nature portfolio

Peer Review File

Non-hazardous and Fully Recyclable Ionic Thermoelectrics for Sustainable Human-Machine Interfaces

Corresponding Author: Professor Benjamin Tee

This file contains all reviewer reports in order by version, followed by all author rebuttals in order by version.

Version 0:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
In this study, an ionic TE hydrogel with high stretchability is fabricated and applied for environment-friendly human-machine interface applications. This is a hot topic and is meaningful for many applications. A hydrogel based on common PAA is fabricated with exceptional mechanical stretchability for human-machine interface. I think a revision is needed for the manuscript. Some comments as follows:
1. The hydrogel has MBAA as a chemical cross-linking agent, so what is the degradation mechanism and what are the degradation products? Why can the hydrogel be formed again when adding acrylic acid and heating it? If the degradation products are still in the hydrogel, should there be a difference in the composition of the hydrogel before and after recycling?
2. In Fig. 2g, how was the mass of the hydrogel measured during the recycling process? How many times can of recycle be realized?
3. Some of the elements in the schematic diagrams are not clear what they represent, e.g., Fig. 2a, Fig. 3b, 3g and 3h, etc.

Reviewer #2

(Remarks to the Author)
This work demonstrated a novel thermoelectric (TE) material enabled by combing a non-toxic salt with PAA polymer, achieving excellent TE performance along with advantages of healing, recyclability and optical transparency. In addition to the TE performance, the ReCLEAR hydrogel doubled as a triboelectric (TENG) material, offering the ability to sense temperature and pressure change simultaneously. The TE and TENG signals' distinction in transient time is easy to separate without complex filtering and decoupling, promising straightforward multimodal signal collection. The authors demonstrated the ReCLEAR in two scenarios: the virtual keyboard and the robot skin.
The ReCLEAR hydrogel's mechanical and electrical performances are characterized rigorously. The application demonstrations are successful and relatable. However, the following issues should be addressed before publication. My concerns and suggestions can be generally divided into the following categories from the highest priority to editorial ones:

A. As a TE material, the Figure of Merit (ZT) and the Seebeck Coefficient are the most important characteristics as they determine how sensitive the material reacts to the temperature change. ReCLEAR has decent Seebeck coefficient (-1.05 mV/K), but the characterization data shows slow response limitations:
1. P10, line 248-249: The temporal change is ~1000 seconds in Fig 3d, if for wearable applications, this translates to less than microvolt per second, or a mV per minute, which is a very small signal change to detect for wearable use with environmental drift. How would this material react in short period of time and small temperature range? Also, what is the applied temperature change in Fig 3, it was not indicated in the caption.
2. Please comment on the possibility to increase response time. Is it a device geometry limitation or materials limitation?

B. The ReCLEAR hydrogel's many advantages are demonstrated, especially the non-toxic and fast recycling process. However, please add more comparison on the self-healing prospects like in Fig S6, S7. For hydrogel, there would be easily contaminants embedded in the materials, and so at what concentration of contaminants may the self-healing be affected?

C. Some figures failed to deliver the message effectively, and some figures have missing information. Also please check grammar throughout the manuscript.

1. Fig. 1a: it's very hard to see the difference between PAA and the trifate anion, either zoom in or make each molecule bigger/simpler. And what is the difference between high temp/low temp zone? Maybe make the contrast of ion concentration more dramatic. Some references for figure examples (All the refs below are not requests to cite and are unrelated to the reviewers, but just examples of how their figures are nicely done.):
a. Nat Commun 13, 221 (2022). Fig. 1a
b. Nat Commun 14, 3246 (2023). Fig. 1a
2. Fig. 1c: this looks like a recreation of reference [39] Sci. Adv. 7, eabe0586 (2021). But whether this is a fair visualization is doubtful: 4 out of 6 axes are yes/partial/no, which makes the figure look out of portion. I suggest using a table for a more straightforward and fair comparison.
3. Fig. 2b: missing the scale bar size.
4. Fig. 3c: there is no difference between the left and the right as the finger approaches. I understand the TENG is shown in 3g later but what's the point of this figure then. Edit refer to Nat Commun 13, 1391 (2022). Fig. 1a-c.
5. Many figures need temperature or input intensity information. Like Fig 3d, 3g, 4,5, the input intensity (temp change) should be put in the caption.
6. Fig. 4c: for the arb. unit response, how is it calculated from the voltage? This is the most important electrical signal, please explain how it is calculated and what signal processing and if any amplifying was used.
7. From Fig. 5b, the hot object is 65 degrees (Celsius? Not specified). Is 60s the onset of the withdraw process, and exactly how far is the distance from the hand approaches the object?
8. P2, line 55, 'inherent toxicity of PEDOT:PSS': add references please. This is counter to many bioelectronics work, where PEDOT:PSS has been implanted in vivo and shown to be bio-compatible.

In general, we think this work presents a promising novel material with great potential in TE and TENG application. But these concerns should be addressed before the manuscript can be accepted for publication.

Reviewer #3

(Remarks to the Author)
I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The questions are well answered and the munuscript can be accepted.

Reviewer #2

(Remarks to the Author)
The revisions have satisfactorily addressed the reviewers' comments.

Reviewer #3

(Remarks to the Author)
I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts.

Re: Nature Communications manuscript #NCOMMS-25-04383A

To the reviewers,

We thank all the reviewers for their insightful and constructive comments on our manuscript. Below, please kindly finds a point-by-point response to the comments. As detailed below, we have carefully revised the main text to address the concerns raised, which are highlighted in blue in the revised manuscript. We believe that the manuscript is much improved as a result.

Reviewer #1:

"In this study, an ionic TE hydrogel with high stretchability is fabricated and applied for environment-friendly human-machine interface applications. This is a hot topic and is meaningful for many applications. A hydrogel based on common PAA is fabricated with exceptional mechanical stretchability for human-machine interface. I think a revision is needed for the manuscript."

Reply: We thank the reviewer for affirming the significance of our work. We appreciate your valuable feedback and have thoroughly revised the manuscript accordingly to enhance its clarity and address the points raised.

1. *The hydrogel has MBAA as a chemical cross-linking agent, so what is the degradation mechanism and what are the degradation products? Why can the hydrogel be formed again when adding acrylic acid and heating it? If the degradation products are still in the hydrogel, should there be a difference in the composition of the hydrogel before and after recycling?*

Reply: We thank the reviewer for the valuable comments on the degradation and recycling about our hydrogel. The **degradation mechanism** of our poly(acrylic acid)

(PAA) based hydrogel through 3 wt% hydrogen peroxide (H_2O_2) is a **free-radical-induced chain scission mechanism**. H_2O_2 generates hydroxyl radicals (·OH), which attack the carbon–carbon backbone of PAA, cleaving it into low-molecular-weight oligomers. The crosslinked network formed by N,N'-methylenebisacrylamide (MBAA) is also disrupted through oxidative cleavage, resulting in the breakdown of the hydrogel matrix into water-soluble products. The main degradation products are **low-molecular-weight PAA oligomers with terminal carboxyl and hydroxyl groups**. This is supported by gel permeation chromatography (GPC) analysis (Table R1 | Table Note 1.1), where the number-average molecular weight decreased from ~19000 g/mol in the pristine hydrogel to ~1407 g/mol after degradation.

The hydrogel can be recycled by adding additional acrylic acid (AA) monomers, water, crosslinker, and initiator, followed by heating to trigger free-radical polymerization. Although the most original carbon double bonds (C=C) are destroyed during degradation, **the newly added AA monomers provide reactive sites for network reconstruction.** Residual oligomers act as fillers, while the regenerated polymer network retains similar chemical functionality to the original. As all degradation products remain in the recycled hydrogel, **its composition slightly differs from that of the pristine one.** However, key functional groups (e.g., carboxyl groups) and the polymer backbone are preserved, resulting in comparable chemical properties of pristine, and recycled hydrogels, supported by fourier-transform infrared (FTIR) analysis (Figure R1 | Figure Note 2.1).

We have included additional notes (Note R1-2 | Supplementary Note 1-2) to further clarify the degradation and recycling mechanisms. In addition, several clips have been added to Movie S1 to visually illustrate the recycling process more clearly.

Note R1 | Supplementary Note 1. Degradation mechanisms of the ReCLEAR hydrogel.

The degradation mechanism of the PAA-based hydrogel using 3 wt% hydrogen peroxide (H_2O_2) is a free-radical-induced chain scission mechanism. H_2O_2 generates hydroxyl radicals (·OH), which attack the carbon–carbon backbone of PAA, cleaving

it into low-molecular-weight oligomers. The crosslinked network formed by N,N'-methylenebisacrylamide (MBAA) is also disrupted through oxidative cleavage, resulting in the breakdown of the hydrogel matrix into water-soluble products. The main degradation products are low-molecular-weight PAA oligomers with terminal carboxyl and hydroxyl groups. This is supported by gel permeation chromatography (GPC) analysis (Table R1 | Table Note 1.1), where the number-average molecular weight decreased from ~19000 g/mol in the pristine hydrogel to ~1407 g/mol after degradation.

Sample name	Retention time (min)	Mn (g/mol)	Mw (g/mol)	Mp (g/mol)	Polydispersity
Pristine-1	14.940	19867	24975	20716	1.257108
Pristine-2	14.983	19400	23550	19922	1.213951
Degraded	17.630	1407	1418	1342	1.008286

Table R1 | Table Note 1.1 Molecular weight analysis of pristine and degraded hydrogels measured by GPC. Mn: number-average molecular weight. Mw: weight-average molecular weight. Mp: peak molecular weight.

Note R2 | Supplementary Note 2: Recycling mechanisms and performance of the ReCLEAR hydrogel.

The hydrogel can be recycled by adding additional acrylic acid (AA) monomers, water, crosslinker, and initiator, followed by heating to trigger free-radical polymerization. Although the most original carbon double bonds (C=C) are destroyed during degradation, the newly introduced AA monomers provide reactive sites for network reconstruction. Residual oligomers act as fillers, while the regenerated polymer network retains similar chemical functionality to the original. As all degradation products remain in the recycled hydrogel, its composition slightly differs from that of the pristine one. However, key functional groups (e.g., carboxyl groups) and the polymer backbone are preserved, resulting in comparable chemical properties of pristine, and recycled hydrogels, supported by fourier-transform infrared (FTIR)

analysis (Figure R1 | Figure Note 2.1).

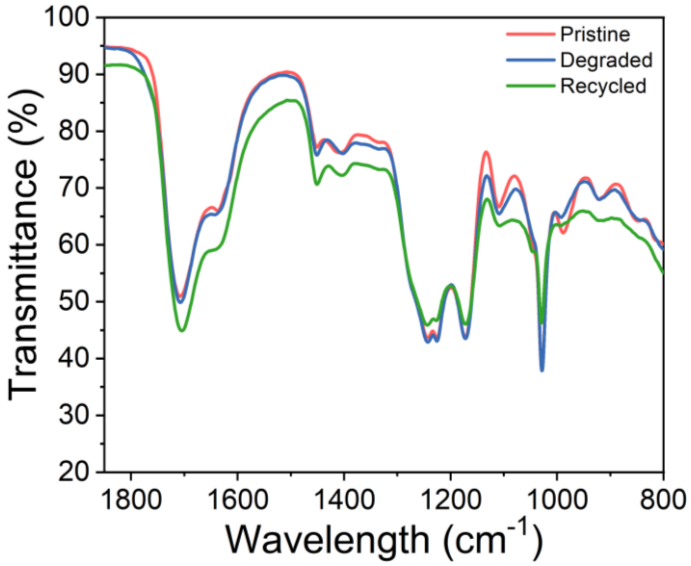

Figure R1 | Figure Note 2.1 FTIR spectra between pristine, degraded and recycled ReCLEAR hydrogel.

All samples show characteristic C=O stretching (~1700 cm^{-1}) and sulfonate (1050–1250 cm^{-1}, ~1030 cm^{-1}) peaks from carboxyl and triflate groups (COO^- and SO_3^-), respectively. The degraded sample shows a small increase in C=C stretching (~1630 cm^{-1}), indicating partial depolymerization and vinyl group regeneration. In the recycled hydrogel, the C=C signal remains, suggesting incomplete re-polymerization. Zn^{2+} coordination contributes to shifts and broadenings in COO^-/C=O regions, while triflate signatures overlap with C–O signal of PAA. These spectral changes validate the chemical transitions during degradation and recycling.

We also revised the Results and the Methods sections accordingly.

Page 5: "The hydrogel achieves 100% degradation within 2-3 days through combined oxidative (3 wt% H_2O_2) and thermal (50-70 °C) conditions via free-radical-induced chain scission. H_2O_2 generates hydroxyl radicals (·OH), which attack the carbon–carbon backbone of hydrogel, cleaving it into water-soluble low-molecular-weight oligomers (Supplementary Note 1). During degradation, the samples become transparent, since the dye undergoes oxidative decolorization. The

degraded solution is thermally concentrated to its initial mass, followed by the reintroduction of acrylic acid monomers, crosslinker, and initiator. Thermal free-radical polymerization subsequently regenerates the hydrogel. The recycling mechanisms and performance are detailed in Supplementary Note 2."

Page 18: "The molecular weight of ReCLEAR hydrogels was characterized using gel permeation chromatography (Agilent, PL-GPC 220)."

2. *In Fig. 2g, how was the mass of the hydrogel measured during the recycling process? How many times can of recycle be realized?*

Reply: We thank the reviewer for raising this important point regarding the recycling process. The mass of the hydrogel during recycling (Fig. 2g) was measured by **carefully transferring the remaining free-standing gel residue to a pre-weighted container**, followed by weighing to determine the residual mass at each stage.

To date, we have tested five recycling cycles, during which the hydrogels exhibited similar molecular weights (Table R2 | Table Note 2.2) and maintained consistent thermoelectric (TE) performance, as shown in Figure Note 2.4 (Figure R3). The slight decrease in TE output is attributed to minor materials loss during the transfer process. Our hydrogel has the promising potential for **recyclability beyond five cycles**. However, after 5 cycles, the hydrogel becomes softer and generates more bubbles, which may begin to affect its subsequent performance.

We have expanded Supplementary Note 2 (Note R2) to provide detailed recycling performance.

The pristine hydrogel weighs approximately 10 g. A minimum of 1 g AA added to the degraded solution can regenerate a hydrogel film, though with low mechanical strength. When more than 1.5 g AA is added, the recycled hydrogel forms a free-standing film with sufficient mechanical integrity for human-machine-interface (HMI) applications. In this study, 2 g AA was added in each recycling cycle to achieve

mechanical strength comparable to the pristine hydrogel. We have successfully tested five recycling cycles. All recycled hydrogels exhibit similar molecular weights (Table Note 2.2), indicate good stability in the recycling process. While the ReCLEAR hydrogel shows potential for recyclability beyond five cycles, the hydrogel becomes softer and generates more bubbles after 5 cycles, the hydrogel, which may begin to affect its subsequent performance.

Sample name	Retention time (min)	Mn (g/mol)	Mw (g/mol)	Mp (g/mol)	Polydispersity
1 st recycled	16.781	2844	3063	3205	1.077083
2nd recycled	16.770	2730	3008	3243	1.101757
3rd recycled	16.769	2993	3177	3248	1.061174
4th recycled	16.691	2611	3005	3526	1.150859
5th recycled	16.659	2984	3267	3645	1.094858

Table R2 | Table Note 2.2 Molecular weight analysis of the ReCLEAR hydrogel with different recycling cycles, measured by GPC.

FTIR spectra of the ReCLEAR hydrogel across five recycling cycles reveal progressive changes in functional group environments (Figure Note 2.3). The 1st recycled film shows higher transmittance at ~1630 cm^{-1} (residual C=C in vinyl groups) and shifted carboxylate/triflate bands (1050-1250 cm^{-1}), indicating partial recovery of the polymer network. From the 2nd to 3rd cycles, spectra stabilize, suggesting reproducible recycling with similar Zn^{2+} coordination. The 4th and 5th cycles exhibit minor spectral shifts in COO^- and SO_3^- regions, reflecting subtle structural reorganizations. Overall, the system achieves chemically stable reusability after the 2nd cycle.

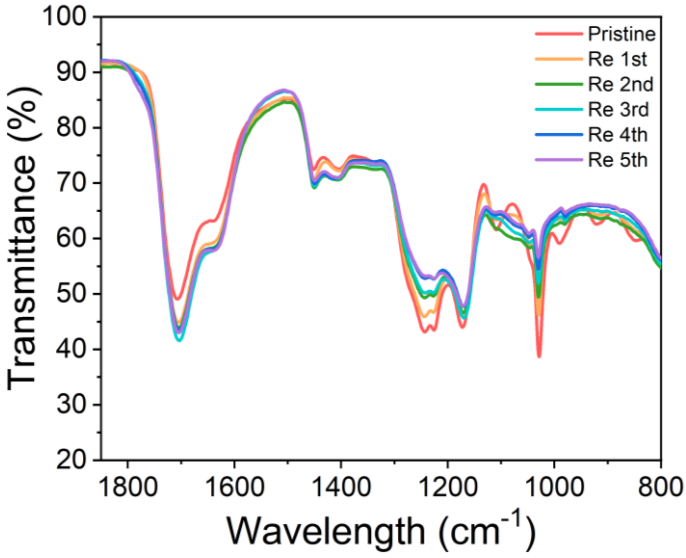

Figure R2 |Figure Note 2.3 FTIR spectra between pristine and recycled ReCLEAR hydrogels over five recycling cycles. Re: recycled.

The hydrogel maintained consistent TE performance over multiple recycling cycles (Figure Note 2.4). The slight increase observed in the second recycled sample is likely due to more stable coordination between Zn^{2+} ions and carboxyl groups. In contrast, the gradual decrease in TE output with additional recycling cycles is attributed to minor material loss during the transfer process.

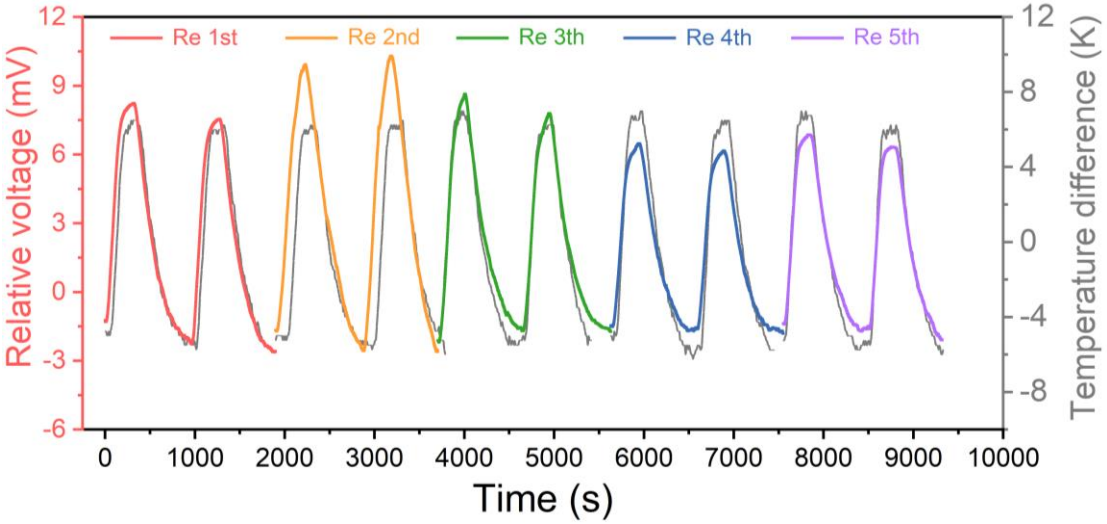

Figure R3 |Figure Note 2.4 Relative thermal voltages of recycled ReCLEAR hydrogels over five recycling cycles. Re: recycled.

We have revised the Results and the Methods sections accordingly.

Page 9: "The hydrogel mass change during a single recycling cycle is shown in Fig. 2g. The ReCLEAR hydrogel demonstrates consistent TE performance over five recycling cycles, with only minor performance loss attributed to slight material loss during transfer (Figure Note 2.4). However, after five cycles, the hydrogel becomes softer and forms more bubbles, which may begin to affect its mechanical stability and TE output in extended recycling."

Page 19: "The hydrogel mass during recycling was measured by weighting the residual free-standing gel transferred to a pre-weighted container."

Page 19: "After complete degradation, the solvent was evaporated at 50 °C to ~ 20 g, transferred to a smaller petri dish, and baked at 70-90 °C into a dry film corresponding to 60%-70% of the initial hydrogel weight. The film was rehydrated with 6 g water and heated at 70 °C for 30 min to yield ~ 15g of low-viscosity solution. Subsequently, 1-2 g AA monomer and 2-3 g water were added and mixed by magnetic stirring, with the AA and water amounts used to tune the mechanical strength of the recycled hydrogel. For hydrogel without $Zn(OTf)_2$, 30 mg APS and 2 mg MBAA were added, while for hydrogel with $Zn(OTf)_2$, 200 mg APS and 10 mg MBAA were added to the mixture for repolymerization at 70 °C for 60 min. The higher APS content compensates for the coordination effect of zinc cations."

3. *Some of the elements in the schematic diagrams are not clear what they represent, e.g., Fig. 2a, Fig. 3b, 3g and 3h, etc.*

Reply: We appreciate the reviewer's feedback on the clarity of the schematic diagrams. In response, we have revised Figures 2a (Figure R4), 3b, 3g, and 3h (Figure R5) to ensure that all elements are clearly labeled and represented.

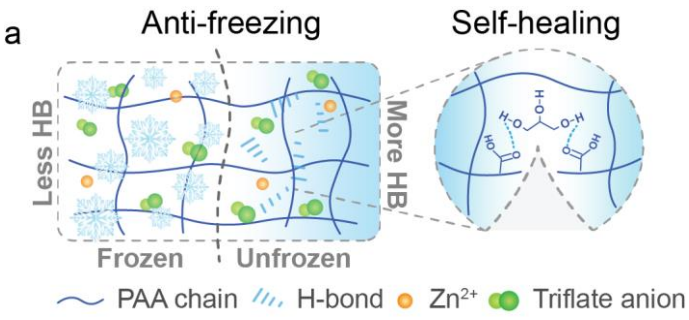

Figure R4 | Fig. 2a Mechanism underlying anti-freezing and self-healing behavior. H-bond/HB: hydrogen bond.

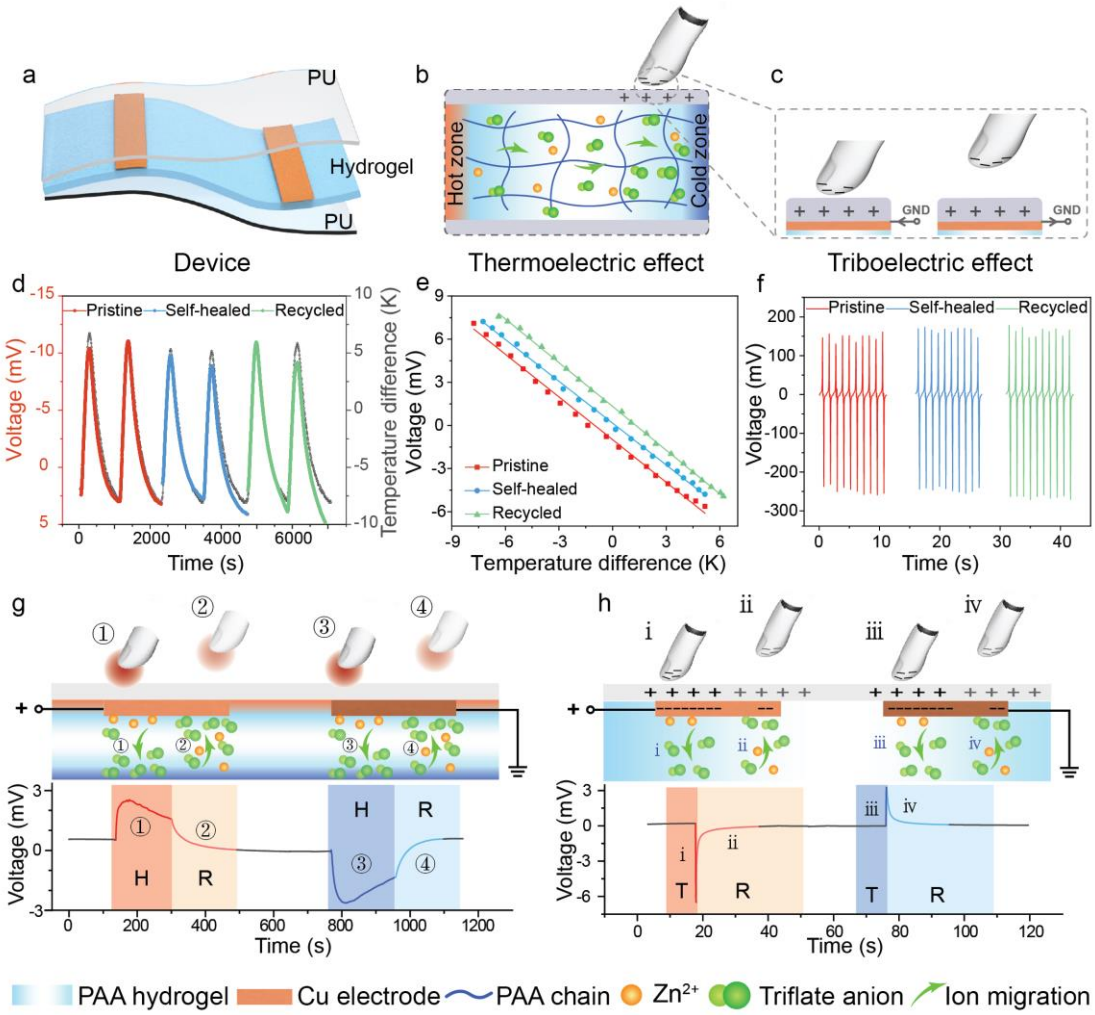

Figure R5 | Fig. 3 Dual-mode electrical performance of ReCLEAR Devices.

Reviewer #2:

"This work demonstrated a novel thermoelectric (TE) material enabled by combing a non-toxic salt with PAA polymer, achieving excellent TE performance along with advantages of healing, recyclability and optical transparency. In addition to the TE

performance, the ReCLEAR hydrogel doubled as a triboelectric (TENG) material, offering the ability to sense temperature and pressure change simultaneously. The TE and TENG signals' distinction in transient time is easy to separate without complex filtering and decoupling, promising straightforward multimodal signal collection. The authors demonstrated the ReCLEAR in two scenarios: the virtual keyboard and the robot skin.

The ReCLEAR hydrogel's mechanical and electrical performances are characterized rigorously. The application demonstrations are successful and relatable. However, the following issues should be addressed before publication. My concerns and suggestions can be generally divided into the following categories from the highest priority to editorial ones:"

Reply: We sincerely thank the reviewer for the positive and detailed evaluation of our work, particularly highlighting the novelty and multifunctionality of the ReCLEAR hydrogel. We appreciate your constructive suggestions and have carefully revised the manuscript to address all listed points.

A. As a TE material, the Figure of Merit (ZT) and the Seebeck Coefficient are the most important characteristics as they determine how sensitive the material reacts to the temperature change. ReCLEAR has decent Seebeck coefficient (-1.05 mV/K), but the characterization data shows slow response limitations:

1. P10, line 248-249: The temporal change is ~1000 seconds in Fig 3d, if for wearable applications, this translates to less than microvolt per second, or a mV per minute, which is a very small signal change to detect for wearable use with environmental drift. How would this material react in short period of time and small temperature range? Also, what is the applied temperature change in Fig 3, it was not indicated in the caption.

Reply: We thank the reviewer for the insightful comment. The temporal change observed in Figure 3d (~1000 seconds) reflects the **testing setup** rather than the

intrinsic response time of the hydrogel. Specifically, the slow temperature ramp is due to the limitations of the Peltier station used in our setup, which was programmed to cycle **from 10 °C to 60 °C over around 5 mins and then return to 10 °C over about 11 mins. Each full cycle thus takes around 960 s**. We chose the Peltier system because it offers a wide and stable temperature range with precise control, which is critical for characterizing thermoelectric performance under well-defined conditions.

To evaluate real-time responsiveness, we conducted additional tests using heat sources with different heating rates. As shown in **Figure R6 | Supplementary Fig. 17**, the hydrogel exhibits a **fast and sensitive TE response** to temperature fluctuations, including under rapid thermal input, confirming its suitability for dynamic and wearable applications. Additionally, our hydrogel responses distinctly even to a 1 K temperature difference, highlighting its potential as a fast and reliable wearable TE material (Figure R7 | Supplementary Fig. 18).

Also, the input distributions of finger temperature and force during short and long press are added in Figure R8 | Supplementary Fig. 27. The caption for Fig. 3 has been revised to specify the detailed temperature variations used in the tests.

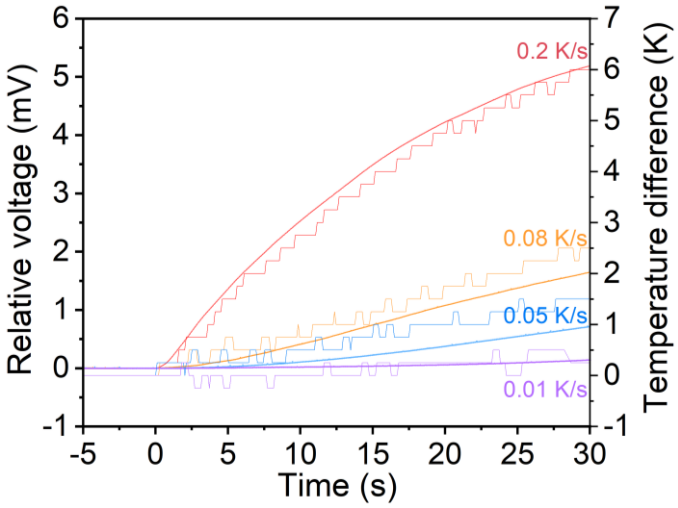

Figure R6 | Supplementary Fig. 17 Rapid TE responses of the ReCLEAR hydrogel under different heating rates. Step-like curves represent the temperature signal, recorded with a resolution of 0.25 K.

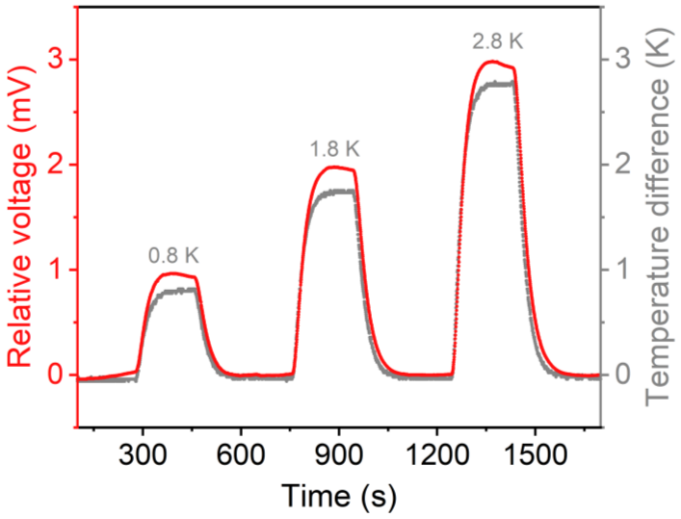

Figure R7 | Supplementary Fig. 18 Sensitive TE responses of the ReCLEAR hydrogel to minor temperature fluctuations.

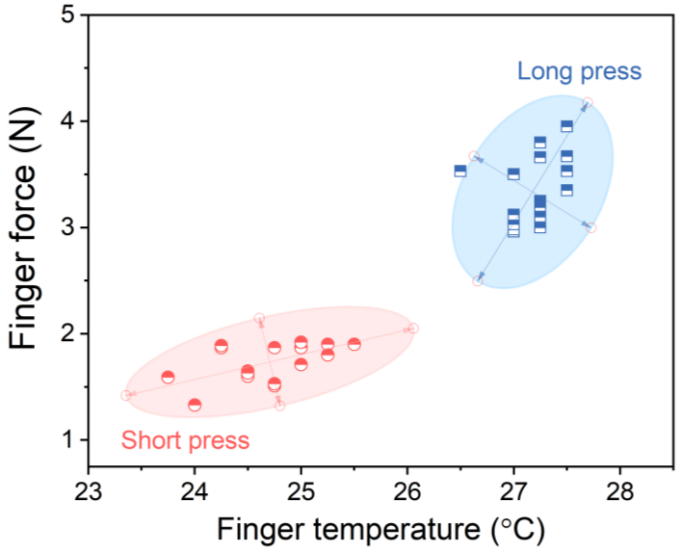

Figure R8 | Supplementary Fig. 27 Input distributions of finger temperature and force during short and long press by hand. The elliptical confidence region represents the 95% 2D confidence ellipse.

We have added new paragraphs to the Results section and revised the caption for Fig. 3 accordingly.

Page 10: "Fig. 3d shows the real-time TE response of pristine, self-healed, and recycled ReCLEAR hydrogels under cyclic temperature changes between 10 °C and 60 °C, producing a temperature difference of approximately –8 °C to +5 °C across the electrodes using a Peltier station. To evaluate response speed, TE

measurements were performed under thermal inputs at varying ramp rates (Supplementary Fig. 17), where the hydrogel exhibited fast and sensitive responses. Additionally, clear and measurable TE outputs were also obtained under minor temperature gradients of 1–3 K (Supplementary Fig. 18), confirming the high thermal sensitivity and suitability of the hydrogel for dynamic and wearable applications."

Page 13: "The input distributions of finger temperature and force during short and long press are shown in Supplementary Fig. 27."

Page 34: "**Fig. 3 Dual-mode electrical performance of ReCLEAR Devices. a,** Schematic of the device structure. **b,** Thermoelectric (TE) sensing mechanism. **c,** Triboelectric (TENG) sensing mechanism. **d,** Real-time TE voltage outputs of pristine, self-healed, and recycled ReCLEAR hydrogels during temperature cycling (10- 60 °C) using Peltier heating, creating –8 °C to +5 °C temperature difference across electrodes. **e,** Extracted thermal voltages from the curves in (d). **f,** TENG responses of pristine, self-healed, and recycled ReCLEAR hydrogels under 10 N applied force. **g,** TE-dominated long-press sensing mechanism (H: hold, R: release). **h,** TENG-dominated short-press sensing mechanism (T: tap, R: release). Input intensity: long press: 3–5 N at 27–28 °C; short press: 1–2 N at 24–25 °C."

2. Please comment on the possibility to increase response time. Is it a device geometry limitation or materials limitation?

Reply: We thank the reviewer for raising this important point regarding the response time. As noted in our response to Comment A.1, the ReCLEAR hydrogel itself exhibits a fast response time. However, to further improve the overall device response time, modifications in **device geometry** can be considered. For instance, **reducing the hydrogel thickness** would shorten the heat diffusion path, thereby enabling faster

thermal response. **Our current hydrogel thickness is ~1 mm**, selected to ensure free-standing integrity and sufficient mechanical strength for HMI applications. Thinner hydrogels could be designed for applications where higher response speed is prioritized over mechanical robustness.

Additionally, decreasing **the electrode distance** can also enhance response time by reducing both thermal diffusion distance and ionic migration time. In our current design, **we used a 1 cm electrode gap** to minimize contact errors and allow stable acquisition of multimodal signals. For applications requiring faster response, this distance can be reduced accordingly.

We have added additional discussion in the Results section.

Page 11: "To further enhance the response speed, reducing the hydrogel thickness and minimizing the electrode spacing can help by shortening the thermal diffusion path and ionic migration distance."

B. The ReCLEAR hydrogel's many advantages are demonstrated, especially the non-toxic and fast recycling process. However, please add more comparison on the self-healing prospects like in Fig S6, S7. For hydrogel, there would be easily contaminants embedded in the materials, and so at what concentration of contaminants may the self-healing be affected?

Reply: We thank the reviewer for this valuable comment. In response, we have added further comparison data on self-healing performance, including 3D surface maps and height profiles of the hydrogel at different self-healing stages within 24 h (Figure R9 | Supplementary Figs. S7).

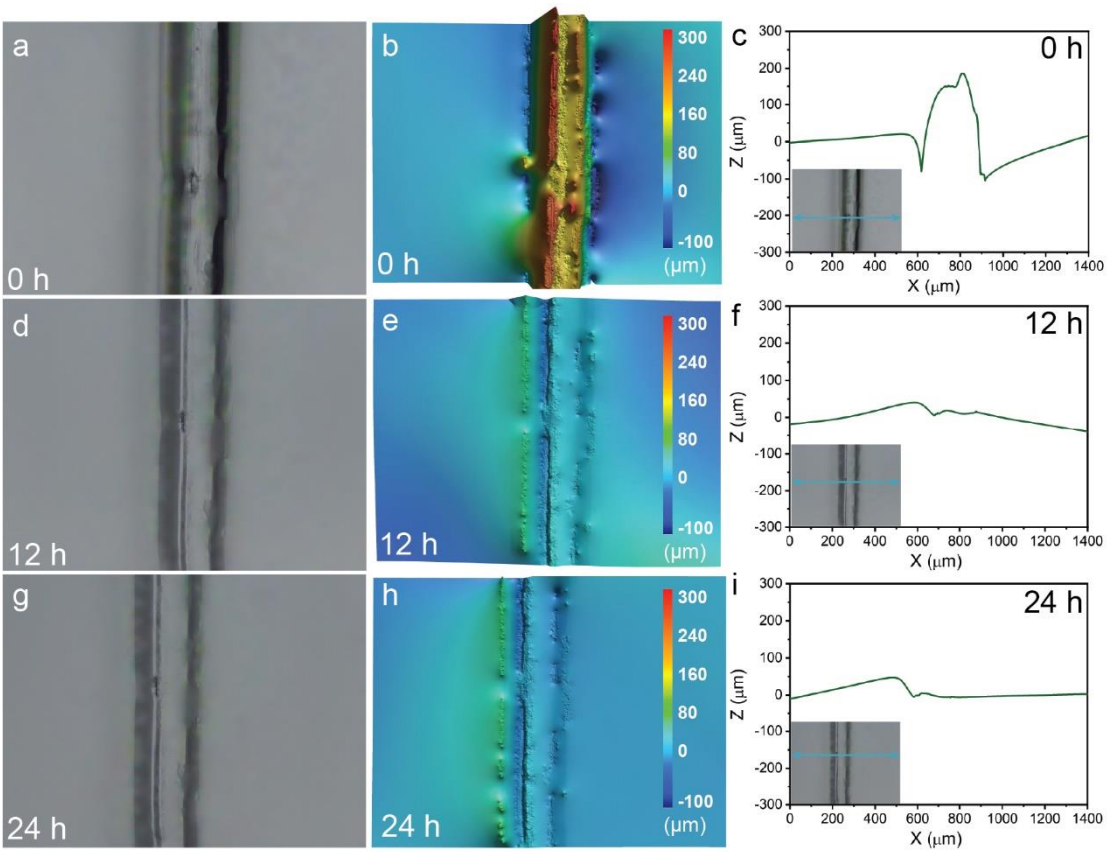

Figure R9 | Supplementary Fig. 7 3D surface maps and corresponding height profiles of the hydrogel at different self-healing stages within 24 h.

Regarding the impact of contamination on self-healing (SH) performance, it is true that embedded contaminants can reduce the effective contact area between fractured surfaces, thereby impeding the healing process. However, in practice, the concentration and types of contaminants are difficult to control or quantify precisely and are rarely discussed directly in literature.

To indirectly assess the influence of contamination, we conducted repeated self-healing experiments. Each hydrogel sample was cut at the same interface and allowed to heal for one day, with the process repeated from one to five times on separate samples. Stress – strain measurements after each healing cycle (Figure R10 | Supplementary Fig. S8) showed that SH performance remained stable for the first two cycles, but decreased by approximately 20%, 30%, and 50% in the third, fourth, and fifth cycles, respectively. As each cut-heal cycle likely introduces additional surface contaminants, these results suggest that self-healing efficiency decreases progressively with increased

contamination.

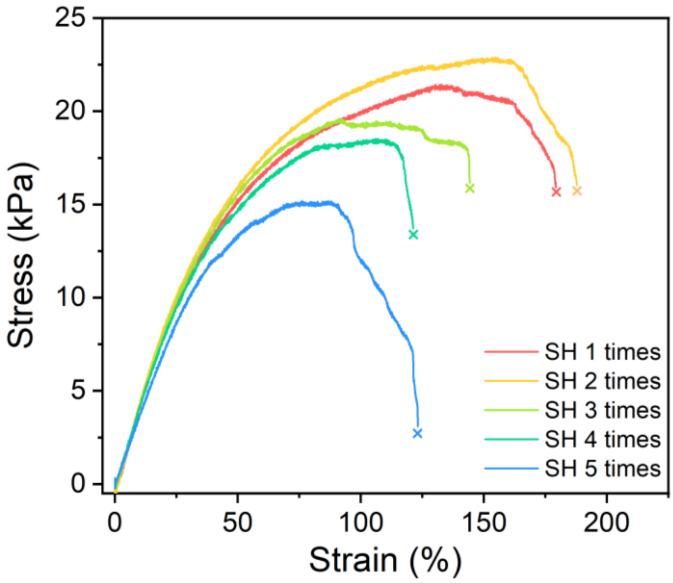

Figure R10 | Supplementary Fig. 8 Self-healing performance of the ReCLEAR hydrogel after 1-5 self-healing cycles, each a 24 h healing period. SH: self-healed.

We have added a new paragraph to the Results section.

Page 7: "3D surface maps and height profiles of the hydrogel at different self-healing stages within 24 h are shown in Supplementary Fig. S7, demonstrating rapid self-healing. To evaluate the durability of self-healing capability, repeated self-healing experiments were conducted (Supplementary Fig. S8). The performance remained stable during the first two cycles but decreased by approximately 20%, 30%, and 50% in the third, fourth, and fifth cycles, respectively. This decline is likely due to cumulative surface contamination, minor material loss, and incomplete chain diffusion during repeated healing. Overall, the hydrogel maintains efficient self-healing in the initial cycles but shows reduced efficiency with multiple repetitions."

C. Some figures failed to deliver the message effectively, and some figures have missing information. Also please check grammar throughout the manuscript.

1. Fig. 1a: it's very hard to see the difference between PAA and the trifate anion, either

zoom in or make each molecule bigger/simpler. And what is the difference between high temp/low temp zone? Maybe make the contrast of ion concentration more dramatic. Some references for figure examples (All the refs below are not requests to cite and are unrelated to the reviewers, but just examples of how their figures are nicely done.):

a. Nat Commun 13, 221 (2022). Fig. 1a

b. Nat Commun 14, 3246 (2023). Fig. 1a

Reply: We thank the reviewer for the valuable suggestions regarding Figure 1a. We have revised the figure accordingly by enlarging and simplifying the molecular structures to clearly distinguish PAA and the triflate anion. The high-temperature zone is the area near the heat source, while the low-temperature zone is cooler, creating the temperature gradient that drives the TE effect. In addition, we enhanced ion concentrations for better visual contrast. We believe the updated figure improves clarity and readability.

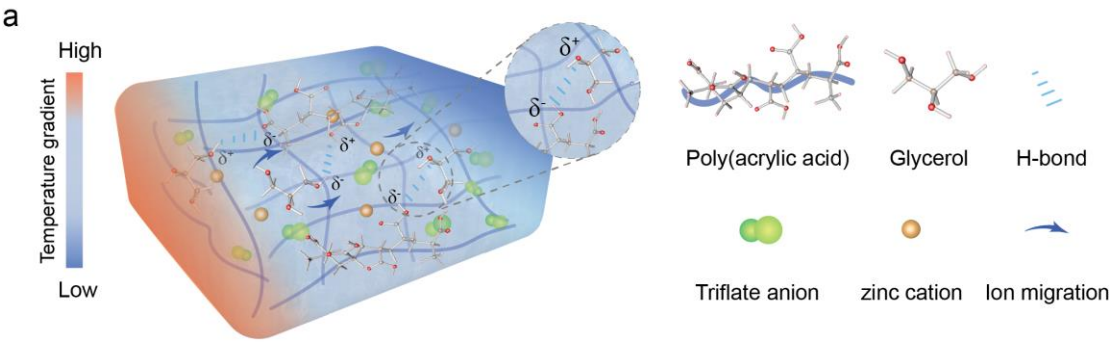

Figure R11 | Fig. 1a Molecular structure of the hydrogel with thermoelectric functionality. H-bond: hydrogen bond.

2. Fig. 1c: this looks like a recreation of reference [39] Sci. Adv. 7, eabe0586 (2021). But whether this is a fair visualization is doubtful: 4 out of 6 axes are yes/partial/no, which makes the figure look out of portion. I suggest using a table for a more straightforward and fair comparison.

Reply: We thank the reviewer for this observation. A table corresponding to Fig. 1c is provided in Supplementary Table 5 (Now move forward to Supplementary Table 1),

which we inadvertently omitted to reference in the manuscript. Among the six comparison criteria, three (non-hazard, recyclability, and self-healing) are qualitative and therefore presented as yes/partial/no, while the other three can be quantified. However, only one reference material reports transparency, and this was not experimentally measured, preventing quantitative comparison. We will revise the manuscript to reference Supplementary Table 1 (Table R3) in the main text and clarify the basis of comparison.

Table R3 | Supplementary Table 1. A detailed comparison between this work and current representative thermoelectric materials for Fig. 1c in the main text.

Materials	Recyclability	Trans-parency	Eco-friendliness	Self-healing	Stretch-ability	*S* (mV/K)	Ref.
PAA/Zn(OTf)$_2$	**Full**	**Full**	**Excellent**	**Yes**	**1500%**	**-1.05**	**This work**
PI/ Bi-Te-Se/ Bi-Sb-Te/	Only PI	No	Toxic	Only PI	120%	-0.145, 0.169	39
BAA/ $Bi_{0.5}Sb_{1.5}Te_3$/ $Bi_2Te_{2.7}Se_{0.3}$	Only BAA	No	Toxic	Only BAA	N.A.	~0.23	40
PI/Bi_2Te_3/Sb_2Te_3	Only PI	No	Toxic	Only PI	50%	-0.186, 0.194	41
PEDOT: PAAMPSA:PA	No	No	Hazardous	Yes	1050%	21.9	22
PVDF-HFP/ BMIM:BF_4/ AgOTf	No	Full	Hazardous	No	N.A.	-26.4	28
Gelatin-KCl-$Fe(CN)_6^{4-/3-}$	No	No	Hazardous	No	200%	17	25
PVDF-HFP/NaTFSI/PC	No	Partially	Hazardous	No	N.A.	20	54

We have revised the Results sections accordingly.

Page 6: "Comparative analysis of current TE materials (Fig. 1c, Supplementary Table 1) highlights the distinct advantages of ReCLEAR, including full recyclability, environmental compatibility, optical transparency, self-healing capability, and stretchability."

3. Fig. 2b: missing the scale bar size.

Reply: We thank the reviewer for pointing this out. The scale bar in Fig. 2b represents 1 cm.

We have updated the figure caption accordingly.

Page 33: "b, Demonstration of anti-freezing performance at -20 ℃ (left) and self-healing properties at room temperature (right). Scale bar: 1 cm."

4. Fig. 3c: there is no difference between the left and the right as the finger approaches. I understand the TENG is shown in 3g later but what's the point of this figure then. Edit refer to Nat Commun 13, 1391 (2022). Fig. 1a-c.

Reply: We thank the reviewer for the insightful comment. We have revised Fig. 3c to better illustrate the TENG functional difference during finger approaches.

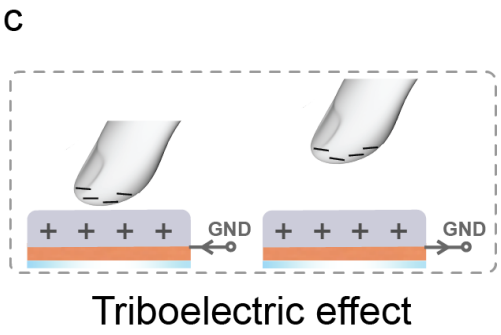

Figure R12 | Fig. 3c Triboelectric (TENG) sensing mechanism.

5. Many figures need temperature or input intensity information. Like Fig 3d, 3g, 4,5, the input intensity (temp change) should be put in the caption.

Reply: We thank the reviewer for this valuable comment. The input intensity for Fig. 3 is provided in our response to Comment A.1. The input intensity information for Figs. 4 and 5 has been added to the figure captions accordingly.

We have updated the figure caption accordingly.

Page 35: "**c,** Time-resolved relative response curves and corresponding triggered outputs across four signal configurations. Finger input intensity: long press, 3–5 N at

27–28 °C; short press, 1–2 N at 24–25 °C."

Page 36: "**b-d,** Real-time thermovoltage curves of pristine, self-healed, and recycled ReCLEAR devices during proximity detection with thermal stimuli: (b) 60 °C, (c) 25 °C, and (d) 10 °C. Critical proximity sensing regions are highlighted by red dashed boundaries."

6. Fig. 4c: for the arb. unit response, how is it calculated from the voltage? This is the most important electrical signal, please explain how it is calculated and what signal processing and if any amplifying was used.

Reply: We thank the reviewer for this constructive comment. Our hydrogel devices are fundamentally high-impedance charge sources, meaning the measured output voltage depends not only on the device but also on the input impedance of the measurement system. To illustrate this, we modeled the device as a voltage source with a series resistor and capacitor (Figure R13).

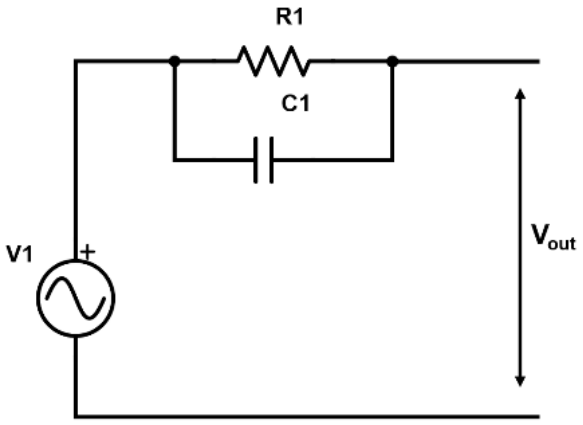

Figure R13. Equivalent voltage model of the ReCLEAR devices

In our experiments, signals were acquired using an Arduino with an ADS1220 ADC (Texas Instruments), which provides an input impedance of ~10 MΩ and **a programmable gain amplifier (PGA) set to 16×. The sensor voltage was calculated with the standard ADC transfer function**:

$$Vdevice = \frac{ADC\ Code}{2^{23} - 1} * (\frac{V_{REF}}{PGA\_Gain})$$

Using a reference voltage of 2.048 V and PGA gain of 16×, this yielded sensor

voltages in the range of ~5–10 mV. No additional amplification or signal processing was applied. The spikes in Fig. 4c represent a separate 3.3 V digital signal from the Arduino, intentionally plotted to illustrate the timing correlation between the response and the triggered event.

Since the measured voltage depends strongly on the input impedance of the acquisition system, the values obtained with the ADS1220 (~10 MΩ) are not directly comparable to those from a high-impedance multimeter such as the Keithley DMM6500. **To address this difference and to facilitate convenient visualization of the signal responses, we present the detected voltages in arbitrary units (a.u.).** This approach ensures consistent comparison of sensor performance under our measurement conditions.

We have revised the Results and Methods sections accordingly.

Page 14: "Because the measured voltage depends on the input impedance of the acquisition system[R1|56], the ADC we used has an input impedance of ~10 MΩ, which is not directly comparable to those from a high-impedance meter such as the Keithley DMM6500. For consistent visualization, we therefore present the detected voltages in arbitrary units (a.u.)."

Page 20: "The ReCLEAR device was connected to a 24-bit ADC converter (Texas Instruments ADS1220) with an input impedance of ~10 MΩ and a programmable gain amplifier (PGA) configured at 16×, which was interfaced and configured via an Arduino Nano 33 IoT. The sensor voltage was calculated using the standard ADC transfer function with a 2.048 V reference, according to the equation: $V = \frac{ADC\ Code}{2^{23}-1} * (\frac{V_{REF}}{PGA\_Gain})$. No additional amplification or filtering was applied. The TENG signal was sampled and accompanied by a 3.3 V digital trigger output for timing correlation. In addition, the Arduino was emulated as a USB keyboard, sending dedicated keystrokes corresponding to the acquired signal pattern."

R1. Cheng, T., Shao, J. & Wang, Z. L. Triboelectric nanogenerators. Nat. Rev. Methods Primer 3, 39 (2023).

7. From Fig. 5b, the hot object is 65 degrees (Celsius? Not specified). Is 60s the onset of the withdraw process, and exactly how far is the distance from the hand approaches the object?

Reply: We thank the reviewer for the helpful comment. We have revised the figure caption to indicate that the unit in the thermal images is **°C**. The current withdrawal process occurs at around 60 s. The slight delay is due to the programmed response speed of the robotic hand, which can be adjusted for faster operation. The distance between the hand and the objects during proximity sensing is approximately **1 cm.**

We have revised the Results section accordingly.

Page 16: "The current proximity distance between the hand and the objects is approximately 1 cm."

Page 16: "The withdrawal process occurs at ~60 s, with the slight delay attributed to the programmed response speed of the robotic hand, which can be adjusted for faster operation."

Page 36: "**b-d,** Real-time thermovoltage responses of pristine, self-healed, and recycled ReCLEAR devices during proximity detection with thermal stimuli at (b) 60 °C, (c) 25 °C, and (d) 10 °C. Critical proximity sensing regions are highlighted by red dashed boundaries. The unit of thermal images: °C."

8. P2, line 55, 'inherent toxicity of PEDOT:PSS': add references please. This is counter to many bioelectronics work, where PEDOT:PSS has been implanted in vivo and shown to be bio-compatible.

Reply: Thank you for this important feedback. It is indeed improper to use "inherent toxicity" for PEDOT:PSS, since it has been extensively demonstrated as biocompatible in numerous bioelectronics applications and in vivo studies. We acknowledge that

characterizing it as having "inherent toxicity" was inaccurate and inconsistent with the well-established literature on its biocompatibility. We will revise this section and instead describe PEDOT:PSS as "intrinsically colored" to better reflect its optical properties that are relevant to our transparency considerations, while maintaining scientific accuracy regarding its well-documented biocompatibility in bioelectronics applications.

We have revised the Results section accordingly.

Page 2: "However, the intrinsic coloration of PEDOT:PSS, PTH and PANi limits their optical transparency, restricting their viability in HMI devices requiring visual interfacing. Alternative conducting polymers like gelatin[R2|25], while potentially offering better optical transparency, typically exhibit inferior TE performance and require chemical doping to enhance their TE performance. This doping requirement introduces significant challenges, as most effective dopants are both hazardous and colored, potentially compromising both device safety and the desired transparency."

R2. Han, C.-G., Qian, X., Li, Q., Deng, B., Zhu, Y., Han, Z., Zhang, W., Wang, W., Feng, S.-P., Chen, G. & Liu, W. Giant thermopower of ionic gelatin near room temperature. *Science* **368,** 1091–1098 (2020).

"In general, we think this work presents a promising novel material with great potential in TE and TENG application. But these concerns should be addressed before the manuscript can be accepted for publication."

Reviewer #3

"I co-reviewed this manuscript with one of the reviewers who provided the listed reports. This is part of the Nature Communications initiative to facilitate training in peer review and to provide appropriate recognition for Early Career Researchers who co-review manuscripts."

Reply: We thank the reviewer and co-reviewer for their time and thoughtful evaluation of our manuscript. We value the constructive feedback provided through this collaborative review.

We have also carefully checked the grammar and other details of the manuscript. We sincerely thank all the reviewers for their constructive feedback, which has helped us substantially improve the quality of this work.