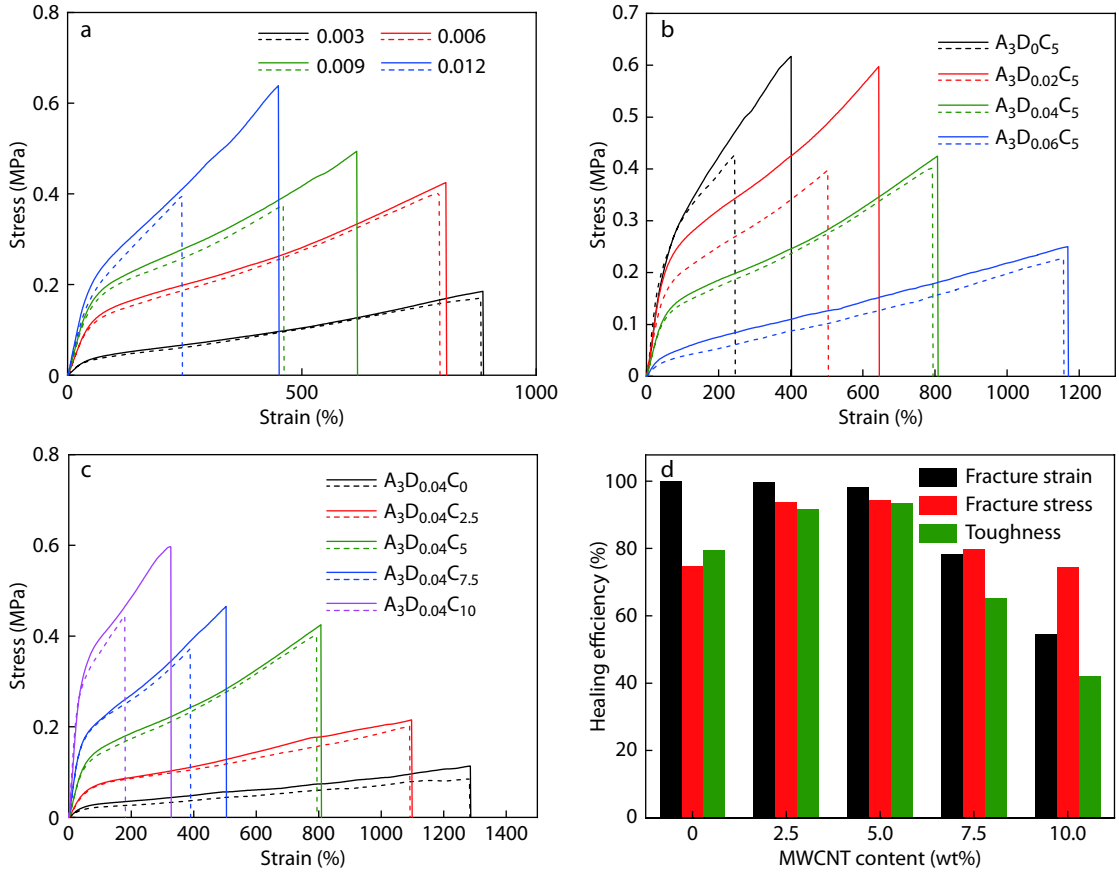

Fig. 2 (a) Stress-strain curves of original (solid line) and self-healing (dashed line) PAA-PDA/CNT hydrogels with different MBA contents; (b) Stress-strain curves of PAA-PDA/CNT hydrogels with different dopamine hydrochloride contents and fixed MBA content of 0.006 g (solid line) and after self-healing (dashed line); (c) Stress-strain curves of the original (solid line) and self-healing (dashed line) of the PAA-PDA/CNT hydrogels with different MWCNT contents; (d) Self-healing efficiency of the fracture strain, fracture stress and toughness of the composite hydrogels.

~60% to ~100%. Thus, the PAA-PDA/CNT hydrogel with dopamine of 0.04 g possesses high mechanical strength and self-healing ability

Next, the effect of MWCNTs on hydrogel properties was studied. After adding MWCNTs, it can be seen that hydrogels can maintain any shapes, while hydrogels without MWCNTs are soft (Fig. S3 in ESI). As the content of MWCNTs increases from 0 wt% to 10 wt%, the stress of the composite hydrogel increases from about 0.1 MPa to 0.6 MPa, and the elongation at break decreases from ~1280% to ~320% (Fig. 2c). This indicates that the increase of the content of MWCNTs improves the stiffness and weakens the toughness of the hydrogel. At the same time, the content of MWCNTs affects the self-healing ability of PAA-PDA/CNT hydrogels. For the hydrogels without MWCNTs, the fracture stress is only 75% of the initial stress. After addition of 2.5 wt% of MWCNTs, the fracture stress reaches 93% of the initial value, suggesting that the carboxyl group on MWCNT forms multiple hydrogen bonding with the polymer chain, which improves the self-healing efficiency of the composite hydrogel. After adding 5 wt% MWCNTs, the self-healing efficiency of the fracture strain, fracture stress and toughness of the composite hydrogel reach 97%, 95%, and 94%, respectively, which are all higher than that of $A_3D_{0.04}C_{2.5}$. This indicates that continuing to increase the content of MWCNTs will improve the self-healing efficiency. However, further increase of MWCNTs (7.5 wt% and 10 wt%) leads to the decline of the self-healing efficiency of the fracture toughness, fracture stress, and strain of the composite hydrogel (Fig. 2d), which can be attributed to that too much amount of MWCNTs hinder the movement of polymer chain, reducing the self-healing efficiency.

PAA-PDA/MWCNTs hydrogels can be stretched and buckled. The cylindrical hydrogels with a diameter of 3 mm can lift off 1 kg of loading without breaking (Fig. 3a). The Young's modulus of hydrogels without MWCNT is only about 50 kPa. With the increase of MWCNT content, the Young's modulus of hydrogels gradually increases. When 10 wt% MWCNT is added, the Young's modulus of hydrogels reaches 800 kPa (Fig. 3b).

The PAA-PDA/CNT hydrogels also possess fatigue resistance as reflected by the stretching cycle. After 20 cycles of stretching, the mechanical properties of $A_3D_{0.04}C_5$ hydrogel do not significantly decline. The maximum stress of the hydrogel at the first stretching cycle can reach 0.25 MPa. After 20 cycles, the maximum stress at the 20th stretching cycle is still 0.22 MPa, which is about 88% of the original value

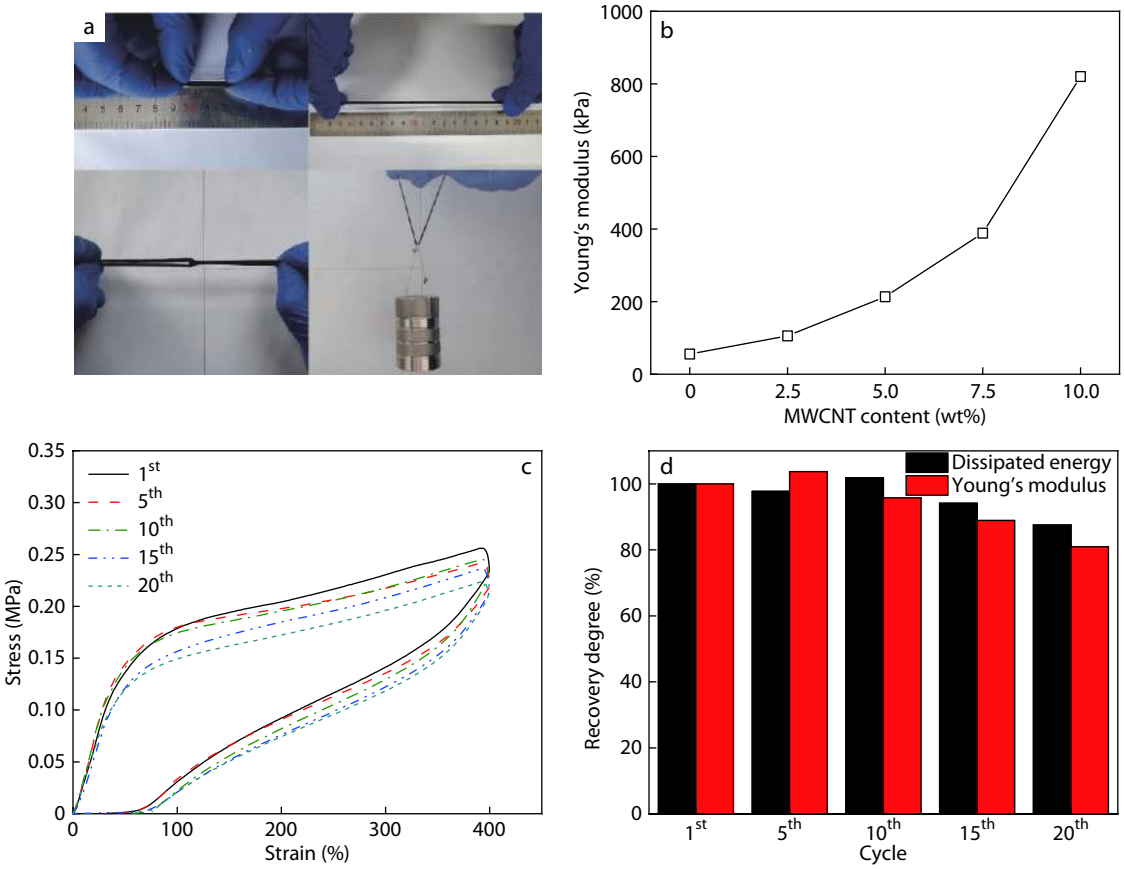

Fig. 3 (a) Photographs of PAA-PDA/CNT hydrogel samples at stretching, buckling and loading of weight; (b) Young's modulus curve of PAA-PDA/CNT hydrogels with different MWCNT content; (c) Cyclic tensile loading-unloading curve of $A_3D_{0.04}C_5$ hydrogel at 400% strain; (d) Recovery degree of dissipated energy and Young's modulus for $A_3D_{0.04}C_5$ after 20 tensile loading-unloading cycles.

(Fig. 3c). As can be seen from Fig. 3(d), after 5 tensile cycles, the toughness is 97% of the original, and even after 20 tensile cycles, its toughness and Young's modulus are still 87% and 80% of the original values. This indicates that PAA-PDA/MWCNT hydrogel has good recovery and tensile fatigue resistance.

The PAA-PDA/CNT conductive hydrogel can be pressed by a finger and quickly restored to its original state after releasing, indicating that the conductive hydrogel has excellent compression recovery properties (Fig. 4a). In order to test the compression performance quantitatively, $A_3D_{0.04}C_5$ hydrogel was compressed to different strains of 20%, 40%, 60%, and 80% (Fig. 4b). The hydrogel can recover to its original state after releasing at 80% strain. Furthermore, the continuous compression cycles at strain of 80% were conducted on the same $A_3D_{0.04}C_5$ hydrogel (Fig. 4c). It can be seen that after 30 compression cycles the stress-strain curves are almost coincident, indicating that $A_3D_{0.04}C_5$ hydrogel has good fatigue resistance, which may be related to the multiple interactions between polymer chains and MWCNTs. Fig. 4(d) summarizes the recovery of the dissipated energy and Young's modulus after each cycle. After five compression cycles, the recovery of the toughness and Young's modulus of the hydrogel is 95% and 98%, respectively. Even after 30 compression cycles, the recovery of the toughness and Young's modulus can still be maintained above 85%. This indicates that $A_3D_{0.04}C_5$ hydrogel will not be greatly affected in the mechanical loading-unloading cycles, and further illustrates the possibility of $A_3D_{0.04}C_5$ hydrogel working in an external pressure environment.

Except for the fatigue resistance and mechanical self-healing ability, the composite conductive hydrogels also show the electrical self-healing ability. When the hydrogel is connected to the conductive circuit, the LED lamp is light on. After the hydrogel is cut off, the LED lamp turns off. When the cut halves are contacted with each other, the lamp is light on immediately (Fig. 5a), indicating that $A_3D_{0.04}C_5$ hydrogel has good electrical self-healing properties.

$A_3D_{0.04}C_5$ hydrogel not only has good electrical self-healing ability, but also has strain response. When the composite hydrogel was stretched to the strain of 200%, 400%, 600%, 800%, the resistance increases to 2, 5, 11, and 17 times of the original resistance. Note that there is a stable platform at each of strain, indicating that the strain response is relatively stable (Fig. 5b). In order to further measure the strain sensing, the hydrogel was stretched to a strain of 200% for multiple cycles, and the change of resistance of $A_3D_{0.04}C_5$ hydrogel was measured (Fig. 5c). It can be seen that when the $A_3D_{0.04}C_5$ hydrogel is stretched to the strain of 200%, the resistance changes to about 2 times of the original resistance. After releasing, the

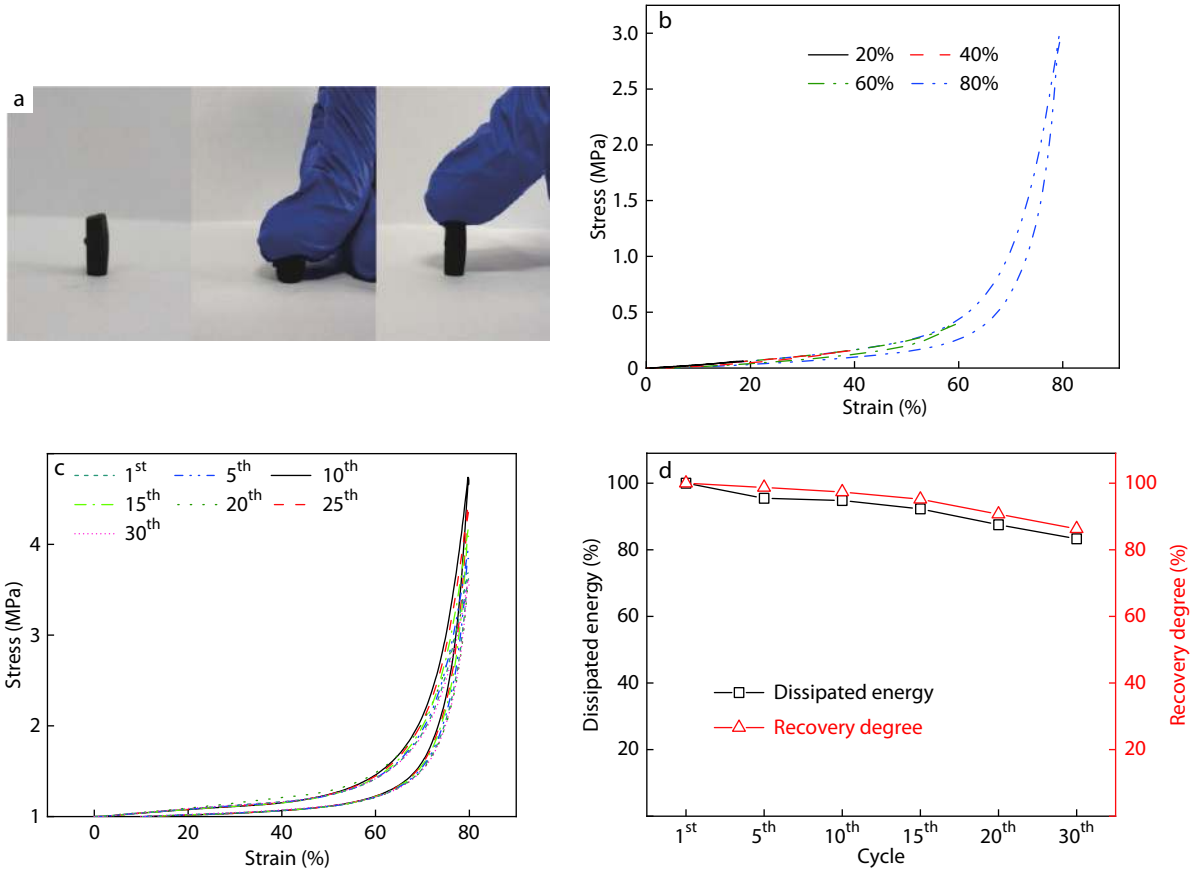

Fig. 4 (a) Photographs of the composite hydrogels before and after compression; (b) Compression curves of $A_3D_{0.04}C_5$ hydrogel under different compression strains; (c) Cyclic compression of $A_3D_{0.04}C_5$ hydrogel at strain of 80%; (d) The degree of recovery of the dissipated energy and Young's modulus of the $A_3D_{0.04}C_5$ hydrogel after 30 compression loading-unloading cycles.

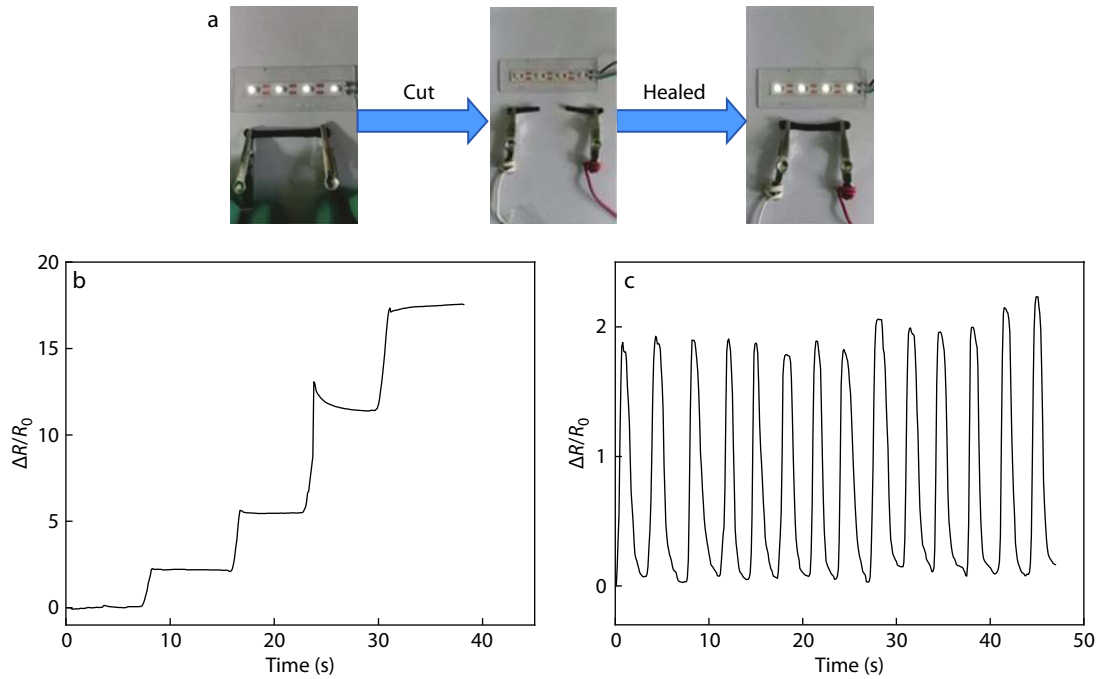

Fig. 5 (a) Photographs of $A_3D_{0.04}C_5$ hydrogel after cutting and healing measurement; (b) Resistance changes of $A_3D_{0.04}C_5$ hydrogel at strain of 200%, 400%, 600%, 800% strain resistance curve; (c) Resistance changes of $A_3D_{0.04}C_5$ hydrogels during stretching-releasing cycles.

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resistance decreases rapidly to the original state. This indicates that $A_3D_{0.04}C_5$ hydrogel has good cyclic stability.

Since the composite hydrogel is strain responsive, it will be motion-sensitive. The $A_3D_{0.04}C_5$ hydrogel strain sensor was attached to the finger joint and connected to the resistance test system (Movie S1 in ESI). By bending the finger of 0°, 30°, 60°, 90° and 0°, the resistance changes at different angles were detected (Fig. 6a). As shown in Fig. 6(b), the changes of resistance increase step by step at the finger bending of 30°, 60°, and 90°. When the finger bends back to 0°, the resistance drops back to the original resistance. When the hydrogel sensor is adhered to the wrist, the resistance change of $A_3D_{0.04}C_5$ hydrogel is regular and stable as the wrist flips over (Fig. 6c). Fig. 6(d) shows that when the strain sensor is attached to the back of the hand and the knuckle of the finger, the resistance changes with the change of clenching motion. This indicates that $A_3D_{0.04}C_5$ hydrogel has good motion transduction and can be used in human skin sensors.

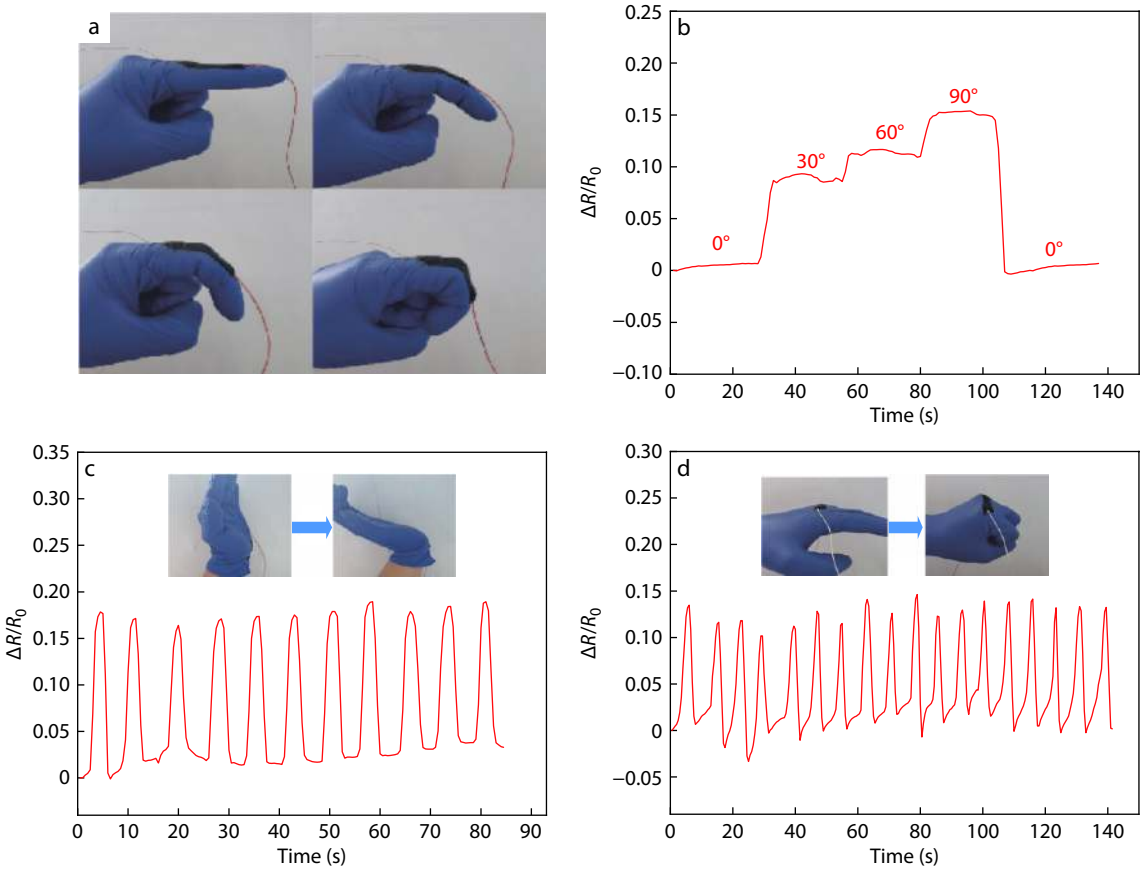

Fig. 6 (a) Photographs of strain sensor with fingers bending of 0°, 30°, 60°, 90° and (b) corresponding resistance changes. The resistance response to the (c) wrist and (d) fist motion. Insets are the photographs of different bent state of wrist and fist.

Fig. 7 Photographs of conductive hydrogel adhered to plastic, glass, rubber, and metal.

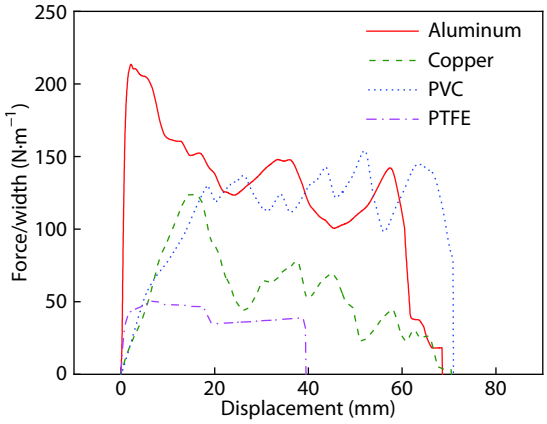

Fig. 8 T peeling curves of PAA-PDA/CNT composite hydrogel on different substrates (aluminum, copper, PVC, PTFE).

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The PAA-PDA/MWCNT hydrogels also have good adhesion and not only can adhere to the human body surface and but also can adhere to other surface. As shown in Fig. 7, the hydrogel can adhere to different surfaces such as plastic, glass, rubber, iron, *etc*. The adhesion performances of PAA-PDA/CNT composite hydrogel to different substrates were also tested by T peeling test. The maximum adhesion strength of PAA-PDA/CNT composite hydrogel to aluminum, copper, poly(vinyl chloride) (PVC) and poly(tetra fluoroethylene) (PTFE) can reach 220, 120, 150, and 50 $N \cdot m^{-1}$, respectively (Fig. 8). These adhesion strengths are comparable to or higher than that of other hydrogels (Table S1 in ESI), indicating the excellent adhesion to different substrates. The good adhesion may be due to the hydrogen bonding and π-π interactions existing in the hydrogels, which makes the hydrogel possible to be used in wearable smart sensors.

CONCLUSIONS

In summary, we have prepared the PAA-PDA/CNT composite hydrogel by the simple random polymerization method. The composite hydrogel has good stretchability (320%–1280%) and compressibility (~80%) as well as good fatigue resistance. The composite hydrogel also shows good mechanical self-healing ability and electrical self-healing ability. In addition, the hydrogel shows good adhesion and can be used as strain sensors for human motion detection.

Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at http://dx.doi.org/10.1007/s10118-020-2472-0.

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