

Cephalopods-inspired Repairable MWCNTs/PDMS Conductive Elastomers for Sensitive Strain Sensor

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Electronic Supplementary Information

Abstract Flexible electronic devices based on reversible bonds for self-curing capabilities arouses extensive interest. However, most of the composite conductive elastomers have the problems of poor mechanical properties and slow recovery of mechanical properties during multiple stretching, which hinder their stability in continuous operation. In this study, hyperbranched-MWCNTs/hyperbranched-PDMS self-healable conductive elastomers inspired by cephalopods were successfully developed. The prepared conductive elastomer exhibited good self-healing ability (91%) at room temperature excited by multiple reversible interactions. The prepared elastomer showed outstanding mechanical properties and anti-fatigue ability, so that it can cope with more arduous tasks. Moreover, the elastomer was sensitive to the change of stress states and can be used as a stable strain sensor. Therefore, the self-repairing conductive elastomer has potential practicability in the fields of human-computer interaction, motion monitoring, soft robot and so on.

Keywords Self-healable; Reversible interactions; Hyperbranched; Anti-fatigue; Strain sensor

Citation: Zhang, K.; Wang, Z.; Liu, Y.; Zhao, H.; Gao, C.; Wu, Y. Cephalopods-inspired repairable MWCNTs/PDMS conductive elastomers for sensitive strain sensor. *Chinese J. Polym. Sci.* 2022, 40, 384–393.

INTRODUCTION

With the rapid growth of industrial demand in motion monitoring, human-computer interaction and other fields, how to fabricate sensitive strain sensors through simple and efficient strategies arouses widespread concern.^[1] The mechanical blending of conductive functional materials with supramolecular system is undoubtedly an ideal low-cost process. However, the devices inevitably suffer mechanical damage in the process of continuous work.^[2] Structural damage of sensors seriously reduce them performance and even cause safety accidents in use.^[3] Therefore, devices with self-healing properties emerge as the times require.

It is well known that intrinsic self-curing materials could self-diagnose internal defects and repair damaged parts.^[4,5] Reversible interactions (such as host-guest interaction,^[6] hydrogen bond,^[7–9] metal-ligand bond,^[10,11] π - π stacking^[12]) and dynamic covalent bonds (such as boron oxygen bond,^[13] D-A reaction,^[14] imine bond,^[15] hydrazide bond,^[16] disulfide bond^[17]) have been widely used in the design of reversible crosslinking networks. The size of conductive nanomaterials is

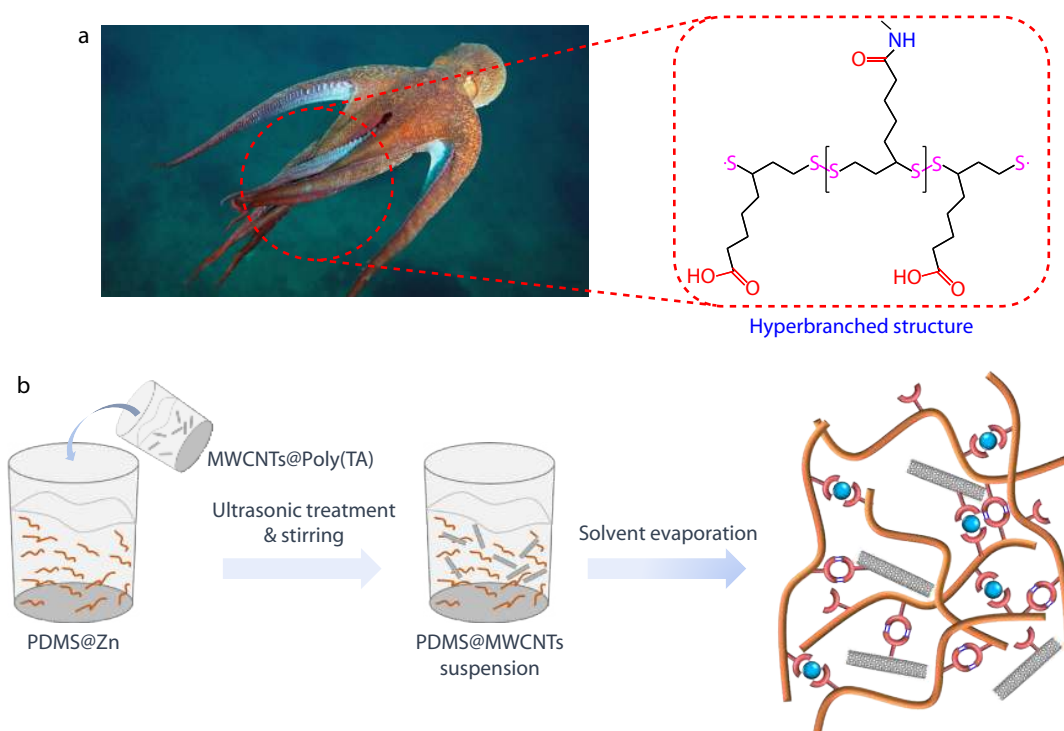
generally larger. Therefore, the incorporation of conductive nanofillers into polymer systems improves the mechanical properties of stretchable materials, but the self-healing efficiency of the elastomer is reduced. To this day, it is still a challenge to develop conductive composites with good mechanical properties and efficient self-curing ability without external stimulation.^[18]

Many conductive nanomaterials (such as functionalized carbon nanotubes,^[19] MXene^[20] and functionalized graphene^[21]) have active groups on their surfaces. Through a series of chemical reactions, we could design the molecular structure of surfaces of nanomaterials. The dynamic bonds between modified nanofillers and polymer segments lead to the formation of ordered dispersed composites. In addition, the self-healing ability of conductive materials will also be improved. We tried to combine hyperbranched strategy with the modification of nanomaterials and polymer segments. Hyperbranched structures have softer branches, similar to the feet of cephalopods (Scheme 1a). This kind of structural design endowed the system with active external functional groups, which made the reversible interaction easier to form.

In this work, a self-healable MWCNTs-PDMS conductive elastomer was prepared by using reversible interaction as the medium to connect the external functions of hyperbranched

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Received October 20, 2021; Accepted November 29, 2021; Published online January 20, 2022



Scheme 1 (a) Design hyperbranched structures inspired by cephalopods; (b) Production process of PDMS@MWCNTs.

structure. Due to the dynamic equilibrium of multiple reversible bonds, conductive elastomer (PDMS@MWCNTs) had good mechanical properties, excellent fatigue resistance and efficient self-healing ability. Well-organized composites were sensitive to the change of stress state and responded linearly to deformation. Furthermore, PDMS@MWCNTs accurately monitored human joint movement. Therefore, self-repairing conductive elastomers based on hyperbranched structure modification as a reliable and sensitive strain sensor have great potential in behavior monitoring, human-machine interaction and other fields.

RESULTS AND DISCUSSION

Structure Design and Characterization

The high-tech life style requires the manufacturing of strain sensors to be convenient and low-cost. In order to meet these requirements, we developed a sensitive and reliable strain sensor through a simple preparation process (Scheme 1b). However, the poor dispersion stability of nanomaterials in polymer is the disadvantage of blending method. Fortunately, the reversible bonds between the surface of nanomaterials and polymer segments promote the uniform dispersion of fillers in the matrix. Cephalopods have a number of soft feet that allow them to move flexibly. Inspired by this, we used the ring-opening polymerization (ROP) of sulfur-containing five membered-rings to endow organosilicon segments and the surface of modified-MWCNTs with high mobility outer carboxyl groups, respectively. The dispersion of designed nanofillers in the polymers was improved by the sacrificial metal-ligand bond between carboxyl groups and metal ions in addition to the interaction between carboxyl groups (Figs. S1 and S2 in the

electronic supplementary information, ESI).^[22] Finally, the conductive elastomers (PDMS@MWCNTs) with outstanding performance were prepared.

The synthetic process of PDMS@Poly(TA) is shown in Fig. S3 (in ESI). In order to confirm that the chain segments of organosilicon with hyperbranched structure were successfully synthesized, we characterized PDMS@Poly(TA) by FTIR spectroscopy (Fig. 1a). The stretching and bending vibration bands of —NH— appear at 3450 and 1546 cm^{-1} , respectively. At the same time, 1641 cm^{-1} is the characteristic band of C=O . The above evidences indicated that peptide bonds were formed. Furthermore, the band of —OH appears in the spectrum. This was the proof of the existence of hyperbranched structure. The organosilicon supramolecular network crosslinked by hydrogen bond lacked toughness. We introduced zinc ions into the polymers and prepared PDMS@Zn elastomers with dual cross-linking. The smooth and uniform surface of the elastomer can be observed by scanning electron microscope (Fig. S4 in ESI). In addition, EDS element maps confirmed that zinc ions were evenly distributed on the surface of the material (Fig. S5 in ESI). The preparation process of hyperbranched MWCNTs with multiple carboxyl terminus is shown in Fig. S6 (in ESI). The characteristic bands of —NH— , C=O , S—S and —OH appear in the FTIR spectrum of MWCNTs@Poly(TA), which were signs of the success of dehydration and ROP (Fig. 1b). As shown in Fig. 1(c), the MWCNTs before and after modification were analyzed by thermogravimetry. In the temperature range of $0\text{--}600\text{ }^{\circ}\text{C}$, MWCNTs hardly decomposed. However, MWCNTs@Poly(TA) exhibited obvious thermal instability. This can be attributed to the thermal decomposition of S—S and terminal carboxyl groups in hyperbranched structure. Meanwhile, the surface of modi-

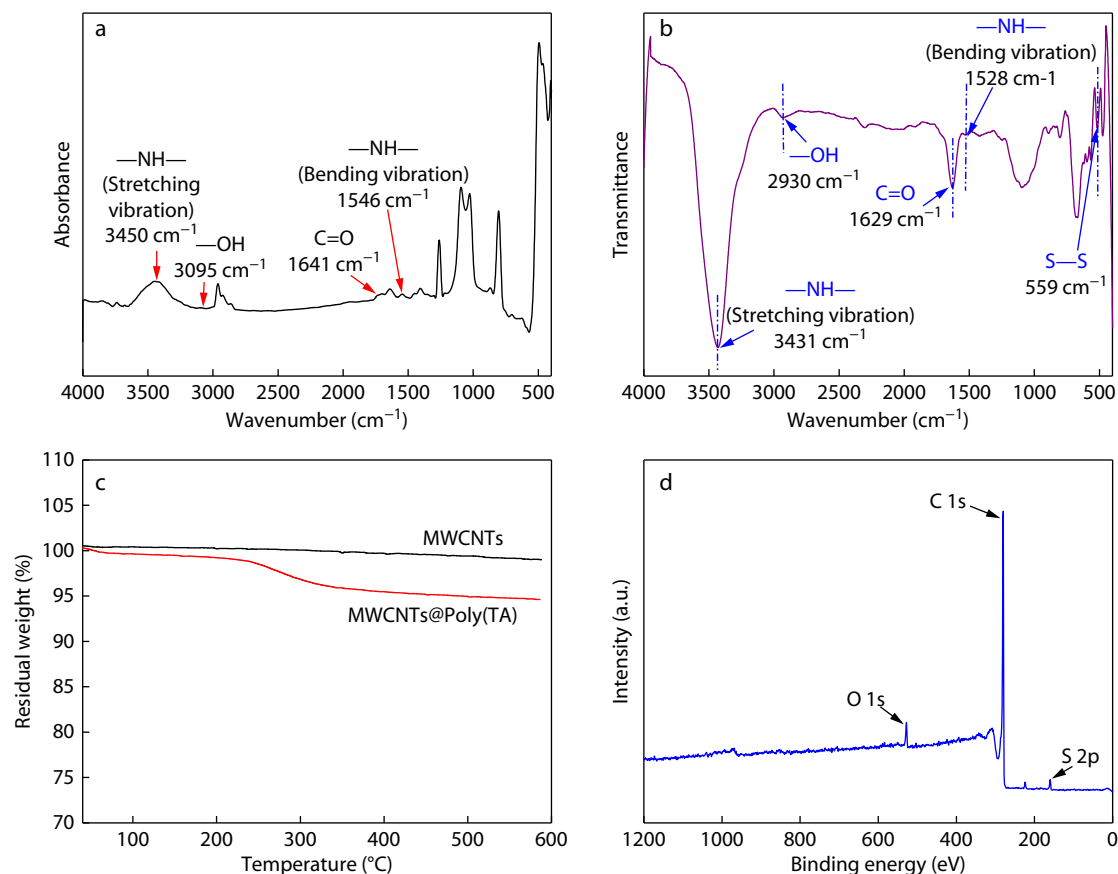


Fig. 1 FTIR spectra of (a) PDMS@Poly(TA) and (b) MWCNTs@Poly(TA); (c) TGA curves of amino functionalized MWCNTs and MWCNTs@Poly(TA); (d) XPS spectrum of MWCNTs@Poly(TA).

fied-MWCNTs was rougher. Therefore, the Raman spectrum of MWCNTs@Poly(TA) showed surface enhanced Raman scattering compared with that of MWCNTs (Fig. S7 in ESI). We observed the element distribution of MWCNTs@Poly(TA) by EDS. As shown in Fig. S8 (in ESI), the appearance of S and O elements on the surface of nanomaterials also proved the success of hyperbranched modification. Moreover, the peaks of O 1s and S 2p clearly appear in XPS spectrum of MWCNTs@Poly(TA), which consolidated our previous conclusion (Fig. 1d). In Fig. S9 (in ESI), the characteristic band of disulfide bond of thionic acid in Raman spectrum disappears after the ROP. This indicated that the ROP between sulfur-containing five membered rings was carried out successfully.^[23]

Mechanical Properties

The process of using puts forward more and more stringent requirements for the mechanical properties of strain sensors.^[24–26] In order to assess the mechanical performances of materials, tensile tests were performed on specimens with different MWCNTs@Poly(TA) content. PDMS elastomers without nanomaterials (PDMS@Zn) exhibit good mechanical properties (Fig. S10 and Table S3 in ESI). The tensile strength of PDMS@1:6 is 0.87 MPa and the elongation at break is 572%. The mechanical properties of the prepared elastomers were not common in supramolecular elastic material based on reversible interaction.^[27–29] The supramolecular network composed of

hydrogen bonds and metal-ligand bonds dissipated the energy generated by external force effectively. Meanwhile, the reversible interactions acted as sacrificial bonds to disperse the concentrated stress.^[30,31] With the increase of zinc ion content, the mechanical properties of the elastomers were raised and the bond energy of metal-ligand bond was stronger. Therefore, more metal-ligand bonds improved the mechanical properties obviously.^[32] The stress-strain curves of PDMS@MWCNTs composites are shown in Fig. 2(a). With the increase of modified-MWCNTs content, the tensile strength of the material is also increased (Table S4 in ESI). This can be attributed to the reinforcing effect of nanofillers on the mechanical properties of elastomers. However, the stretchability of PDMS@MWCNTs is negatively correlated with the content of MWCNTs@Poly(TA), which might be due to the fact that nanoscale filler hindered the slipping of organosilicon segments. It is worth noting that the tensile strength of PDMS@MWCNTs-10 is as high as 1.77 MPa, and the maximum strain is 348%. Such classy mechanical properties rarely appeared in previous reports about self-repairing flexible conductive materials, which also made PDMS@MWCNTs-10 meet the needs of most applications.^[33–39] PDMS@MWCNTs-14 had a tensile strength as high as 3.08 MPa. Nevertheless, the elongation at break of the material was only 130%, which was difficult to cope with the special application requirements. Therefore, we chose PDMS@MWCNTs-10 with outstanding tensile strength and stretchability as the object of

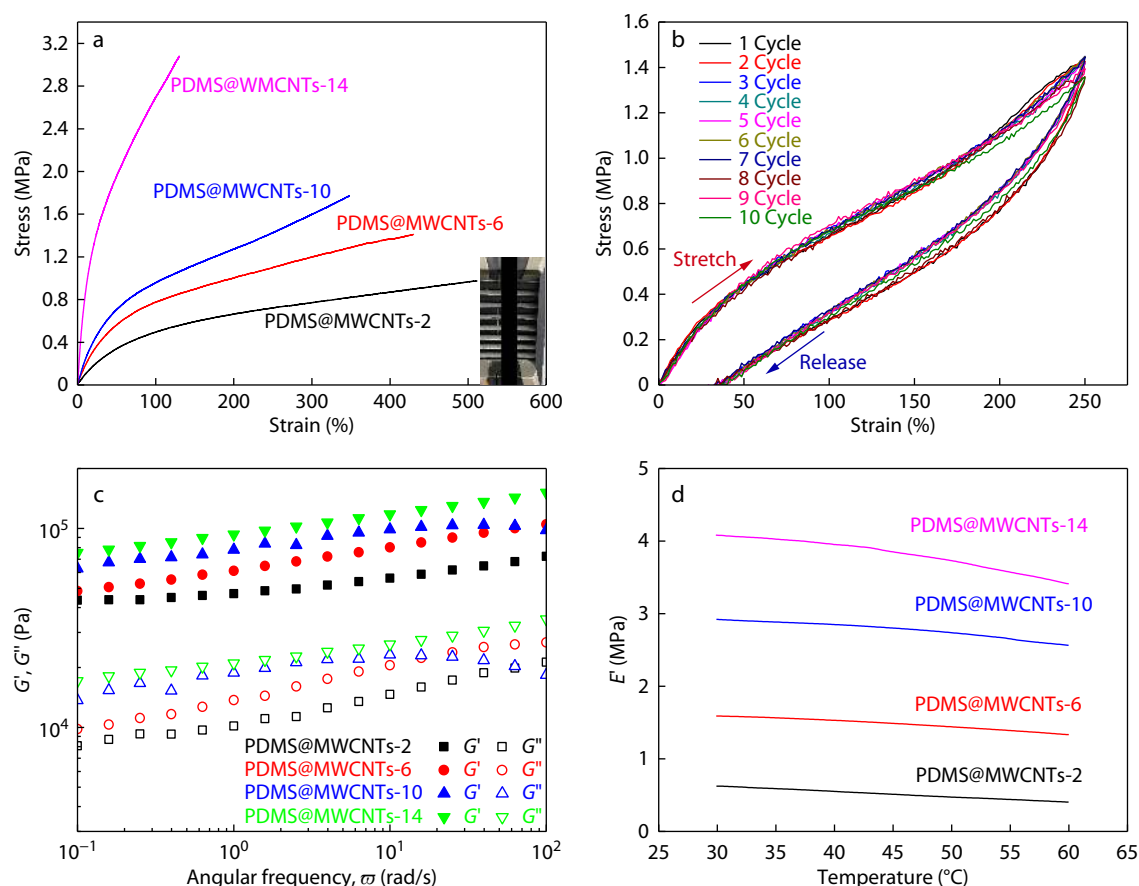


Fig. 2 (a) Stress-strain curves of PDMS@MWCNTs with different nanofillers contents; (b) Cyclic stress-strain curves of PDMS@MWCNTs-10; (c) Frequency-dependent rheological tests of PDMS@MWCNTs with different nanofiller contents at 25 $^{\circ}\text{C}$; (d) Temperature-dependent DMA tests of PDMS@MWCNTs with different nanofiller contents.

performances evaluation.

The mechanical properties of most of strain sensors fabricated by simple process cannot be recovered immediately when they are subjected to continuous deformation. This can be attributed to the uneven dispersion of nanomaterials and the hysteresis of reconstruction after dynamic bond fracture. The fatigue resistance of the prepared conductive elastomer was analyzed by cyclic tensile test. After the PDMS@MWCNTs-10 was stretched to 250% strain at the speed of 50 mm/min, the sample was immediately pulled back to the original state at the same speed. When the first load-unload process was finished, the next cycle was started promptly. As shown in Fig. 2(b), PDMS@MWCNTs-10 still maintains its original mechanical properties after repeated cyclic stretching. The excellent fatigue resistance of the sample depended on the efficient reconstruction of the broken reversible bonds.^[10,40,41] Meanwhile, the hysteresis loops indicated that the hydrogen bonds and metal-ligand bonds effectively dissipated the energy brought by the external force in the tensile process.^[22,42]

The frequency-dependent rheological test of PDMS@Zn at room temperature is shown in Fig. S11 (in ESI). The storage modulus (G') increases with the increase of zinc ion content. For PDMS@MWCNTs, the G' was directly proportional to the content of modified-MWCNTs (Fig. 2c). These were consistent

with the conclusion drawn from stress-strain curves. At the same time, all the storage modulus are obviously higher than the loss modulus. This indicated that both PDMS@Zn and PDMS@MWCNTs were elastic at room temperature. As shown in Fig. S12 (in ESI), the G' and η^* of PDMS@MWCNTs-10 decrease with the increase of temperature, which was because the flow capacity of polymer segments was positively correlated with temperature. Simultaneously, the hydrogen bonds in conductive elastomer dissociated with the increase of temperature, which further promoted this phenomenon. In addition, temperature dependent DMA measurements were performed on PDMS@Zn series elastomers, and the results verify the conclusion of rheological tests (Fig. S13 in ESI). The glass transition temperatures (T_g) of PDMS@Zn with different zinc ion contents are shown in Fig. S14 (in ESI). With the increase of zinc ions, the T_g was also raised. This was due to the raise of metal-ligand bonds, which improved the crosslinking density of supramolecular network. As shown in Fig. 2(d), the storage modulus (E') of the conductive elastomer increases with more MWCNTs@Poly(TA). We assumed that this was related to the blocking effect of nanofillers on the flow of supramolecular segments. Furthermore, the T_g of PDMS@MWCNTs was proportional to the content of modified-MWCNTs, which proved this conjecture (Fig. S15 and Table S4 in ESI).

Self-healing Properties

How to make nanocomposites achieve harmonious self-healing ability similar to organisms is a hot topic at present.^[4,43] However, nanofillers hinder the fluidity of polymer segments, which is contradictory to the self-healing performance.^[44,45] We observed the repair effect of damaged PDMS@MWCNTs-10 under different time periods at room temperature by stereomicroscope. After 20 h of self-healing, the appearance of the wound was almost invisible (Fig. 3a and Fig. S16 in ESI). In addition, completely broken sample can still be bent and stretched after repair (Fig. S17 in ESI). In order to quantify the self-healing performance of conductive elastomer. Tensile tests were performed on the samples before and after self-curing. As shown in Fig. 3(b), the fully fractured elastomer after 20 h of self-repairing exhibited similar mechanical properties as intact sample. Meanwhile, the self-healing efficiency of PDMS@

MWCNTs-10 is positively correlated with the repair time, and the maximum self-curing efficiency is 91% (Fig. 3c). It is a reliable way to apply rheological analysis to the study of self-repairing properties of flexible materials.^[46–48] As shown in Fig. 3(d), the PDMS@MWCNTs-10 before and after self-healing were tested by strain-dependent rheological measurements. The G' of the repaired sample is almost the same as that of the original one. When the oscillation strain switched regularly between 0.5% and 300%, the G' and η^* of the conductive elastomer also sharply rose and suddenly declined (Fig. 3e). This was one of the effective evidences that PDMS@MWCNTs had good self-repairing ability. Furthermore, whether the repairable material could carry out the disconnection-connection process continuously is particularly important. As shown in Figs. S18 and S19 (in ESI), the mechanical properties of PDMS@MWCNTs-10 are still restored to 77% after six successive repairs. Therefore,

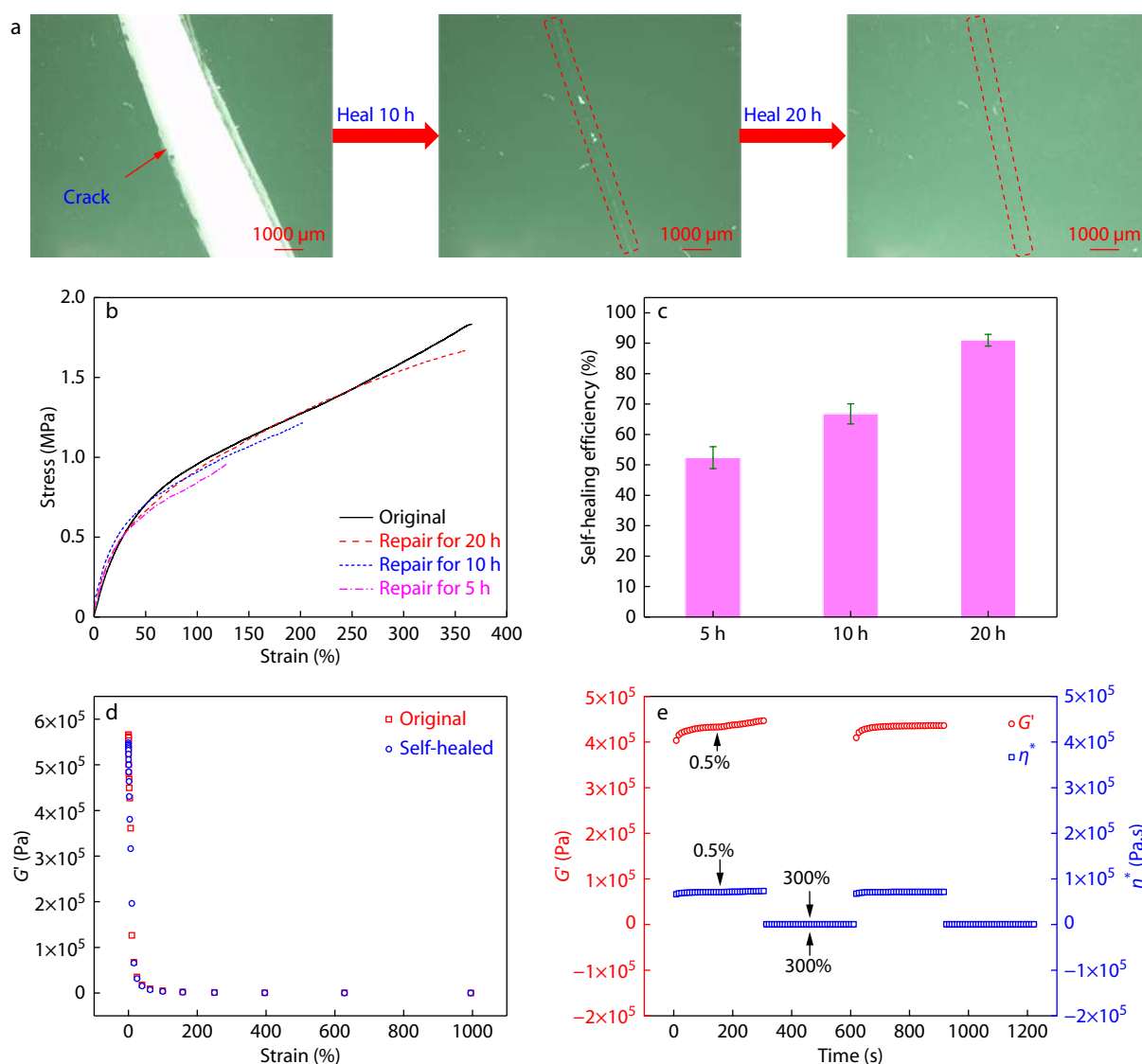


Fig. 3 (a) The wound healing process of PDMS@MWCNTs-10 observed by stereomicroscope; (b) Stress-strain curves of PDMS@MWCNTs-10 before and after repaired; (c) Self-healing efficiency of PDMS@MWCNTs-10 under different repair time periods; (d) Strain-dependent rheological tests of PDMS@MWCNTs-10 before and after self-healed; (e) Cyclic G' and η^* of PDMS@MWCNTs-10 as alternate step strain switched from 0.5% strain to 300% strain with a fixed 300 s interval.

the conductive elastomers prepared by us can work steadily over a long time.

The outstanding self-healing properties under room temperature of PDMS@MWCNTs were attributed to the hyper-branched structures of the surface of nanomaterials and supramolecular segments, which endowed the composite system with a lot of hydrogen bonds and metal-ligand bonds (Fig. 4a). These reversible interactions efficiently reconstructed after fracture. In addition, the molecular structure of the conductive elastomer was analyzed by temperature-dependent FTIR spectroscopy. At 30 °C, the band of —OH appears at 3446 cm^{-1} , and the characteristic band of C=O is 1636 cm^{-1} (Figs. 4b and 4c). When the temperature crept up to 70 °C, the band position of C=O does not change. However, when the temperature rose from 30 °C to 70 °C, the band position of —OH moves from 3446 cm^{-1} to 3459 cm^{-1} . This indicated that temperature affected the disassociation and recombination of the hydrogen-bonding interaction provided by —COOH .^[49] Meanwhile, the reversibility of hydrogen bonds could be achieved at room temperature.^[50,51]

Sensor Performance Evaluation

Conductivity reflected the conductivity of materials. The conductivities of PDMS@MWCNTs were shown in Fig. 5(a) and Table S4 (in ESI). When the proportion of conductive nanomaterials increased, the conductivity of the composite elastomers was also raised. Among them, the conductivity of PDMS@MWCNTs-10 is $2.96 \times 10^{-3}\text{ S/cm}$. Moreover, the resistance changes of PDMS@MWCNTs during stretching to 250% elongation are recorded (Fig. 5b), of which the response resistance shows a linear change. This was due to the well-organized nano-supramolecular composite system. When the conductive elastomer was subjected to external force and deformation, the polymer segments moved, which slowly widened the distance between MWCNTs@Poly(TA).^[34,52] At the same time, the GF value of PDMS@MWCNTs-10 (0%–250% strain) is 3.87. We compared PDMS@MWCNTs-10 with the previously reported self-healable strain sensors, and found that the comprehensive properties of the conductive elastomer we prepared were more advantageous (Fig. 5c).^[34,53–68]

In order to further evaluate the ability of the conductive elastomer as a wearable strain sensor to monitor human motion, we fixed the PDMS@MWCNTs-10 on the joints of

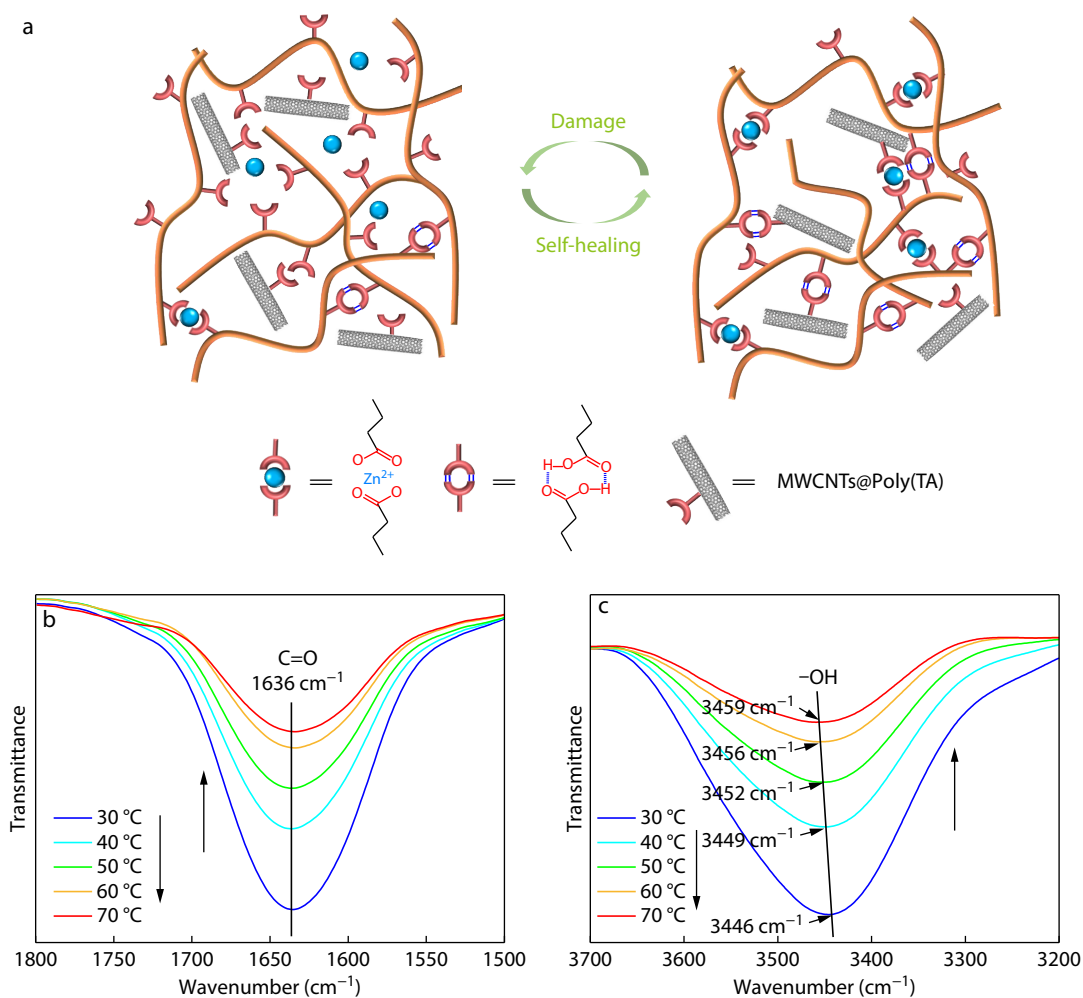


Fig. 4 (a) Self-healing mechanism of conductive elastomers; (b, c) Temperature-dependent FTIR spectra of PDMS@MWCNTs.

the volunteer and recorded the real-time I - t curve during the joint movement through the electrochemical workstation. When the joint bent, the stress states of sample were

changed, and the resistance altered. Subsequently, Ohm's law ($R=U/I$) was used to calculate the real-time resistance change. As shown in Figs. 6(a)–6(c), the $\Delta R/R_0$ curves corres-

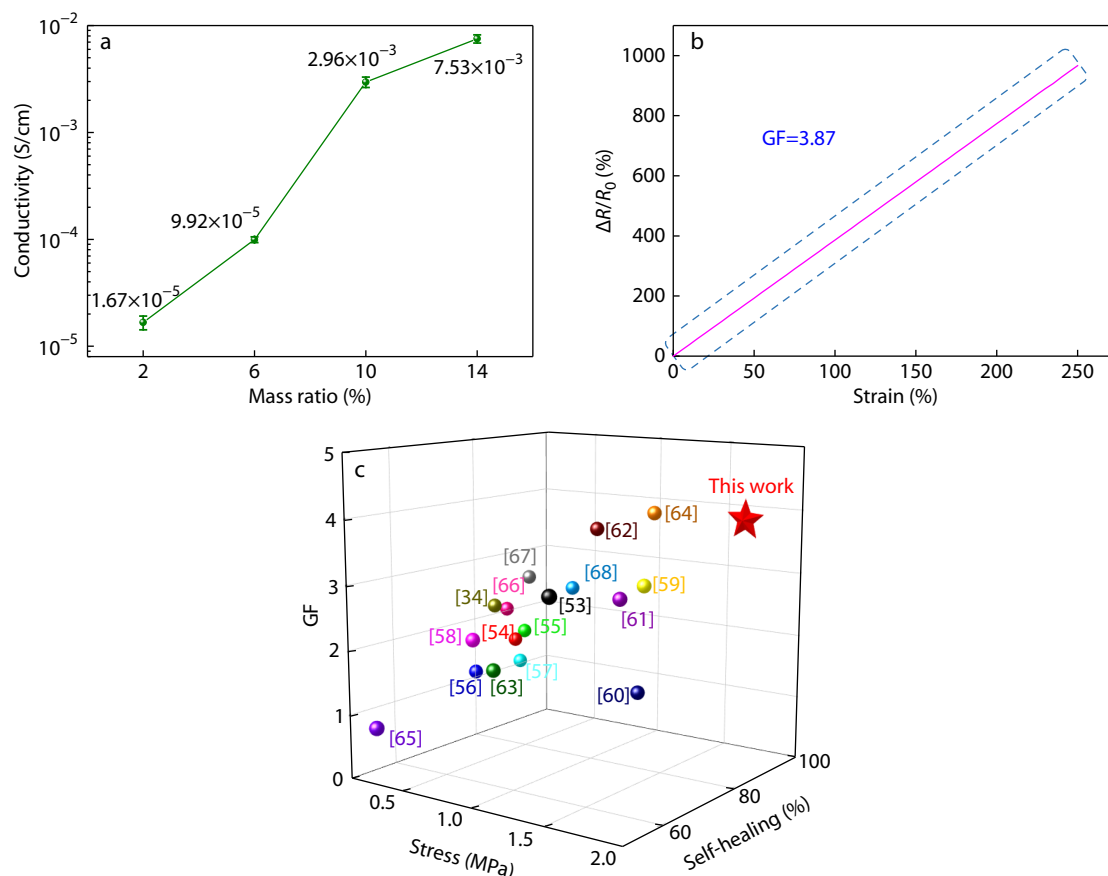


Fig. 5 (a) Conductivity of PDMS@MWCNTs with different nanofillers content; (b) The functional relationship between strain and $\Delta R/R_0$ in PDMS@MWCNTs-10; (c) Comparison of comprehensive performance between PDMS@MWCNTs-10 and recently reported self-curing strain sensors.

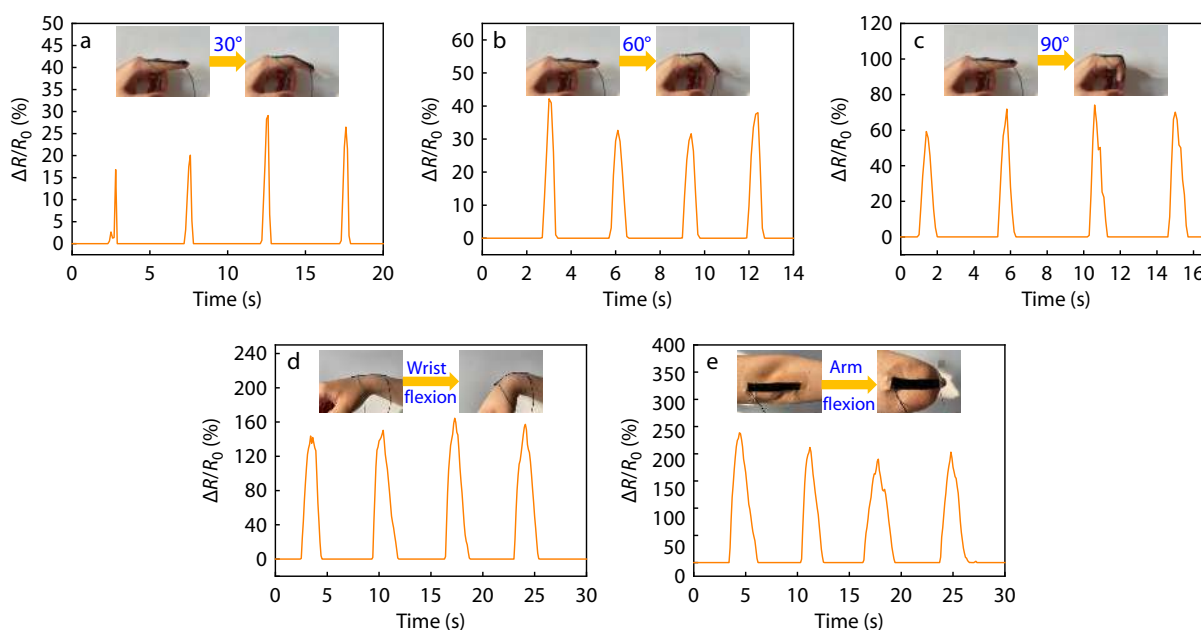


Fig. 6 PDMS@MWCNTs-10 was used to monitor joint movement: finger bending (a) 30°, (b) 60° and (c) 90°; (d) Wrist bending; (e) Elbow bending.

ponding to continuous finger bending of 30°, 60° and 90° were recorded, respectively. Based on the same test method, the wrist and elbow bending motions were successfully monitored (Figs. 6d and 6e). The results showed that PDMS@MWCNTs-10 could monitor human movement accurately and stably.

CONCLUSIONS

Inspired by the flexible feet of cephalopods, MWCNTs@Poly(TA) were linked with polymer segments through multiple reversible interactions with hyperbranched structures. Through this novel strategy, we fabricated well-organized conductive elastomers with good mechanical properties. The tensile strength of PDMS@MWCNTs with 10 wt% nanofiller was 1.77 MPa and the maximum strain was 348%. With the help of the dynamic reversibility of hydrogen bond and metal ligand bond, the repair efficiency of elastomer at room temperature was 91%. In addition, the GF value of PDMS@MWCNTs-10 (0–250% strain) was 3.8673, and the elastomer accurately monitored human movement. We believe that the self-healing PDMS@MWCNTs conductive elastomer based on hyperbranched structure modification could meet the industrial requirements of strain sensors applied in human-computer interaction, motion monitoring and other fields by virtue of simple and low-cost preparation process.

NOTES

The authors declare no competing financial interest.



Electronic Supplementary Information

Electronic supplementary information (ESI) is available free of charge in the online version of this article at <http://doi.org/10.1007/s10118-022-2674-8>.

ACKNOWLEDGMENTS

This work was financially supported by Shandong Provincial Natural Science Foundation (No. ZR2019QB019), the National Natural Science Foundation of China (No. 51872150), Shandong Provincial Natural Science Foundation (No. ZR2018MB034), Key Laboratory of Special Functional Aggregated Materials, Ministry of Education, P. R. China, “QingChuang Science and Technology Plan” Project of Colleges and Universities in Shandong Province (No. 2020KJC005).

REFERENCES

- Liu, X.; Su, G.; Guo, Q.; Lu, C.; Zhou, T.; Zhou, C.; Zhang, X. Hierarchically structured self-healing sensors with tunable positive/negative piezoresistivity. *Adv. Funct. Mater.* **2018**, *28*, 1706658.
- Urban, M. W.; Davydovich, D.; Yang, Y.; Demir, T.; Zhang, Y.; Casabianca, L. Key-and-lock commodity self-healing copolymers. *Science* **2018**, *362*, 220–225.
- Guo, Q.; Huang, B.; Lu, C.; Zhou, T.; Su, G.; Jia, L.; Zhang, X. A cephalopod-inspired mechanoluminescence material with skin-like self-healing and sensing properties. *Mater. Horiz.* **2019**, *6*, 996–1004.
- Li, S.; Zhou, X.; Dong, Y.; Li, J. Flexible self-repairing materials for wearable sensing applications: elastomers and hydrogels. *Macromol. Rapid. Commun.* **2020**, *41*, e2000444.
- Wu, H. T.; Jin, B. Q.; Wang, H.; Wu, W. Q.; Cao, Z. X.; Yuan, Z. Y.; Huang, Y.; Li, W. H.; Huang, G. S.; Liao, L. S.; Wu, J. R. A robust self-healing polyurethane elastomer enabled by tuning the molecular mobility and phase morphology through disulfide bonds. *Chinese J. Polym. Sci.* **2021**, *39*, 1299–1309.
- Wang, Z.; Ren, Y.; Zhu, Y.; Hao, L.; Chen, Y.; An, G.; Wu, H.; Shi, X.; Mao, C. A rapidly self-healing host-guest supramolecular hydrogel with high mechanical strength and excellent biocompatibility. *Angew. Chem. Int. Ed.* **2018**, *57*, 9008–9012.
- Chen, Y.; Kushner, A. M.; Williams, G. A.; Guan, Z. Multiphase design of autonomic self-healing thermoplastic elastomers. *Nat. Chem.* **2012**, *4*, 467–472.
- Cordier, P.; Tournilhac, F.; Soulie-Ziakovic, C.; Leibler, L. Self-healing and thermoreversible rubber from supramolecular assembly. *Nature* **2008**, *451*, 977–980.
- Wang, Y.; Huang, X.; Zhang, X. Ultrarobust, tough and highly stretchable self-healing materials based on cartilage-inspired noncovalent assembly nanostructure. *Nat. Commun.* **2021**, *12*, 1291.
- Li, C. H.; Wang, C.; Keplinger, C.; Zuo, J. L.; Jin, L.; Sun, Y.; Zheng, P.; Cao, Y.; Lissel, F.; Linder, C.; You, X. Z.; Bao, Z. A highly stretchable autonomous self-healing elastomer. *Nat. Chem.* **2016**, *8*, 618–624.
- Wang, Y.; Guo, Q.; Su, G.; Cao, J.; Liu, J.; Zhang, X. Hierarchically structured self-healing actuators with superfast light- and magnetic-response. *Adv. Funct. Mater.* **2019**, *29*, 1906198.
- Mei, J. F.; Jia, X. Y.; Lai, J. C.; Sun, Y.; Li, C. H.; Wu, J. H.; Cao, Y.; You, X. Z.; Bao, Z. A highly stretchable and autonomous self-healing polymer based on combination of Pt...Pt and π - π Interactions. *Macromol. Rapid Commun.* **2016**, *37*, 1667–1675.
- Lai, J. C.; Mei, J. F.; Jia, X. Y.; Li, C. H.; You, X. Z.; Bao, Z. A stiff and healable polymer based on dynamic-covalent boroxine bonds. *Adv. Mater.* **2016**, *28*, 8277–8282.
- Ye, L.; Zhang, S. F.; Lin, Y. C.; Min, J. K.; Ma, L.; Tang, T. Synthesis and characterization of butyl acrylate-based graft polymers with thermo-responsive branching sites via the Diels-Alder reaction of furan/maleimide. *Chinese J. Polym. Sci.* **2018**, *36*, 1011–1018.
- Lei, T.; Chen, X.; Pitner, G.; Wong, H. S.; Bao, Z. Removable and recyclable conjugated polymers for highly selective and high-yield dispersion and release of low-cost carbon nanotubes. *J. Am. Chem. Soc.* **2016**, *138*, 802–805.
- Debnath, S.; Ujjwal, R. R.; Ojha, U. Self-healable and recyclable dynamic covalent networks based on room temperature exchangeable hydrazide Michael adduct linkages. *Macromolecules* **2018**, *51*, 9961–9973.
- Peng, W. L.; You, Y.; Xie, P.; Rong, M. Z.; Zhang, M. Q. Adaptable interlocking macromolecular networks with homogeneous architecture made from immiscible single networks. *Macromolecules* **2020**, *53*, 584–593.
- Deng, H.; Lin, L.; Ji, M.; Zhang, S.; Yang, M.; Fu, Q. Progress on the morphological control of conductive network in conductive polymer composites and the use as electroactive multifunctional materials. *Prog. Polym. Sci.* **2014**, *39*, 627–655.
- Lv, Z.; Huang, X.; Fan, D.; Zhou, P.; Luo, Y.; Zhang, X. Scalable manufacturing of conductive rubber nanocomposites with ultralow percolation threshold for strain sensing applications. *Compos. Commun.* **2021**, *25*, 100685.
- Lukatskaya, M. R.; Mashtalir, O.; Ren, C. E.; Dall'Agnese, Y.; Rozier,

- P.; Taberna, P. L.; Naguib, M.; Simon, P.; Barsoum, M. W.; Gogotsi, Y. Cation intercalation and high volumetric capacitance of two-dimensional titanium carbide. *Science* **2013**, *341*, 1502–1505.
- 21 Cheng, H.; Huang, Y.; Cheng, Q.; Shi, G.; Jiang, L.; Qu, L. Self-healing graphene oxide based functional architectures triggered by moisture. *Adv. Funct. Mater.* **2017**, *27*, 1703096.
 - 22 Huang, J.; Tang, Z.; Yang, Z.; Guo, B. Bioinspired interface engineering in elastomer/graphene composites by constructing sacrificial metal-ligand bonds. *Macromol. Rapid Commun.* **2016**, *37*, 1040–1045.
 - 23 Wang, Y.; Sun, S.; Wu, P. Adaptive ionogel paint from room-temperature autonomous polymerization of α -thioctic acid for stretchable and healable electronics. *Adv. Funct. Mater.* **2021**, *31*, 2101494.
 - 24 Lin, Y.; Zhang, H.; Liao, H.; Zhao, Y.; Li, K. A physically crosslinked, self-healing hydrogel electrolyte for nano-wire PANI flexible supercapacitors. *Chem. Eng. J.* **2019**, *367*, 139–148.
 - 25 Zhao, P.; Yin, C.; Zhang, Y.; Chen, X.; Yang, B.; Xia, J.; Bian, L. Mussel cuticle-mimetic ultra-tough, self-healing elastomers with double-locked nanodomains exhibit fast stimuli-responsive shape transformation. *J. Mater. Chem. A* **2020**, *8*, 12463–12471.
 - 26 Fernandes, D. F.; Majidi, C.; Tavakoli, M. Digitally printed stretchable electronics: a review. *J. Mater. Chem. C* **2019**, *7*, 14035–14068.
 - 27 Chen, L.; Peng, H.; Wei, Y.; Wang, X.; Jin, Y.; Liu, H.; Jiang, Y. Self-healing properties of PDMS elastomers via guanine and cytosine base pairs. *Macromol. Chem. Phys.* **2019**, *220*, 1900280.
 - 28 Liu, Y.; Zhang, K.; Sun, J.; Yuan, J.; Yang, Z.; Gao, C.; Wu, Y. A type of hydrogen bond cross-linked silicone rubber with the thermal-induced self-healing properties based on the nonisocyanate reaction. *Ind. Eng. Chem. Res.* **2019**, *58*, 21452–21458.
 - 29 Liu, Z.; Hong, P.; Huang, Z.; Zhang, T.; Xu, R.; Chen, L.; Xiang, H.; Liu, X. Self-healing, reprocessing and 3D printing of transparent and hydrolysis-resistant silicone elastomers. *Chem. Eng. J.* **2020**, *387*, 124142.
 - 30 Wu, S.; Fang, S.; Tang, Z.; Liu, F.; Guo, B. Bioinspired design of elastomeric vitrimers with sacrificial metal-ligand interactions leading to supramechanical robustness and retentive malleability. *Mater. Design* **2020**, *192*, 108756.
 - 31 Liu, J.; Wang, S.; Tang, Z.; Huang, J.; Guo, B.; Huang, G. Bioinspired engineering of two different types of sacrificial bonds into chemically cross-linked *cis*-1,4-polyisoprene toward a high-performance elastomer. *Macromolecules* **2016**, *49*, 8593–8604.
 - 32 Tian, M.; Zuo, H.; Wang, J.; Ning, N.; Yu, B.; Zhang, L. A silicone elastomer with optimized and tunable mechanical strength and self-healing ability based on strong and weak coordination bonds. *Polym. Chem.* **2020**, *11*, 4047–4057.
 - 33 Guo, K.; Zhang, D. L.; Zhang, X. M.; Zhang, J.; Ding, L. S.; Li, B. J.; Zhang, S. Conductive elastomers with autonomic self-healing properties. *Angew. Chem. Int. Ed.* **2015**, *54*, 12127–12133.
 - 34 Han, J.; Wang, H.; Yue, Y.; Mei, C.; Chen, J.; Huang, C.; Wu, Q.; Xu, X. A self-healable and highly flexible supercapacitor integrated by dynamically cross-linked electro-conductive hydrogels based on nanocellulose-templated carbon nanotubes embedded in a viscoelastic polymer network. *Carbon* **2019**, *149*, 1–18.
 - 35 Hsu, H. H.; Liu, Y.; Wang, Y.; Li, B.; Luo, G.; Xing, M.; Zhong, W. Mussel-inspired autonomously self-healable all-in-one supercapacitor with biocompatible hydrogel. *ACS Sustain. Chem. Eng.* **2020**, *8*, 6935–6948.
 - 36 Liu, J.; Song, H.; Wang, Z.; Zhang, J.; Zhang, J.; Ba, X. Stretchable, self-healable, and reprocessable chemical cross-linked ionogels electrolytes based on gelatin for flexible supercapacitors. *J. Mater. Sci.* **2019**, *55*, 3991–4004.
 - 37 Liu, L.; Han, Y.; Lv, S. Design of self-healing and electrically conductive silk fibroin-based hydrogels. *ACS Appl. Mater. Interfaces* **2019**, *11*, 20394–20403.
 - 38 Ren, K.; Cheng, Y.; Huang, C.; Chen, R.; Wang, Z.; Wei, J. Self-healing conductive hydrogels based on alginate, gelatin and polypyrrole serve as a repairable circuit and a mechanical sensor. *J. Mater. Chem. B* **2019**, *7*, 5704–5712.
 - 39 Xin, Y.; Peng, H.; Xu, J.; Zhang, J. Ultrauniform embedded liquid metal in sulfur polymers for recyclable, conductive, and self-healable materials. *Adv. Funct. Mater.* **2019**, *29*, 1808989.
 - 40 Wang, D.; Xu, J.; Chen, J.; Hu, P.; Wang, Y.; Jiang, W.; Fu, J. Transparent, mechanically strong, extremely tough, self-recoverable, healable supramolecular elastomers facilely fabricated via dynamic hard domains design for multifunctional applications. *Adv. Funct. Mater.* **2019**, *30*, 1907109.
 - 41 Wang, D.; Wang, Z.; Ren, S.; Xu, J.; Wang, C.; Hu, P.; Fu, J. Molecular engineering of a colorless, extremely tough, superiorly self-recoverable, and healable poly(urethane-urea) elastomer for impact-resistant applications. *Mater. Horiz.* **2021**, *8*, 2238–2250.
 - 42 Ducrot, E.; Chen, Y.; Bulters, M.; Sijbesma, R. P.; Creton, C. Toughening elastomers with sacrificial bonds and watching them break. *Science* **2014**, *344*, 186–189.
 - 43 Benight, S. J.; Wang, C.; Tok, J. B. H.; Bao, Z. Stretchable and self-healing polymers and devices for electronic skin. *Prog. Polym. Sci.* **2013**, *38*, 1961–1977.
 - 44 Sanka, R. V. S. P.; Krishnakumar, B.; Leterrier, Y.; Pandey, S.; Rana, S.; Michaud, V. Soft self-healing nanocomposites. *Front. Mater.* **2019**, *6*, 137.
 - 45 Kumar, V.; Kessler, M. R. Self-healing polymer nanocomposite material: a review. *Polymer* **2015**, *69*, 369–383.
 - 46 Zhang, Z.; Gao, Z.; Wang, Y.; Guo, L.; Yin, C.; Zhang, X.; Hao, J.; Zhang, G.; Chen, L. Eco-friendly, self-healing hydrogels for adhesive and elastic strain sensors, circuit repairing, and flexible electronic devices. *Macromolecules* **2019**, *52*, 2531–2541.
 - 47 Hong, Y.; Kim, J. M.; Jung, H.; Park, K.; Hong, J.; Choi, S. H.; Kim, B. S. Facile synthesis of poly(ethylene oxide)-based self-healable dynamic triblock copolymer hydrogels. *Biomacromolecules* **2020**, *21*, 4913–4922.
 - 48 Wang, Y.; Xie, R.; Li, Q.; Dai, F.; Lan, G.; Shang, S.; Lu, F. A self-adapting hydrogel based on chitosan/oxidized konjac glucomannan/AgNPs for repairing irregular wounds. *Biomater. Sci.* **2020**, *8*, 1910–1922.
 - 49 Xu, J.; Chen, J.; Zhang, Y.; Liu, T.; Fu, J. A fast room-temperature self-healing glassy polyurethane. *Angew. Chem. Int. Ed.* **2021**, *60*, 7947–7955.
 - 50 Song, Y.; Liu, Y.; Qi, T.; Li, G. L. Towards dynamic but supertough healable polymers through biomimetic hierarchical hydrogen-bonding interactions. *Angew. Chem. Int. Ed.* **2018**, *57*, 13838–13842.
 - 51 Wang, D.; Ren, S.; Chen, J.; Li, Y.; Wang, Z.; Xu, J.; Jia, X.; Fu, J. Healable, highly thermal conductive, flexible polymer composite with excellent mechanical properties and multiple functionalities. *Chem. Eng. J.* **2021**, 133163.
 - 52 Guo, Q.; Zhang, X.; Zhao, F.; Song, Q.; Su, G.; Tan, Y.; Tao, Q.; Zhou, T.; Yu, Y.; Zhou, Z.; Lu, C. Protein-inspired self-healable Ti_3C_2 MXenes/rubber-based supramolecular elastomer for intelligent sensing. *ACS Nano* **2020**, *14*, 2788–2797.
 - 53 Fang, Y.; Xu, J.; Gao, F.; Du, X.; Du, Z.; Cheng, X.; Wang, H. Self-healable and recyclable polyurethane-polyaniline hydrogel toward flexible strain sensor. *Compos. Part B-Eng.* **2021**, *219*, 108965.
 - 54 Searle, T.; Sencadas, V.; Greaves, J.; Alici, G. Room-temperature self-healing piezoresistive sensors. *Compos. Sci. Technol.* **2021**, *211*, 108856.
 - 55 Han, J.; Ding, Q.; Mei, C.; Wu, Q.; Yue, Y.; Xu, X. An intrinsically self-healing and biocompatible electroconductive hydrogel based on nanostructured nanocellulose-polyaniline complexes embedded

- in a viscoelastic polymer network towards flexible conductors and electrodes. *Electrochim. Acta* **2019**, *318*, 660–672.
- 56 Wei, P.; Chen, T.; Chen, G.; Liu, H.; Mugaanire, I. T.; Hou, K.; Zhu, M. Conductive self-healing nanocomposite hydrogel skin sensors with antifreezing and thermoresponsive properties. *ACS Appl. Mater. Interfaces* **2020**, *12*, 3068–3079.
 - 57 Wang, Y.; Huang, H.; Wu, J.; Han, L.; Yang, Z.; Jiang, Z.; Wang, R.; Huang, Z.; Xu, M. Ultrafast self-healing, reusable, and conductive polysaccharide-based hydrogels for sensitive ionic sensors. *ACS Sustain. Chem. Eng.* **2020**, *8*, 18506–18518.
 - 58 Wang, L.; Gao, G.; Zhou, Y.; Xu, T.; Chen, J.; Wang, R.; Zhang, R.; Fu, J. Tough, adhesive, self-healable, and transparent ionically conductive zwitterionic nanocomposite hydrogels as skin strain sensors. *ACS Appl. Mater. Interfaces* **2019**, *11*, 3506–3515.
 - 59 Yin, J.; Pan, S.; Wu, L.; Tan, L.; Chen, D.; Huang, S.; Zhang, Y.; He, P. A self-adhesive wearable strain sensor based on a highly stretchable, tough, self-healing and ultra-sensitive ionic hydrogel. *J. Mater. Chem. C* **2020**, *8*, 17349–17364.
 - 60 Zhao, L.; Jiang, B.; Huang, Y. Self-healable polysiloxane/graphene nanocomposite and its application in pressure sensor. *J. Mater. Sci.* **2018**, *54*, 5472–5483.
 - 61 Zhou, Z.; Qian, C.; Yuan, W. Self-healing, anti-freezing, adhesive and remoldable hydrogel sensor with ion-liquid metal dual conductivity for biomimetic skin. *Compos. Sci. Technol.* **2021**, *203*, 108608.
 - 62 Yan, Q.; Zhou, M.; Fu, H. Study on mussel-inspired tough TA/PANI@CNCs nanocomposite hydrogels with superior self-healing and self-adhesive properties for strain sensors. *Compos. Part B-Eng.* **2020**, *201*, 108356.
 - 63 Jing, X.; Mi, H. Y.; Peng, X. F.; Turng, L. S. Biocompatible, self-healing, highly stretchable polyacrylic acid/reduced graphene oxide nanocomposite hydrogel sensors via mussel-inspired chemistry. *Carbon* **2018**, *136*, 63–72.
 - 64 Liang, Y.; Sun, X.; Lv, Q.; Shen, Y.; Liang, H. Fully physically cross-linked hydrogel as highly stretchable, tough, self-healing and sensitive strain sensors. *Polymer* **2020**, *210*, 123039.
 - 65 Wang, Y.; Zhang, H.; Zhang, H.; Chen, J.; Li, B.; Fu, S. Synergy coordination of cellulose-based dialdehyde and carboxyl with Fe³⁺ recoverable conductive self-healing hydrogel for sensor. *Mat. Sci. Eng. C-Mater.* **2021**, *125*, 112094.
 - 66 Qiao, H.; Qi, P.; Zhang, X.; Wang, L.; Tan, Y.; Luan, Z.; Xia, Y.; Li, Y.; Sui, K. Multiple weak H-bonds lead to highly sensitive, stretchable, self-adhesive, and self-healing ionic sensors. *ACS Appl. Mater. Interfaces* **2019**, *11*, 7755–7763.
 - 67 Gao, Z.; Li, Y.; Shang, X.; Hu, W.; Gao, G.; Duan, L. Bio-inspired adhesive and self-healing hydrogels as flexible strain sensors for monitoring human activities. *Mat. Sci. Eng. C-Mater.* **2020**, *106*, 110168.
 - 68 Jing, X.; Feng, P.; Chen, Z.; Xie, Z.; Li, H.; Peng, X. F.; Mi, H. Y.; Liu, Y. Highly stretchable, self-healable, freezing-tolerant, and transparent polyacrylic acid/nanochitin composite hydrogel for self-powered multifunctional sensors. *ACS Sustain. Chem. Eng.* **2021**, *9*, 9209–9220.