nature portfolio

Peer Review File

Solid-liquid interface charge transfer for generation of H2O2 and energy

Corresponding Author: Professor Hongzhi Wang

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 work, the authors reported an interesting device based on contact electrification, which can be employed to synthesize H2O2 and simultaneously generate electrical energy with an output power of over 5.8 kW/m3. They suggested that the electron transfer at the solid-liquid interface plays the central role, and that the performance is related to the electronegativity of the solid phase. Overall, this work can broaden the application of contact electrification and add to the toolbox of wave energy harvesting technology. However, only after addressing the following issues can I recommend the publication of this manuscript in Nature Communications.

1. The application of FEP in generating H2O2 via water-solid contact electrification has already been demonstrated recently (Ref. 18 of this manuscript). That study has also indicated the critical role of interfacial electron transfer for forming the hydroxyl radicals, which can finally lead to the production of H2O2. The relevant mechanisms have even been proposed in some earlier studies (Ref. 15 and 16), with a focus on the formation of radicals on FEP at different conditions. Although these studies have utilized ultrasonication to generate H2O2, I believe the underlying mechanism is quite the same as that proposed in the present work. The corresponding part of this manuscript should therefore be rewritten and a more comprehensive comparison with those previous studies must be provided.

2. The authors should verify the quantification accuracy of H2O2 concentration by some other means, such as the potassium iodide method in combination with NMR. Quantification of the OH radicals should also be provided.

3. It is mentioned in this manuscript that PFDTMS enhances the electronegativity of the solid phase surface. However, the authors did not provide any solid evidence for this statement.

4. The voltage presented in Figure 2d is different from that in Figure 3b. Is the condition changed? More details should be provided here.

5. Figure 3b shows that voltage and current decrease rapidly as a function of H2O2 concentration. The authors should give an explanation on why voltage and current remain nearly unchanged in the stability test in Figure 3f, given that there should be a nonnegligible amount of H2O2 accumulated after experimentation for 7 days.

6. OH- anions are consumed in the formation of H2O2. Does it mean that the pH in the liquid phase will decrease during operation? Some information should be provided in this regard, as well as the corresponding influence on performance.

7. The formation of H2O2 is an oxidation reaction using OH- as the reactant. Then what is the reduction reaction occurring in this device? The amount of reduction products should be provided so as to support the measured values of H2O2 concentration.

Reviewer #2

(Remarks to the Author)
This work introduced a dual-functional device for generation of H2O2 and energy, introducing the interface of H2O2

generated mechanism as well as the relatively strong energy harvesting performance. However, this work is not very innovative. Although the mechanism of hydrogen peroxide generation is not very clear, this work does not propose a fundamental mechanism improvement. In addition, the correlation between energy output and hydrogen peroxide production was not strong. Therefore, this work is not suitable for published in Nature Communications at the present stage unless it has been further improved..
1. Innovation. Compared with previous work (Nat. Commun. 13, 130 (2022); Adv. Mater. 35, 2304387 (2023)), this work is not very innovative. What is the mechanism of free radical production? Are free radicals affected by the presence of oxygen and the breaking of bonds? These are very fundamental questions that need to be analyzed in detail.
2. This work is linked to H2O2 as an energy harvesting device for water. However, the production of H2O2 is very trace and does not affect the actual device output very much.
3. Does the generation of hydrogen peroxide have an effect on the degradation performance of the output of triboelectric devices?

Reviewer #3

(Remarks to the Author)
Thank you for giving me the opportunity to review the paper of Hu Y. et al, entitled “Solid-liquid interface charge transfer for generator of H2O2 and energy”. The paper herein presents a system capable of simultaneously generating hydrogen peroxide and electrical energy from mechanical energy. To do so, the system relies on the use of charge transfers induced by solid-liquid triboelectrification, the concept of contact-electro-catalysis discovered in Zhong Lin Wang’s group, and a design for the electrical generator that is inspired by the droplet generator of Wang Zuankai’s research group. Although there are some obvious issues that would be difficult to solve for reaching practical applications of this device regarding the collection of the hydrogen peroxide produced, the concept is interesting and worth exploring.
While I do not see many problems with the experimental part concerning the engineering, sometimes it is very obvious that some of the basic science behind the experiments is not well understood, such as the interpretation of the results of figure 2e (see question 2e). This should absolutely be corrected before considering publication.
When it comes to the literature review, while it is rather thorough overall, the way it is cited in the manuscript is sometimes inconsistent (see question 2), and need to be improved. Some other issues concerning the way the literature review is conducted are much more concerning. Sometimes papers are not properly cited where they should obviously be (see itemized questions below). For example, in several instances, the main body of manuscript is written in a way that makes the reader believe it is presenting an original thought, while they are actually drawn from the literature cited in the introduction (see itemized questions below). Moreover, it seems, from the way the paper is written, that the corpus cited has not been in some instances well understood. I believe it has been understood, actually, from the rest of the main body of the text, but this needs to be improved in order not to confuse future readers and cause misunderstanding of concepts related to the topic. I understand that the requirement in terms of conciseness makes it difficult to express clearly, but these clarifications are needed.
The paper cannot be accepted for publication as is, but could be after this round of review. Below, you will find a point-by-point, but not exhaustive, list of the issues that needs to be corrected for this paper to be suitable for publication. You should not only correct the specific issues I mentioned below, but to also correct similar ones you will find by yourself based on the ones I already pointed out.
1. In the introduction, you first talk about solid—liquid interfaces, and charge transfers and evocate that the charge could be radicals, citing the papers of Bartosz’ group. These papers are talking about the nature of the charges responsible for the chemical activity of polymers tribocharged by solid-solid friction. To avoid confusion for new readers, who may think it is related to solid-liquid contact electrification, it would be wise to revise this passage and make it clearer on that matter.
2. Line 45, concerning reference 18 and 19, I am confused as to why they are referred to as Wang et al. The first authors are Berbille A. for one and Zhao J. for the other. Moreover, these two papers do not share the same last author. This should be corrected as to reflect the authors contribution to the corpus appropriately. Please, also check other citations.
3. Line 50, “Electron transfer at the solid-liquid interface not only induces chemical reactions within the liquid phase but also involves the transfer of a amounts of energy.” Please correct “a amounts of energy” for “energy” or “an amount of energy”. Regardless, chemical reactions are a form of transfer of energy (mechanical to chemical here). The transfer of electrons is the result of an input of mechanical energy in the thermodynamic system, that then undergoes a change to find equilibrium. I believe you want to evocate electrical power when you employ the term “energy”. I am afraid the wording employed here may confuse some readers. You could improve this by completing the sentence and adding that “[it] can take the form of electrical signals when electrodes are part of the system” or, something in this spirit. Same issue on Line 111.
4. Citations are missing for the statements of Line 75, 76, 80-84. Moreover, the type of mechanism proposed in fig 1b has already been proposed in other works. Including, but not only, Adv. Funct. Mater. 2024, 34, 2315817. https://doi.org/10.1002/adfm.202315817 and by other papers already cited, such as ref 18 and 19.
5. Line 117, “this design ressemble that of a field-effect transistor”, while true it also resembles the design of the droplet generator of Wang Zuankai’s group cited as Ref 22 (Nature 578, 392–396 (2020). https://doi.org/10.1038/s41586-020-1985-6). I strongly suggest the authors cite this work there. As well. There are many similar issues throughout the text where the writing leads the reader to think an original idea is presented, while it is the adaptation of the work of others. This is most probably an honest mistake, but this kind of issues needs to be addressed as they can mislead future readers.
6. I fail to understand how figure 2e is conducive of electron transfer. It is conducive to a transfer of charge, but the KPFM method cannot distinguish electrons from ions. To do so, you would need to reproduce a similar experiment to that of Lin et al. from citation 10, which you did conduct fully here. The data showed does not prove that electrons were transferred, only that a charge has been transferred (electrons, ions, or radicals). Please correct this issue, either by completing this experiment, or by drawing the proper conclusions.
7. In line 196, you observed a decrease of the electrical output from the generator when the concentration of hydrogen

peroxide increases. Could you explain why?
8. Line 232, it would be preferable to replace “H2O2 preparation” by “H2O2 production” or “H2O2 generation”.
9. Concerning the results of fig. 4b, it would be interesting to conduct a capture experiment, i.e., comparing the rate of the original degradation reaction with the same experiment conducted in presence of radical scavengers (EDTA, p-Benzoquinone, AgNO3, ter-butanol, hindering the effects of holes, superoxide anions, electrons, and hydroxyle radicals, respectively). Thus, you could compare the results from your experiments and those previously presented in ref 16. I expect the results could be different, and could help you distinguishing your paper from previous publications on contact electro catalysis. Same could be done concerning H2O2 production.
10. For the power generation application, you employed a rectifier bridge rather than more advanced and power efficient solutions, such as power management systems designed by Harmon W. et al. that caters specifically to the needs of TENGs (Nano Energy 71, 104642 (2020), https://doi.org/10.1016/j.nanoen.2020.104642). Why did you make this choice ?
11. This is only a suggestion, but have you though about use your device as water purifier, not for dye contamination, but for bacterial (such as e.coli) ? The fact the dye can be degraded quickly, and that you can generate H2O2, indicate that it may have a good potential for decontamination of water from this type of organism.

Reviewer #4

(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)
All my comments have been fully addressed. This paper can now be published in the current version.

Reviewer #2

(Remarks to the Author)
All my previous considerations have been resolved. The level of this work has been greatly improved and can be accepted by Nature Communications.

Reviewer #3

(Remarks to the Author)
The authors have addressed all the questions I was concerned. I recommend its publication in NC as it is.

Reviewer #4

(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.

Solid-liquid interface charge transfer for generation of H_2O_2 and energy

We sincerely thank the reviewers for their careful and thorough review, which are indeed very helpful to make the paper more solid and smooth. We have revised our manuscript very carefully in the light of their suggestions and comments.

The following responses have been prepared to address all of the reviewers' comments in a point-by-point fashion. (Comments in black, responses in blue):

Response to Reviewer #1

General comment: *In this work, the authors reported an interesting device based on contact electrification, which can be employed to synthesize H_2O_2 and simultaneously generate electrical energy with an output power of over 5.8 kW/m^3. They suggested that the electron transfer at the solid-liquid interface plays the central role, and that the performance is related to the electronegativity of the solid phase. Overall, this work can broaden the application of contact electrification and add to the toolbox of wave energy harvesting technology. However, only after addressing the following issues can I recommend the publication of this manuscript in Nature Communications.*

Response: Thank you for your review and we appreciate your feedback. We have carefully revised the manuscript according to your comments.

1. The application of FEP in generating H_2O_2 via water-solid contact electrification has already been demonstrated recently (Ref. 18 of this manuscript). That study has also indicated the critical role of interfacial electron transfer for forming the hydroxyl radicals, which can finally lead to the production of H_2O_2. The relevant mechanisms have even been proposed in some earlier studies (Ref. 15 and 16), with a focus on the formation of radicals on FEP at different conditions. Although these studies have utilized ultrasonication to generate H_2O_2, I believe the underlying mechanism is quite the same as that proposed in the present work. The corresponding part of this manuscript should therefore be rewritten and a more comprehensive comparison with those previous studies must be provided.

Response: Thank you for your professional comments. In this paper, we align with the

majority of the perspectives presented by Wang's group regarding the phenomenon of spontaneous H_2O_2 generation in water. While the generation of H_2O_2 through water flow is a common occurrence, the underlying mechanism and production efficiency require further investigation. We have revised the corresponding section of the manuscript as follows: "Although the mechanism behind the spontaneous generation of H_2O_2 at the solid-liquid interface remains controversial, it is widely accepted that interfacial electron transfer leads to the synthesis of H_2O_2. This suggests that when the electrode is part of the solid-liquid system, electron transfer not only generates electrical signals but may also lead to the generation of non-catalytic H_2O_2 in the liquid phase." For our device, "by designing a cyclic sliding structure between the liquid and solid phases, the electrical properties of the solid-liquid interface can be continuously collected, and the occurrence of interfacial chemical reactions can be enhanced. Moreover, by studying the electron donors and electron transfer products in the liquid phase, the electrical performance output of the solid-liquid power generation system can be further improved." We have revised the section related to H_2O_2 in the introduction and Fig. 2. The focus is on investigating the solid-liquid electrical properties and the impact of H_2O_2 production at the solid-liquid interface on electrical performance.

In order to make a more comprehensive comparison with previous studies, we have compiled relevant literature on the mechanism of spontaneous generation of H_2O_2 at this interface, as shown in Table R1. In current research, the spontaneous generation of H_2O_2 at the water interface is categorized into liquid-gas and liquid-solid interfaces. For the generation of H_2O_2 at the liquid-gas interface, studies suggest that it results from the combination of ·OH radicals spontaneously formed from OH- under the influence of the internal electric field at the surface of neutral droplets (Proc. Natl. Acad. Sci. 116, 19294-19298 (2019), Proc. Natl. Acad. Sci. 117, 30934-30941 (2020)). However, the roles of N_2, O_2, and O_3 in H_2O_2 production remain a subject of debate.

In the preparation of H_2O_2 at the liquid-solid interface, it is essential to first consider the composition of the interfacial transferred charge (electrons and ions). For SiO_2, studies have demonstrated that charge transfer at the SiO_2-water interface involves both electron and ion transfer (Nat. Commun. 11, 399 (2020)), with KPFM tests confirming that electron transfer is predominant. In Zare's group's study on microfluidic injection at the SiO_2-water interface, the hydroxyl groups on the SiO_2 surface were labeled with ^{18}O, and the presence of $H_2{}^{18}O_2$ was detected after solid-liquid friction (Proc. Natl. Acad. Sci. 119, 2209056119 (2022)). It is hypothesized that

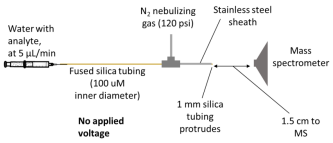
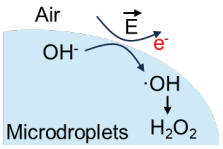
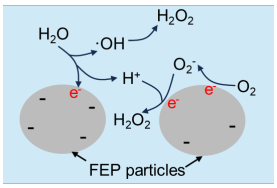
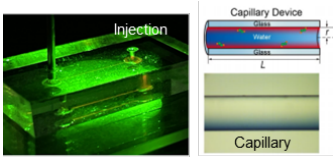
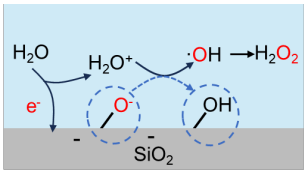
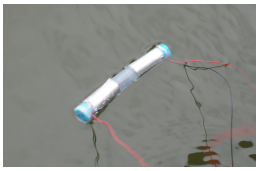
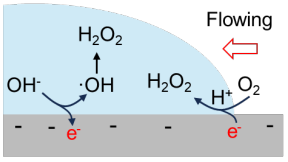
electrons from H_2O are transferred to the SiO_2 surface to obtain H_2O^+, which then undergoes ion exchange with Si-^{18}O- to generate Si-OH and free radicals $\cdot^{18}OH$, and finally obtain $H_2{}^{18}O_2$.

Wang's group selected FEP nanoparticles as the solid-phase material and employed external ultrasound to induce continuous vibration and rotation of the FEP nanoparticles in water, ensuring an optimal solid-liquid friction contact area (Adv. Mater. 35, 2304387 (2023)). Notably, they proposed an explanation for the continuous generation of H_2O_2: electrons in the water are continually transferred to the FEP surface, forming ·OH, while O_2 continuously obtains electrons on the FEP surface and transforms into O_2^-. This ongoing electron transfer cycle facilitates the continuous production of H_2O_2.

In our experiment, based on the thermal excitation of surface electrons at a high temperature of 513 K (Nat. Commun. 11, 399 (2020)), we used KPFM to measure the surface electrical properties during the solid-liquid friction and thermal excitation cycle (Fig. R1, R2). Multiple high-temperature treatments at 513 K caused the surface potential to nearly return to its initial value, indicating that in our experiment, electron transfer dominated the solid-liquid friction. Regarding the mechanism of H_2O_2 production, we largely concur with Wang's group perspective. Based on the oxidizing property of O_2, it can extract electrons from the solid surface, thereby diminishing the surface electrical properties of the material (ACS Nano. 14, 17354-17364 (2020)). The difference is that it may be because the relative contact area of water flow is much smaller than the relative contact area between nanoparticles and water. In our experiment, it was found that H_2O_2 would reach a critical value.

In our solid-liquid power generation device, H_2O_2 is produced as a result of solid-liquid friction electron transfer. But excessive H_2O_2 can impact electron transfer, leading to a decrease in electrical performance. Unlike ions that directly influence solid-liquid interface performance, H_2O_2 does not affect electrical energy when the solid-liquid charge is balanced. For specific experiments and analyses, please refer to Question 5.

Table R1: Mechanism of spontaneous generation of H_2O_2.

Ref	System	H_2O_2 preparation method	Device diagram	H_2O_2 production mechanism
1, 2	Liquid /Gas	Spraying droplets		
3, 4	Liquid /Solid	Particle/water ultrasound		
5	Liquid /Solid	Microfluidics injection		
Our work	Liquid /Solid	Water flow		

1. Lee, J. K. et al. *Proc. Natl. Acad. Sci.* **116**, 19294-19298 (2019).
2. Lee, J. K. et al. *Proc. Natl. Acad. Sci.* **117**, 30934-30941 (2020).
3. Berbille, A. et al. *Adv. Mater.* **35**, 2304387 (2023).
4. Zhao, J. et al. *Angew. Chem. Int. Ed. Engl.* **62**, 202300604 (2023).
5. Chen, B. et al. *Proc. Natl. Acad. Sci.* **119**, 2209056119 (2022).

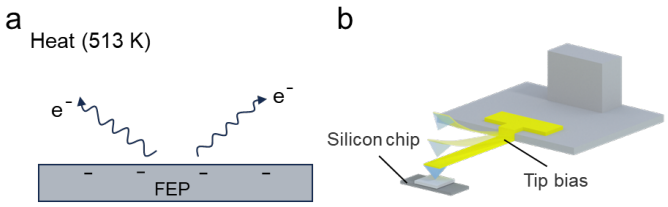


Fig. R1 KPFM test of solid surface potential a Thermal emission of electrons on solid surface. **b** Schematic of the apparatus for KPFM measurement of solid surface potential.

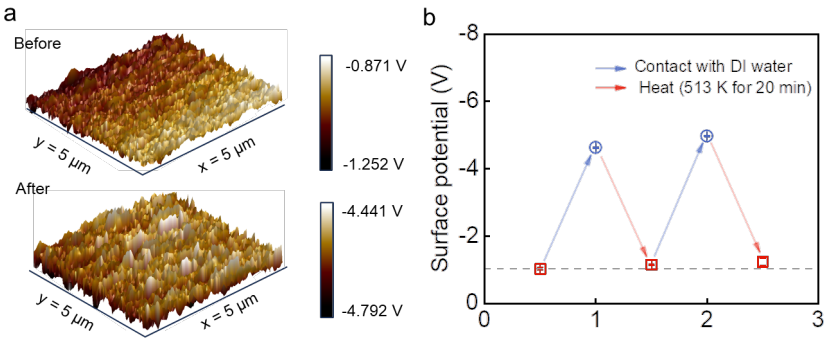


Fig. R2 KPFM potential change diagram before and after solid-liquid friction.

- **Our revision to the manuscript:**

We have revised the section related to H_2O_2 in the manuscript. Based on the phenomenon of H_2O_2 production through solid-liquid electron transfer, we investigated the impact of the H_2O_2 generation at the solid-liquid interface on the electrical properties. In the revised supplementary materials, we added Table. R1 as Table. S1, and added Fig. R1, R2 as Fig. S2, S4 for more comprehensive comparison with previous studies. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

2. The authors should verify the quantification accuracy of H_2O_2 concentration by some other means, such as the potassium iodide method in combination with NMR. Quantification of the ·OH radicals should also be provided.

Response: Thank you very much for your professional advice. In addition to the potassium titanium oxalate (PTO) method, the KI method (Chemosphere. 270, 129448 (2021)) and the potassium permanganate method (Angew. Chem. Int. Edit. 62, e202300604 (2023)) are also commonly used for quantitative testing of H_2O_2. As for the detection of H_2O_2 using NMR (Proc. Natl. Acad. Sci. USA. 119, e2121542119 (2022)), this method is often used qualitatively (Adv. Mater. 35, 2304387 (2023)) at low H_2O_2 concentrations due to limitations in equipment requirements and sensitivity. Therefore, in the experiment, to further verify the accuracy of the H_2O_2 concentration, we incorporated the KI and potassium permanganate methods for quantitative testing of H_2O_2 in water.

On the other hand, the quantification of hydroxyl radicals is also a major challenge in the field of catalysis due to hydroxyl radicals are short lived (≈10^{-9} s) (Free Radical

Biol. Med. 12, 169-173 (1992)) and highly reactive. In recent years, electron paramagnetic resonance (EPR) testing has become a widely accepted qualitative method. However, direct quantification of hydroxyl radicals remains challenging. In the experiment, we added O-phenylenediamine (OPD) and used ultraviolet absorption spectroscopy to characterize changes in radical concentration. The specific experiment is as follows:

- **H_2O_2 quantitative test.**

KI Method: Under the catalysis of ammonium molybdate, H_2O_2 and I ions undergo a redox reaction, and the change in absorbance is detected using UV-visible spectroscopy (Fig. R3). The mixed solution displays two absorption peaks at 287 nm and 350 nm. The calculated H_2O_2 concentrations before and after the modification of the inner wall of the tube are approximately 7.55 μM and 17.29 μM, respectively.

Potassium Permanganate Method: Under acidic conditions, H_2O_2 reacts with potassium permanganate in a redox reaction, and the change in absorbance is detected using UV-visible spectroscopy (Fig. R4). The absorbance at 525 nm is used as the characteristic value, and a standard curve is constructed based on the corresponding hydrogen peroxide concentrations. The calculated H_2O_2 concentrations before and after modification are approximately 7.5 μM and 17.62 μM, respectively.

We also repeated the test using the **PTO method** (Fig. R5) and calculated that the H_2O_2 concentrations before and after tube modification were 7.92 μM and 18.09 μM, respectively (Fig. R3). In summary, we used the above three methods to more accurately quantify H_2O_2 in flowing water.

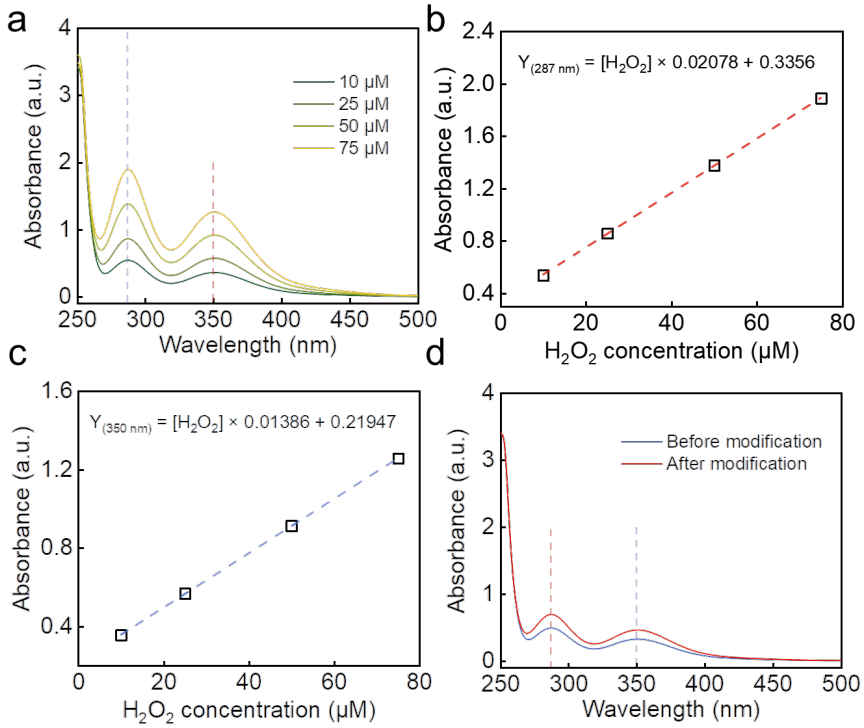


Fig. R3 KI method for quantification of H_2O_2. **a** UV spectrum of H_2O_2 aqueous solution titrated with KI, with H_2O_2 concentrations of 10 μM, 25 μM, 50 μM, and 75 μM. **b** Calibration curve of absorption at 287 nm acquired from the UV absorption spectrum. **c** Calibration curve of absorption at 350 nm acquired from the UV absorption spectrum. **d** UV spectra of water titrated with KI after solid-liquid friction cycles (before and after modification of the inner wall of the tube).

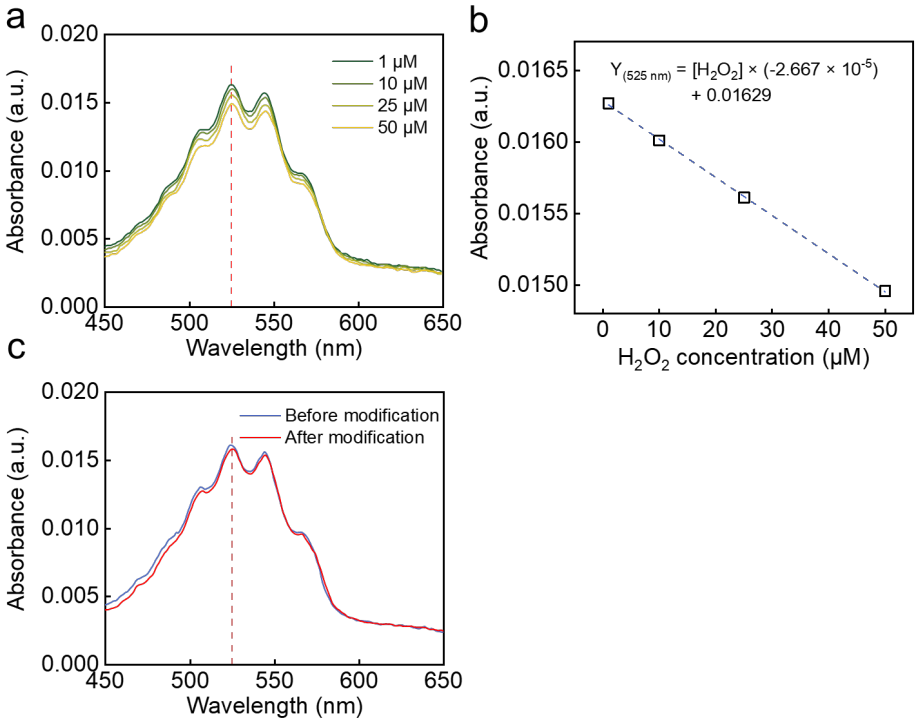


Fig. R4 Potassium permanganate method for quantification of H_2O_2. a UV spectrum of H_2O_2 aqueous solution titrated with potassium permanganate, with H_2O_2 concentrations of 1 μM, 10 μM, 25 μM, and 50 μM. **b** Calibration curve of absorption at 525 nm acquired from the UV absorption spectrum. **c** UV spectra of water titrated with potassium permanganate after solid-liquid friction cycles (before and after modification of the inner wall of the tube).

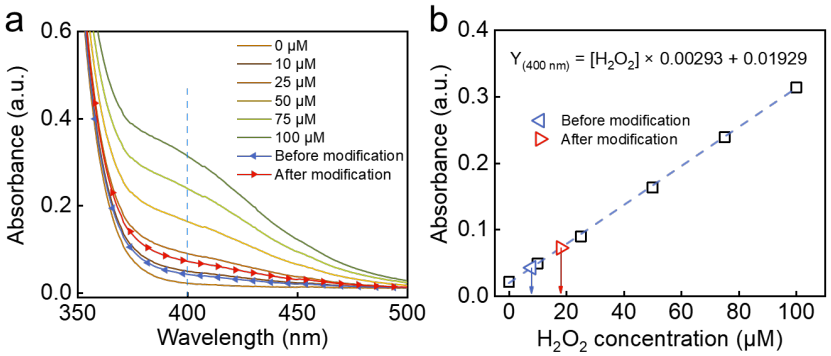


Fig. R5 PTO method for quantification of H_2O_2 a The absorption spectrum of an aqueous PTO solution with added H_2O_2. Examples microdroplet spectra in red and blue. **b** Calibration curve of absorption at 400 nm acquired from the UV absorption spectrum.

- **Testing changes in ·OH concentration.**

We used OPD as a detection probe for ·OH. OPD can be oxidized by ·OH to generate diaminophenothiazine (DAP). Fig. R6a displays the UV absorption spectra for different water flow cycles, demonstrating that an increase in the number of circulations correlates with a rise in ·OH concentration. Notably, when water flow ceases, the ·OH concentration drops significantly within just a few minutes (Fig. R6b). This is due to the cessation of electron transfer and the short lifetime of ·OH.

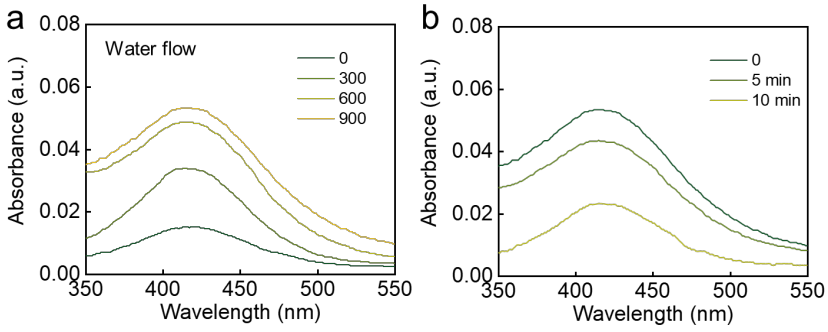


Fig. R6 Changes in ·OH concentration a The friction cycle affects the concentration of ·OH produced. **b** UV absorption spectra at various time intervals after the friction cycle stopped.

- **Our revision to the manuscript:**

We have replaced the original figures for "PTO method for testing H_2O_2" and updated Fig. R5a, b to Fig. 2g, h in the revised manuscript. Additionally, we added Fig. R3 as Fig. S19, added Fig. R4 as Fig. S20, and added Fig. R6 as Fig. S27 in the revised supplementary materials. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

3. It is mentioned in this manuscript that PFDTMS enhances the electronegativity of the solid phase surface. However, the authors did not provide any solid evidence for this statement.

Response: We believe that the increased electronegativity following the modification will facilitate solid-liquid charge transfer, thereby enhancing the electrical properties. As illustrated in Fig. R7, the electrical properties improved from 221.5 V and 74.5 μA to 255.1 V and 85.4 μA after modification.

To further support the view that PFDTMS enhances the electronegativity of the solid surface, we added two additional characterizations: a solid surface potential test and a solid-liquid charge transfer test.

Surface potential test: We treated the tube in a high-temperature oven at 513 K for 15 minutes, which caused electrons to be thermally excited and emitted from the surface. This treatment ensured that the surface potential of the inner wall of the tube remained roughly consistent before and after modification. Then, we tested the surface potential of the inner wall of the tube after cyclic water flow. As shown in Fig. R8, the potential stabilized after approximately 200 cycles, with the surface potentials being about -600 V before modification and -820 V after modification. This indicates that the modification enhances the tube's ability to acquire charge from water, thereby improving its electronegativity.

Solid-liquid charge transfer test: The solid-liquid single-electrode design is a simple method for evaluating solid-liquid charge transfer capability (ACS Nano, 14, 17565-17573 (2020)) and can be used to compare the electronegativity of solid materials. As shown in Fig. R9, the charge in the tube increased from 21 nC to 29.3 nC before and after modification. This indicates that the inner wall of the modified tube acquires more charge from the water during cyclic flow and possesses greater electronegativity.

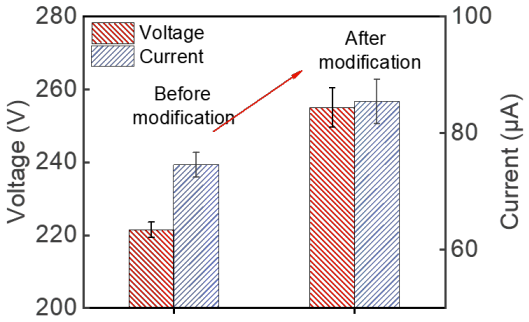


Fig. R7 Alterations in voltage and current characteristics before and after modification

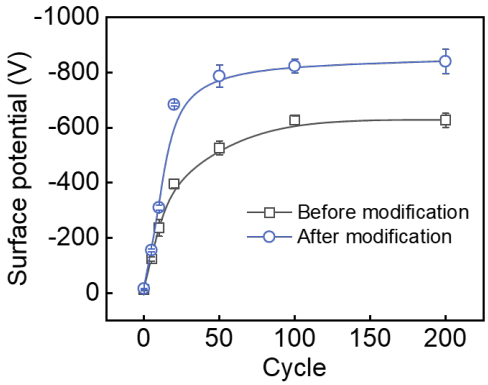


Fig. R8 Solid surface potential test

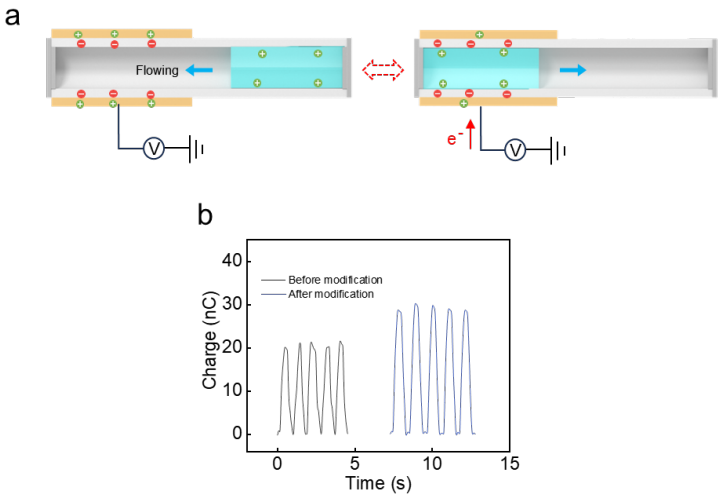


Fig. R9 Solid-liquid charge transfer test. a Single electrode solid-liquid generator. **b** Solid-liquid charge transfer before and after modification.

- **Our revision to the manuscript:**

We added Fig. R8 as Fig. S16c. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

4. The voltage presented in Figure 2d is different from that in Figure 3b. Is the condition changed? More details should be provided here.

Response: Thanks for your valuable suggestions. To further enhance electrical performance, in addition to the structural design of the electrodes (Fig. S2), we improved performance by adding an isolation layer around the tube and modifying the inner wall of the tube (Fig. R10). Fig. 2d of the manuscript compares the impact of the isolation layer on electrical performance, while the voltage data presented in Fig. 3b reflect the performance improvements resulting from both the isolation layer and the inner modifications.

To provide a clearer comparison of changes in electrical performance, we have reorganized Fig. 2d and S17, as shown in Fig. R10. The addition of an isolation layer around the tube and modifications to the inner wall of the tube have both significantly enhanced electrical performance.

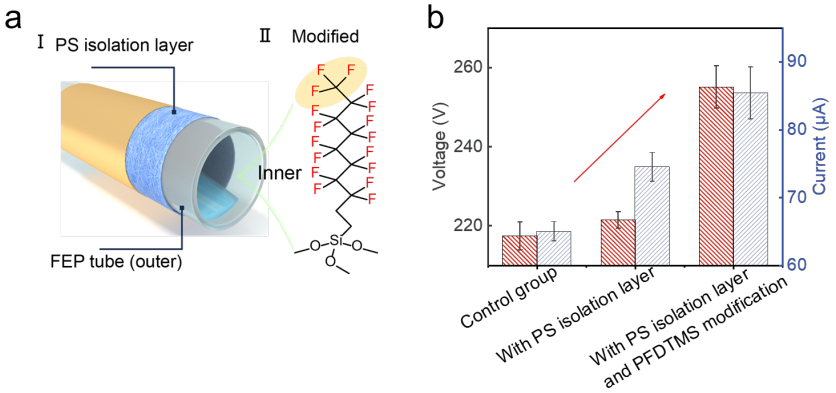


Fig. R10 Effect of tube inner wall modification and isolation layer on electrical properties. a Sealing tube structure design. **b** Electrical performance output

5. Figure 3b shows that voltage and current decrease rapidly as a function of H_2O_2 concentration. The authors should give an explanation on why voltage and current remain nearly unchanged in the stability test in Figure 3f, given that there should be a nonnegligible amount of H_2O_2 accumulated after experimentation for 7 days.

Response: Thank you for your professional comments. First, in the stability test shown in Fig. 3f, we demonstrated that H_2O_2 does not accumulate continuously, but instead

reaches a critical value. The stable electrical signal output over seven days is due to the dominance of the induced charge in the system, with the strength of the electrical signal being related to the electrostatic induction on the solid surface. Second, the addition of H_2O_2 in Fig. 3b leads to a decrease in voltage and current performance because the excessive addition of H_2O_2 affects electron transfer at the solid-liquid interface and the accumulation of charge density on the solid surface, resulting in a decline in electrical performance. The changes in H_2O_2 concentration at the solid-liquid interface and the effects of H_2O_2 on the solid-liquid electrical properties are as follows:

- **The concentration of H_2O_2 reaches a critical value:**

As shown in Fig. R11, the H_2O_2 generated from solid-liquid electron transfer does not accumulate indefinitely but gradually reaches saturation. In the relevant literature (Angew. Chem. Int. Edit. 62, e202300604 (2023)), where H_2O_2 concentration can increase steadily over an extended period without reaching a critical value, this difference may be due to the solid-liquid contact area. The relative contact area of water on a flow plane is considerably smaller than that between nanoparticles and water. Therefore, there was no significant accumulation of H_2O_2 on day 7.

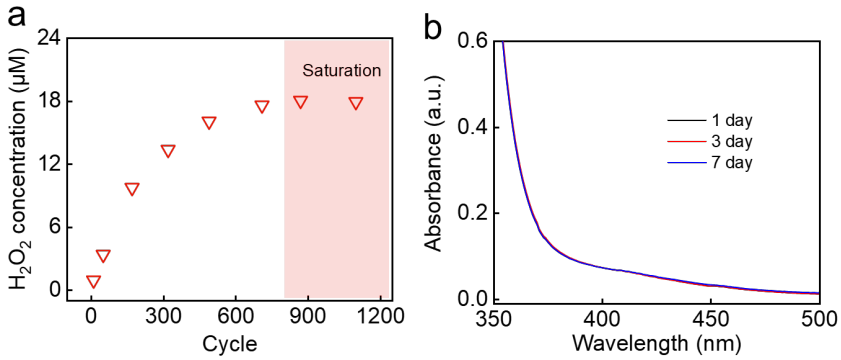


Fig. R11 The concentration of H_2O_2 reaches a critical value. a The friction cycle affects the concentration of H_2O_2 produced. **b** UV spectrum of PTO added to water after phase friction (the friction time was 1 day, 3 day and 7 day).

- **Effect of H_2O_2 on solid-liquid electrical properties:**

Solid-liquid power generation consists of the charging stage and the saturation stage (Nature, 578, 392-396 (2020)). In the charging stage, periodic contact between the solid and liquid phases causes electrons to transfer from the liquid to the solid phase. During this stage, the electrical signal arises from contact electrification and electrostatic induction. As the solid phase charge density accumulates, the electrical performance gradually increases. When the solid-phase charge density approaches saturation and the solid-liquid electron transfer reaches equilibrium, the system enters

the saturation stage (Fig. R12). At this point, the electrical signal, driven by electrostatic induction, reaches its maximum and stabilizes. The solid-phase charge density during the saturation stage is the key factor influencing electrical performance output.

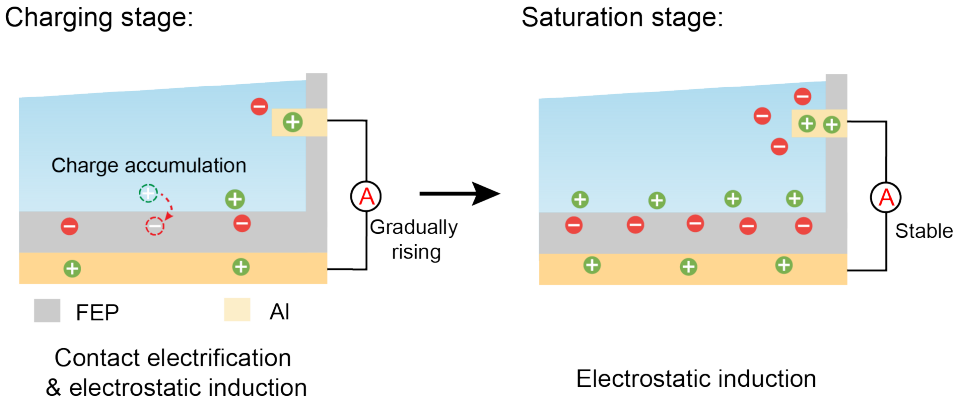


Fig. R12 Solid-liquid power generation consists of the charging stage and the saturation stage.

Effect of H_2O_2 on solid-liquid electron transfer (charging stage): In the experiment, we tested the electrical performance output of deionized water and 0.1 mM H_2O_2 during the solid-liquid friction process, as well as the change in solid surface potential after friction. During the "charging stage", as solid-phase charge density accumulated, the voltage signal gradually increased to reach equilibrium. However, the addition of H_2O_2 weakened the voltage performance output (Fig. R13a). This effect is due to the presence of H_2O_2, which reduces electron transfer, resulting in a change in solid surface potential from -840 V to -512V (Fig. R13b, c).

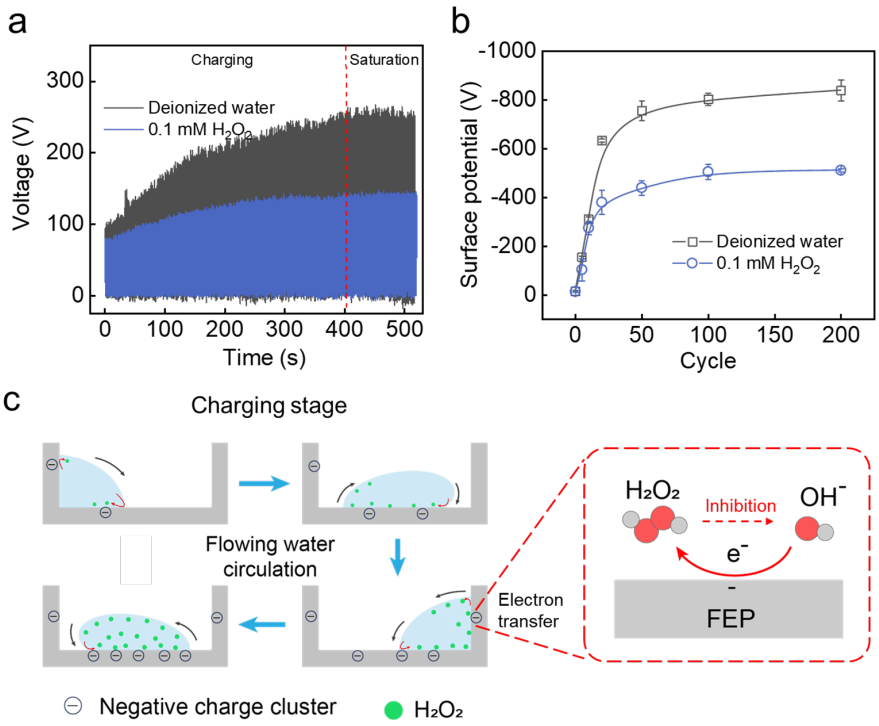


Fig. R13 Effect of H_2O_2 on solid-liquid properties. a Effect of H_2O_2 on voltage performance of solid-liquid power generation (charging stage and saturation stage). **b** Effect of H_2O_2 on solid surface potential. **c** Electron transfer generates H_2O_2, and an excess amount of H_2O_2 has the potential to inhibit electron transfer.

Effect of H_2O_2 on solid-liquid charge balance system (saturation stage): It is noteworthy that, unlike ions that directly affect solid-liquid interface performance by intervening in the double electrical layer, H_2O_2 does not impact the electrical properties of the solid-liquid system after surface charge balance is achieved. We designed the following comparative experiments: Experiment I served as the control group, where the voltage reached 255 V (Fig. R14a) after solid-liquid friction charge balance was achieved. Next, we removed the water from the tube, obtaining both the tube with solid-liquid friction charge balance and the water. Experiment II involved adding 0.1 mM H_2O_2 to the friction tube; Experiment III consisted of injecting the friction water into a tube heated to 513 K (thermally excited electrons).

In Experiments I and II, the solid phase was at charge saturation, and the additional H_2O_2 did not significantly affect the electrical performance output, indicating that H_2O_2 does not impact the electrical properties during the "saturation stage" (Fig. R14b). However, in Experiment III, there was a noticeable decrease in electrical performance. This decline is attributed to the presence of a small amount of H_2O_2 in the water after

solid-liquid friction, which affects the solid-liquid electron transfer during the "charging stage", leading to a reduction in electrical performance.

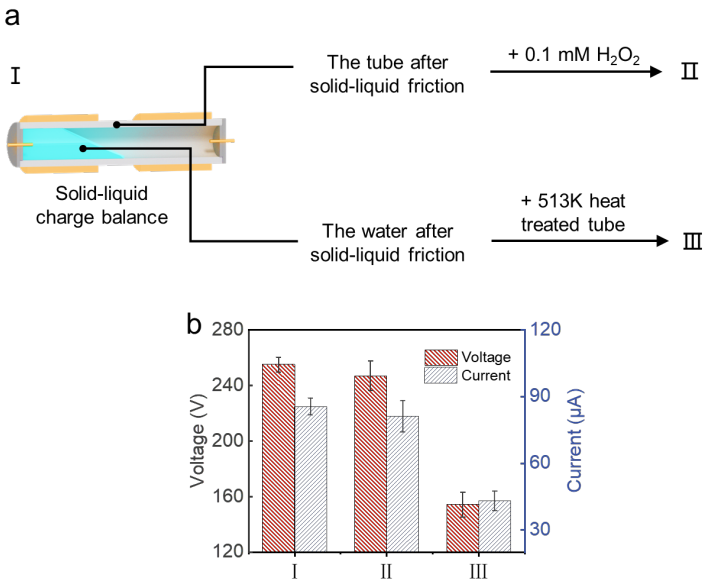


Fig. R14 Effect of H_2O_2 on the solid-liquid electrical properties in the charging and saturation stages. a Experiment I Control group; Experiment II 0.1 mM H_2O_2 was added to the tube after solid-liquid friction; Experiment III Electron thermal excitation tube was added with water after solid-liquid friction. **b** Experiment I, II and III voltage and current performance.

- **Our revision to the manuscript:**

We added Fig. R11b as Fig. S23, added Fig. R12 as Fig. S24, added Fig. R13 as Fig. S28, and added Fig. R14 as Fig. S29. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

6. OH^- anions are consumed in the formation of H_2O_2. Does it mean that the pH in the liquid phase will decrease during operation? Some information should be provided in this regard, as well as the corresponding influence on performance.

Response: We agree with your perspective. The pH decreases with the consumption of OH^- anions. As shown in Fig. R15, after achieving charge transfer equilibrium, the pH of the water decreases from 6.84 to 6.79.

Acidity has a significant adverse effect on electrical properties (Fig. R16a). Since the electrical properties of the solid-liquid interface are positively correlated with the surface charge density of the solid phase, we enhance the charge transfer capacity at

this interface by increasing the electronegativity of the solid phase and boosting the electron donors in the liquid phase. Conversely, acidic solutions result in lower OH^- concentrations, which is not conducive to the accumulation of surface charge on the solid phase. As shown in the Fig. R16b, after achieving charge transfer equilibrium in an acidic environment, the surface potential of the solid phase is low, leading to a decrease in electrical properties.

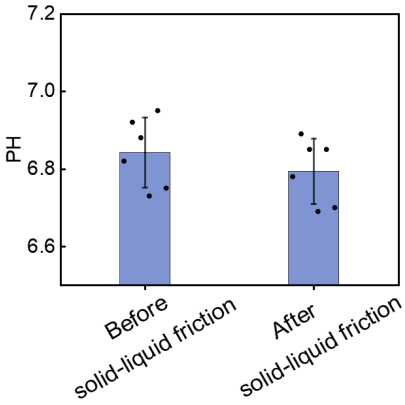


Fig. R15 Liquid pH changes before and after solid-liquid friction

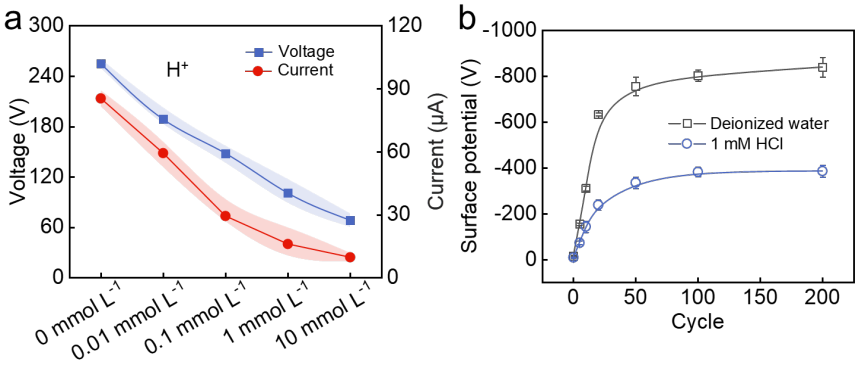


Fig. R16 Effect of acid on solid-liquid electrical properties. a Effect of HCl concentration in liquid phase on electrical properties. **b** After solid-liquid friction, the solid surface potential.

- **Our revision to the manuscript:**

We added Fig. R16b as Fig. S30. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

7. The formation of H_2O_2 is an oxidation reaction using OH^- as the reactant. Then what is the reduction reaction occurring in this device? The amount of reduction products should be provided so as to support the measured values of H_2O_2 concentration.

Response: During the formation of H_2O_2 at the solid-liquid interface, current research widely agrees that O_2 participates in the reduction reaction (Angew. Chem. Int. Edit. 62, e202300604 (2023)). This is due to the oxidative properties of O_2, enabling it to gain electrons from the solid surface, thereby reducing the surface electrical properties of the material (ACS Nano 14, 17354-17364 (2020)).

In the reduction reaction of this device, O_2 loses electrons and converts into superoxide radicals (Adv. Mater. 35, 2304387 (2023)). In fact, about 9×10^{-8} mol of H was generated in our tube, with a maximum O_2 consumption of 4.5×10^{-8} mol. In a sealed tube, excluding the water proportion, the O_2 content in the air is about 7.75×10^{-5} mol, so the oxygen consumption remains below 0.058%. Due to sensor sensitivity limitations, accurately measuring this small change in O_2 is challenging.

Response to Reviewer #2

General comment: *This work introduced a dual-functional device for generation of H_2O_2 and energy, introducing the interface of H2O2 generated mechanism as well as the relatively strong energy harvesting performance. However, this work is not very innovative. Although the mechanism of hydrogen peroxide generation is not very clear, this work does not propose a fundamental mechanism improvement. In addition, the correlation between energy output and hydrogen peroxide production was not strong. Therefore, this work is not suitable for published in Nature Communications at the present stage unless it has been further improved.*

Response: Thank you for your comment, we appreciate your feedback. We have done our best to address the issues raised. The responses to each of your questions are provided below. Before answering the main comment, we would like to respond to the concern regarding innovation and the correlation between energy output and H_2O_2 production.

- **Innovation in the structure and mechanism:**

Structure: Solid-liquid power generation includes two methods: water droplet power generation and water flow power generation (Table. R2). Wang Zuankai 's group proposed a transistor-like structure that greatly improved the electrical output of water droplet power generation (Nature 578, 392-396 (2020)). However, the instability of water droplets and the difficulty in precisely controlling droplet positioning hinder continuous and efficient energy collection (Adv. Mater. 33, 2105761 (2021)). Additionally, parasitic capacitance between the upper electrode and the solid phase limits the energy collection capacity when integrating multiple units (Energ. Environ. Sci. 15, 2916-2926 (2022)). While water flow power generation can provide stable energy output, its current performance remains relatively low (ACS Nano 15, 13200-13208 (2021)).

In this paper, we designed a solid-liquid power generation device by enhancing the transistor-like structure, charge isolation layer, and solid-phase surface modification. Power generation efficiency is enhanced in three ways: optimizing circuit design, reducing internal charge loss, and increasing solid-liquid charge transfer efficiency. The design of separating the inserted electrode from the dielectric material greatly reduces the parasitic capacitance. This approach also overcomes the challenges of instability and difficulty in collecting power from water droplets.

Mechanism: In solid-liquid contact charged systems, liquid-phase charging is a

common phenomenon. While the literature has demonstrated the existence of electron transfer at the solid-liquid interface by studying the surface charge of the solid phase, the underlying mechanism of electron transfer in the liquid phase remains uncertain. Material selection and structural development hinge on understanding the mechanism, which is crucial for enhancing performance.

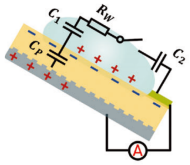
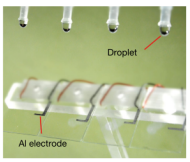
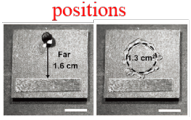
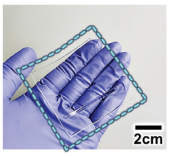
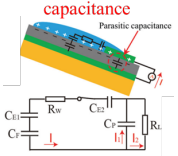
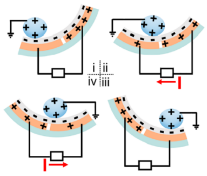
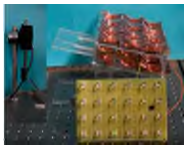
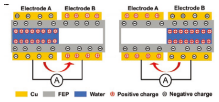
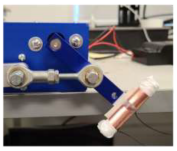
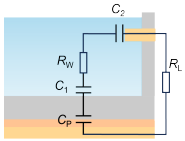
In recent years, studies have demonstrated that H_2O_2 can be spontaneously generated at the solid-liquid interface (Table R3). Although the exact mechanism of H_2O_2 generation remains controversial, it is generally accepted that interfacial electron transfer leads to the synthesis of H_2O_2. In particular, Wang Zhonglin's group proposed that FEP particles act as catalysts under ultrasonic conditions (Adv. Mater. 35, 2304387 (2023)), where H_2O and O_2 continuously generate H_2O_2 through electron exchange on the FEP surface.

We demonstrated that solid-liquid interface electron transfer is the predominant process. Based on the phenomenon of H_2O_2 produced by circulating water flow in the experiment, and supported by studies of electrical properties. First, we proposed that OH^-, rather than H_2O, serves as the electron donor in the liquid phase. The liquid phase acquires a negative charge due to the consumption of OH^- during solid-liquid electron transfer. Second, H_2O_2 is the product of liquid-phase electron transfer. However, through solid-liquid friction cycles, the concentration of this spontaneously generated H_2O_2 eventually reaches a critical value and no longer increases. Third, we further proposed and demonstrated that in the solid-liquid power generation system, increasing the concentration of the electron donor OH^- in the liquid phase enhances solid-liquid electrical performance. On the other hand, the addition of H_2O_2 influences solid-liquid electron transfer.

- **The correlation between energy output and H_2O_2 production:**

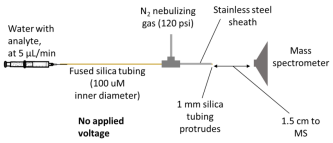
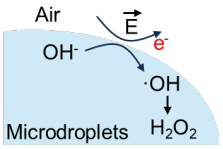
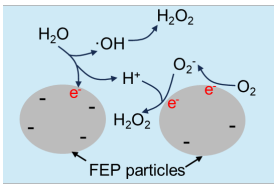
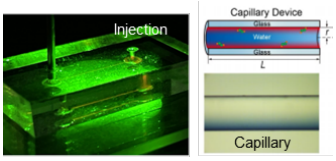
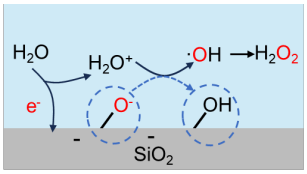
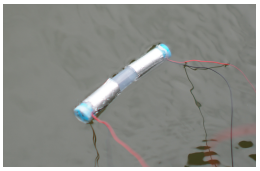
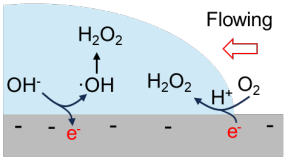
(1) Solid-liquid electron transfer results in the generation of liquid phase H_2O_2 and the accumulation of charge in the solid phase; (2) Increasing the concentration of the electron donor OH^- enhances the electrical performance output; (3) Adding H_2O_2 will result in a decrease in the energy output of the solid-liquid system.

Response Table R2: Comparison of various solid-liquid generators.

Ref.	System	Mechanism	Device diagram	Voltage (V)	Current (μA)	Defect
6	Water drops			143.5	213.7	I External continuous water titration 
7	Water drops			90	20	II Special titration positions 
8	Water drops			45	15	III Parasitic capacitance 
9	Water Flow			77	0.052	Lower electrical output
10	Water Flow			223	0.33	
Our work	Water Flow			312.5	103.8	

6. Xu, W. et al. *Nature* **578**, 392-396 (2020).
7. Liang, F. et al. *Adv. Energy Mater.* **12**, 2102991 (2022).
8. Jang, S. et al. *Adv. Funct. Mater.* 2411350 (2024).
9. Wei, X. et al. *ACS Nano* **15** 13200-13208 (2021).
10. Wu, H. et al. *Adv. Energy Mater.* **11**, 2100038 (2021).

Response Table R3: Mechanism of spontaneous generation of H_2O_2.

Ref	System	H_2O_2 preparation method	Device diagram	H_2O_2 production mechanism
11, 12	Liquid /Gas	Spraying droplets		
13, 14	Liquid /Solid	Particle/water ultrasound		
15	Liquid /Solid	Microfluidics injection		
Our work	Liquid /Solid	Water flow		

11. Lee, J. K. et al. *Proc. Natl. Acad. Sci.* **116**, 19294-19298 (2019).
12. Lee, J. K. et al. *Proc. Natl. Acad. Sci.* **117**, 30934-30941 (2020).
13. Berbille, A. et al. *Adv. Mater.* **35**, 2304387 (2023).
14. Zhao, J. et al. *Angew. Chem. Int. Ed. Engl.* **62**, 202300604 (2023).
15. Chen, B. et al. *Proc. Natl. Acad. Sci.* **119**, 2209056119 (2022).

- **Our revision to the manuscript:**

We added Table R3 as Table S1 in the supplementary materials. Corresponding changes have been marked in red in the revised supplementary materials and manuscript.

1. Innovation. Compared with previous work (Nat. Commun. 13, 130 (2022); Adv. Mater. 35, 2304387 (2023)), this work is not very innovative. What is the mechanism of free radical production? Are free radicals affected by the presence of oxygen and the

breaking of bonds? These are very fundamental questions that need to be analyzed in detail.

Response: The innovation of this work lies not in the H_2O_2 generation mechanism, but in the improvement of the solid-liquid energy harvesting device through structural design and the study of the solid-liquid electron transfer mechanism, which enables stable and efficient energy harvesting.

- **Innovation in comparison to related studies**

In the field of solid-liquid power generation (Table R2), it is challenging for water droplet energy harvesters to accurately control the water droplets and ensure stable (Adv. Mater. 33, 2105761 (2021)), high output (current > 15 μA). Additionally, parasitic capacitance limits the integration of such devices (Energ. Environ. Sci. 15, 2916-2926 (2022)). On the other hand, water flow energy harvesters achieve stable energy harvesting but suffer from low electrical output (current < 1 μA). In this work, we designed a solid-liquid power generation device by enhancing the transistor-like structure, charge isolation layer, and solid-phase surface modification. The power generation efficiency is improved from three aspects: optimizing circuit design, reducing internal charge loss and improving solid-liquid charge transfer efficiency. The design of separating the upper electrode from dielectric materials greatly reduces parasitic capacitance and facilitates device integration. As a wave energy harvester, stable and efficient energy harvesting is thereby achieved (Table. R4).

Solid-liquid electron transfer mechanism: The ionization energy of OH^- is much lower than that of H_2O (J. Phys. Chem. Lett. 11, 1789-1794 (2020)), making it easier for OH^- to lose electrons. During the electron transfer process at the solid-liquid interface, OH^- in the liquid phase acts as an electron donor, losing electrons and converting into ·OH, which then recombines to form H_2O_2. The concentration of H_2O_2 will eventually reach a critical value (Fig. R17). Based on this solid-liquid electron transfer mechanism leading to H_2O_2 production, we propose the following correlation between the components in the liquid phase and the performance of solid-liquid power generation:

(1) Solid-liquid electron transfer results in the generation of liquid phase H_2O_2 and the accumulation of charge in the solid phase. (2) Increasing the concentration of the electron donor OH^- enhances the electrical performance output. (3) Adding H_2O_2 will result in a decrease in the energy output of the solid-liquid system.

Table R4. Comparison of power output performance of HEG and related wave energy harvesting devices.

References	Type of device	Energy source (solid-liquid or solid-solid)	Peak Power Density (W/m^3)	Device volume (cm^3)
16	TENG	S-L	0.228 W/m^3	39.7 cm^3
17	TENG	S-S	0.91 W/m^3	15.386 cm^3
18	TENG	S-S	6.67 W/m^3	17.54 cm^3
19	TENG	S-L	13.1 W/m^3	11.3 cm^3
20	TENG/EMG	S-S	18.98 W/m^3	170 cm^3
21	TENG/EMG	S-S	31.6 W/m^3	523.58 cm^3
22	TENG/EMG	S-S	162.01 W/m^3	170 cm^3
23	TENG	S-S	200 W/m^3	30000 cm^3
24	TENG	S-S	358 W/m^3	400 cm^3
Our work	TENG	S-L	Half ≈ 2877 W/m^3 Single ≈ 5754 W/m^3	17.66 cm^3

16. Ouyang, R. et al. *Nano Energy* **102**, 107749 (2022).
17. Zhang, Q. et al. *Nano Energy* **103**, 107810 (2022).
18. Jung, H. et al. *Nano Energy* **99**, 107365 (2022).
19. Wu, H. et al. *Adv. Energy Mater.* **11**, 2100038 (2021).
20. Han, C. et al. *Adv. Funct. Mater.* **32**, 2205011 (2022).
21. Hong, H. et al. *Energ. Environ. Sci.* **15**, 621-632 (2022).
22. Zhu, C. et al. *Adv. Energy Mater.* **13**, 2301665 (2023).
23. Zhang, C. et al. *Adv. Energy Mater.* **11**, 2003616 (2021).
24. Zhang, C. et al. *Adv. Funct. Mater.* **32**, 2111775 (2022).

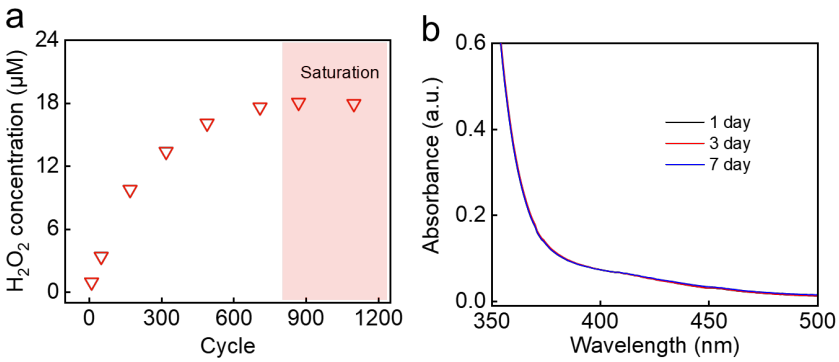


Fig. R17 The concentration of H_2O_2 reaches a critical value. a The friction cycle affects the concentration of H_2O_2 produced. **b** UV spectrum of PTO added to water after phase friction (the friction time was 1 day, 3 day and 7 day).

- **Mechanism of free radical generation:**

Due to electron transfer at the solid-liquid interface, OH^- loses electrons as an electron donor in the liquid phase, resulting in the production of ·OH. O_2, being an oxidizing agent, can acquire electrons from the solid surface and transform into superoxide radicals, which in turn leads to a decrease in the electrical properties of the material surface.

We investigated the effect of ·OH and superoxide radicals on H_2O_2 production using free radical scavengers. The addition of p-benzoquinone (superoxide radical scavenger) reduced H_2O_2 production to 9.87 μM, while the introduction of tert-butano (·OH scavenger) lowered the liquid-phase H_2O_2 concentration to 1.16 μM. These results indicate that hydroxyl radicals play a dominant role in H_2O_2 formation.

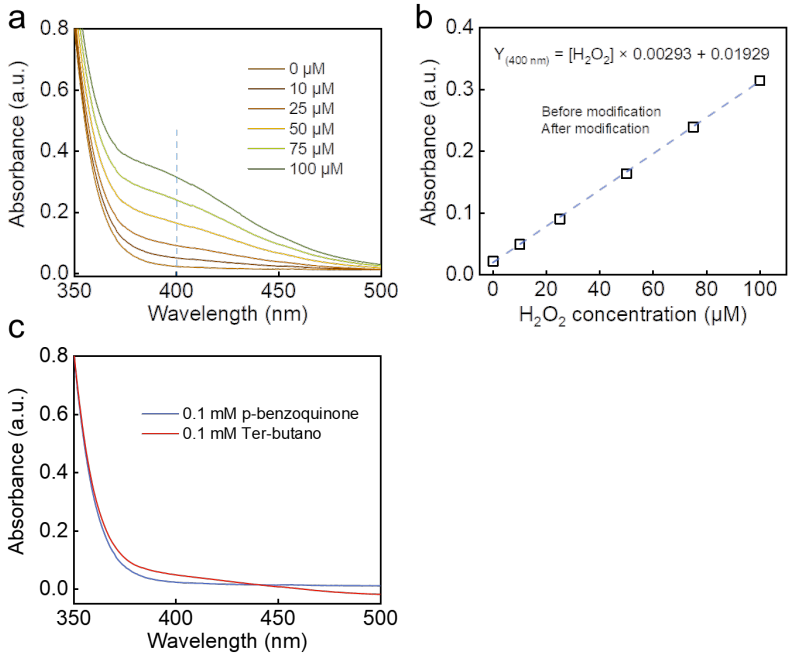


Fig. R18 Effects of free radical scavengers on H_2O_2 production

- **Effects of oxygen and bond breaking on free radicals:**

The presence of oxygen can indeed affect free radical generation, as it promotes the formation of superoxide radicals. However, an increase in oxygen concentration can degrade the surface electrical properties of the solid phase (ACS Nano 14, 17354-17364 (2020)), which is not conducive to the liquid-solid electron transfer to produce •OH. On the other hand, bond breaking, particularly during solid-liquid mechanical interactions at the interface, may lead to the formation of free radicals.

We agree that a more detailed examination of how the presence of oxygen and bond breaking affect the generation and reactivity of free radicals is important for understanding the spontaneous H_2O_2 production. However, as our study focuses on solid-liquid power generation, our primary interest lies in the relationship between H_2O_2 production and electrical properties, as well as exploring ways to enhance the electron donors in the liquid phase to improve electron transfer efficiency.

- **Our revision to the manuscript:**

We added Fig. R17 as Fig. S23 and added Fig. R18 as Fig. S21. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

2. This work is linked to H_2O_2 as an energy harvesting device for water. However, the production of H_2O_2 is very trace and does not affect the actual device output very much.

Response: We agree with your view that the yield of H_2O_2 is very trace. However, we believe that the trace amounts of H_2O_2 generated at the solid-liquid interface do have a certain impact on the electrical performance. By adding 0.1 mM of tert-butanol to the liquid phase to scavenge hydroxyl radicals, we were able to reduce the H_2O_2 yield (Fig. R), which in turn led to an improvement in the electrical performance (Fig. R19).

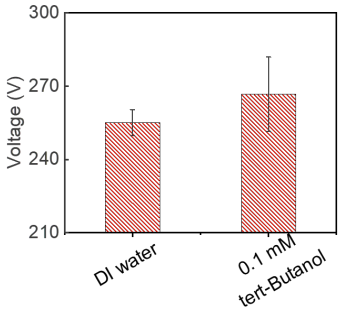


Fig. R19 Effect of tert-butanol on electrical performance output

To further investigate the effect of H_2O_2 on electrical properties, we examined the mechanism of solid-liquid power generation, dividing it into the charging stage and the saturation stage. We then studied the impact of H_2O_2 on electrical properties at each stage. The specific experiments and conclusions are as follows:

- **Mechanism of solid-liquid power generation:**

Solid-liquid power generation consists of the charging stage and the saturation stage (Nature, 578, 392-396 (2020)). In the charging stage, periodic contact between the solid and liquid phases causes electrons to transfer from the liquid to the solid phase. During this stage, the electrical signal arises from contact electrification and electrostatic induction. As the solid phase charge density accumulates, the electrical performance gradually increases. When the solid-phase charge density approaches saturation and the solid-liquid electron transfer reaches equilibrium, the system enters the saturation stage (Fig. R20). At this point, the electrical signal, driven by electrostatic induction, reaches its maximum and stabilizes. The solid-phase charge density during the saturation stage is the key factor influencing electrical performance output.

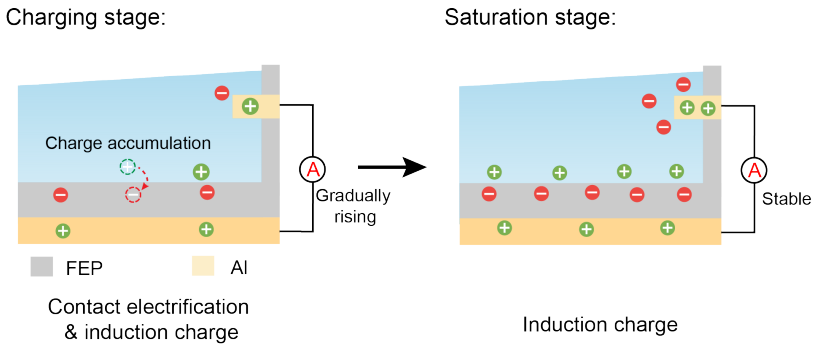


Fig. R20 Solid-liquid power generation consists of the charging stage and the saturation stage.

- **Effect of H_2O_2 on solid-liquid electron transfer (charging stage):**

In the experiment, we tested the electrical performance output of deionized water and 0.1 mM H_2O_2 during the solid-liquid friction process, as well as the change in solid surface potential after friction. During the "charging stage", as solid-phase charge density accumulated, the voltage signal gradually increased to reach equilibrium. However, the addition of H_2O_2 weakened the voltage performance output (Fig. R21a). This effect is due to the presence of H_2O_2, which reduces electron transfer, resulting in a change in solid surface potential from -840 V to -512V (Fig. R21b).

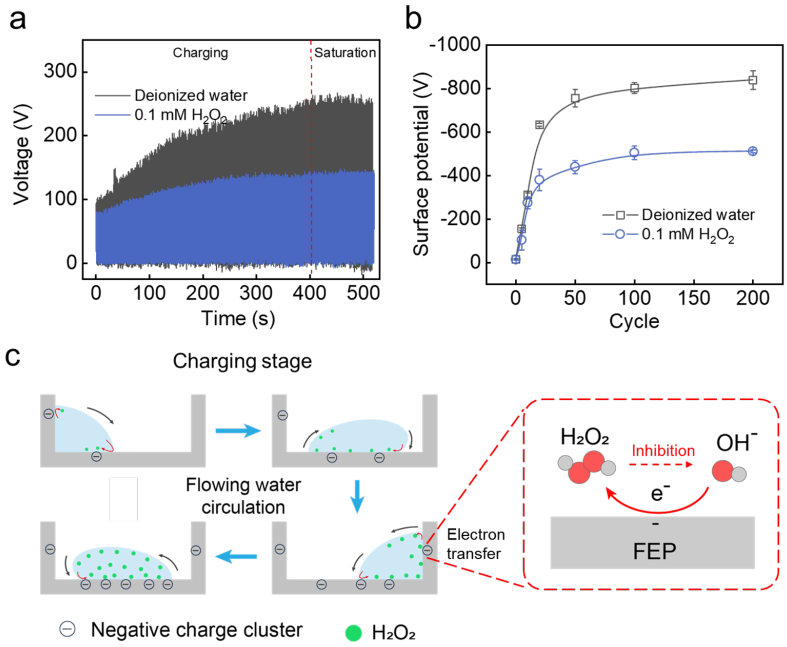


Fig. R21 Effect of H_2O_2 on solid-liquid properties. a Effect of H_2O_2 on voltage performance of solid-liquid power generation (charging stage and saturation stage). **b** Effect of H_2O_2 on solid surface potential. **c** Electron transfer generates H_2O_2, and an excess amount of H_2O_2 has the potential to inhibit electron transfer.

- **Effect of H_2O_2 on solid-liquid charge balance system (saturation stage):**

It is noteworthy that, unlike ions that directly affect solid-liquid interface performance by intervening in the double electrical layer, H_2O_2 does not impact the electrical properties of the solid-liquid system after surface charge balance is achieved. We designed the following comparative experiments: Experiment I served as the control group, where the voltage reached 255 V (Fig. R22a) after solid-liquid friction charge balance was achieved. Next, we removed the water from the tube, obtaining both the tube with solid-liquid friction charge balance and the water. Experiment II involved adding 0.1 mM H_2O_2 to the friction tube; Experiment III consisted of injecting the friction water into a tube heated to 513 K (thermally excited electrons).

In Experiments I and II, the solid phase was at charge saturation, and the additional H_2O_2 did not significantly affect the electrical performance output, indicating that H_2O_2 does not impact the electrical properties during the "saturation stage" (Fig. R22b). However, in Experiment III, there was a noticeable decrease in electrical performance. This decline is attributed to the presence of a small amount of H_2O_2 in the water after solid-liquid friction, which affects the solid-liquid electron transfer during the "charging stage", leading to a reduction in electrical performance.

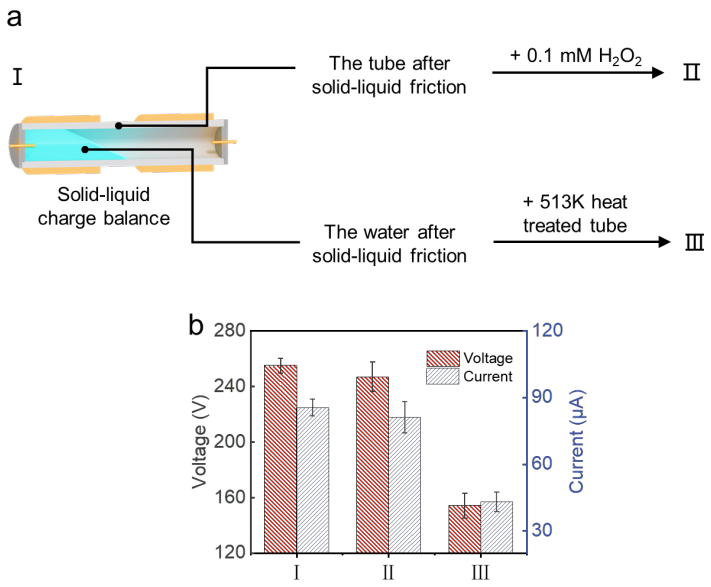


Fig. R22 Effect of H_2O_2 on the solid-liquid electrical properties in the charging and saturation stages. a Experiment I Control group; Experiment II 0.1 mM H_2O_2 was added to the tube after solid-liquid friction; Experiment III Electron thermal excitation tube was added with water after solid-liquid friction. **b** Experiment I, II and III voltage and current performance.

- **Our revision to the manuscript:**

We added Fig. R20 as Fig. S24, added Fig. R21 as Fig. S28 and added Fig. R22 as Fig. S29. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

3. Does the generation of hydrogen peroxide have an effect on the degradation performance of the output of triboelectric devices?

Response: We believe this will impact the degradation performance. As mentioned in the response to question 1, H_2O_2 will gradually reach a critical value during the solid-liquid friction cycle. Additionally, the increasing concentration of H_2O_2 will affect solid-liquid electron transfer, resulting in a decrease in free radical generation. The experiment is as follows:

In the methyl orange degradation experiment, the process primarily relies on active free radicals, such as hydroxyl radicals, generated at the solid-liquid interface. We assessed the degradation performance by introducing tert-butyl alcohol (a hydroxyl radical scavenger) and H_2O_2. As shown in the Fig. 25, the degradation rates decreased

to 27.3% and 54.1%, respectively.

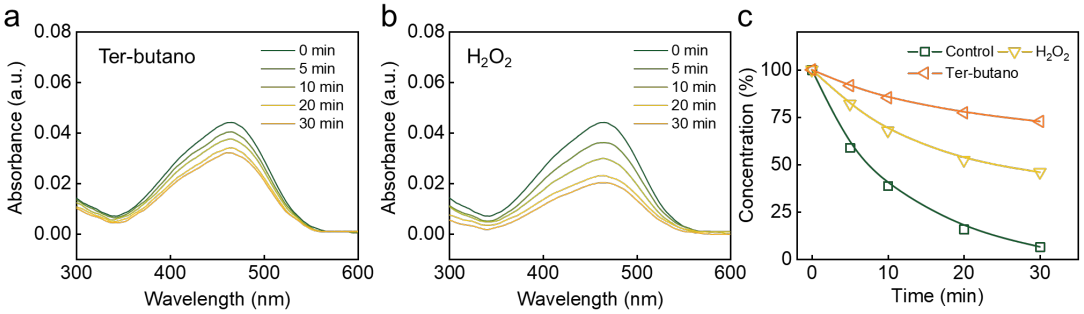


Fig. R23 Effects of 1 mM tert-Butanol and H_2O_2 on the degradation of methyl orange

- **Our revision to the manuscript:**

We added Fig. R23 as Fig. S33. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

Response to Reviewer #3

General comment: *Thank you for giving me the opportunity to review the paper of Hu Y. et al, entitled "Solid-liquid interface charge transfer for generator of H_2O_2 and energy". The paper herein presents a system capable of simultaneously generating hydrogen peroxide and electrical energy from mechanical energy. To do so, the system relies on the use of charge transfers induced by solid-liquid triboelectrification, the concept of contact-electro-catalysis discovered in Zhong Lin Wang's group, and a design for the electrical generator that is inspired by the droplet generator of Wang Zuankai's research group. Although there are some obvious issues that would be difficult to solve for reaching practical applications of this device regarding the collection of the hydrogen peroxide produced, the concept is interesting and worth exploring.*

While I do not see many problems with the experimental part concerning the engineering, sometimes it is very obvious that some of the basic science behind the experiments is not well understood, such as the interpretation of the results of figure 2e (see question 2e). This should absolutely be corrected before considering publication.

When it comes to the literature review, while it is rather thorough overall, the way it is cited in the manuscript is sometimes inconsistent (see question 2), and need to be improved. Some other issues concerning the way the literature review is conducted are much more concerning. Sometimes papers are not properly cited where they should obviously be (see itemized questions below). For example, in several instances, the main body of manuscript is written in a way that makes the reader believe it is presenting an original thought, while they are actually drawn from the literature cited in the introduction (see itemized questions below). Moreover, it seems, from the way the paper is written, that the corpus cited has not been in some instances well understood. I believe it has been understood, actually, from the rest of the main body of the text, but this needs to be improved in order not to confuse future readers and cause misunderstanding of concepts related to the topic. I understand that the requirement in terms of conciseness makes it difficult to express clearly, but these clarifications are needed.

The paper cannot be accepted for publication as is, but could be after this round of review. Below, you will find a point-by-point, but not exhaustive, list of the issues that needs to be corrected for this paper to be suitable for publication. You should not only correct the specific issues I mentioned below, but to also correct similar ones you will

find by yourself based on the ones I already pointed out.

Response: Thanks for your review and we appreciate your feedback. For Fig. 2e, we designed a more detailed and accurate KPFM test based on the relevant literature (Nat. Commun. 11, 399 (2020)) and demonstrated that electron transfer at the solid-liquid interface is dominant in our system (Question 6). Additionally, we sincerely apologize for the oversight in properly citing references. We have carefully reviewed and corrected the citation format in the text and marked the relevant references for non-original mechanisms and theories. We have carefully revised the manuscript according to your comments. The replies to each of your concern are listed below.

1. In the introduction, you first talk about solid—liquid interfaces, and charge transfers and evocate that the charge could be radicals, citing the papers of Bartosz' group. These papers are talking about the nature of the charges responsible for the chemical activity of polymers tribocharged by solid-solid friction. To avoid confusion for new readers, who may think it is related to solid-liquid contact electrification, it would be wise to revise this passage and make it clearer on that matter.

Response: Thank you for your valuable comment. To better clarify the distinctions between solid-solid and solid-liquid charge transfer, we have revised the introduction as follows: "In fact, even at solid-solid interfaces, there remains controversy over whether the transferred charge involves electrons, ions, or free radicals. At solid-liquid interfaces, the fluidity and dispersion of liquids, along with ion adsorption, introduce even greater uncertainty." Corresponding changes have been marked in red in the revised manuscript.

2. Line 45, concerning reference 18 and 19, I am confused as to why they are referred to as Wang et al. The first authors are Berbille A. for one and Zhao J. for the other. Moreover, these two papers do not share the same last author. This should be corrected as to reflect the authors contribution to the corpus appropriately. Please, also check other citations.

Response: Thank you for your careful comment. We revised it to "Wang's group and Fan's group" to distinguish these two references and updated the citation format for the other references. Corresponding changes have been marked in red in the revised

manuscript.

3. Line 50, "Electron transfer at the solid-liquid interface not only induces chemical reactions within the liquid phase but also involves the transfer of a amounts of energy." Please correct "a amounts of energy" for "energy" or "an amount of energy". Regardless, chemical reactions are a form of transfer of energy (mechanical to chemical here). The transfer of electrons is the result of an input of mechanical energy in the thermodynamic system, that then undergoes a change to find equilibrium. I believe you want to evocate electrical power when you employ the term "energy". I am afraid the wording employed here may confuse some readers. You could improve this by completing the sentence and adding that "[it] can take the form of electrical signals when electrodes are part of the system" or, something in this spirit. Same issue on Line 111.

Response: Thank you for your valuable comment. In the revised manuscript, we revised them to "electron transfer at the solid-liquid interface not only initiates chemical reactions within the liquid phase but also generates electrical signals when electrodes are part of the system," and "electron transfer at the solid-liquid interface can generate electrical signals when electrodes are included in the system". Corresponding changes have been marked in red in the revised manuscript.

4. Citations are missing for the statements of Line 75, 76, 80-84. Moreover, the type of mechanism proposed in fig 1b has already been proposed in other works. Including, but not only, Adv. Funct. Mater. 2024, 34, 2315817. https://doi.org/10.1002/adfm.202315817 and by other papers already cited, such as ref 18 and 19.

Response: Thank you for your valuable comments. We cited the references in the relevant sections. In the original manuscript, Fig. 1b presents a surface state model used to characterize electron transfer between solid and liquid. This model is widely recognized in the field of contact electrification. We have transferred it to the supplementary material. Corresponding changes have been marked in red in the supplementary material.

5. Line 117, "this design ressemble that of a field-effect transistor", while true it also

resembles the design of the droplet generator of Wang Zuankai's group cited as Ref 22 (Nature 578, 392–396 (2020). https://doi.org/10.1038/s41586-020-1985-6). I strongly suggest the authors cite this work there. As well. There are many similar issues throughout the text where the writing leads the reader to think an original idea is presented, while it is the adaptation of the work of others. This is most probably an honest mistake, but this kind of issues needs to be addressed as they can mislead future greaders.

Response: In terms of structural design, we refer to the design of the droplet generator design from Wang Zuankai's group but have implemented several improvements. These include adding a PS isolation layer and converting the unstable titration-based power generation into a continuous liquid flow system. We have added references to relevant literature in the revised manuscript, with corresponding changes marked in red.

6. I fail to understand how figure 2e is conducive of electron transfer. It is conducive to a transfer of charge, but the KPFM method cannot distinguish electrons from ions. To do so, you would need to reproduce a similar experiment to that of Lin et al. from citation 10, which you did conduct fully here. The data showed does not prove that electrons were transferred, only that a charge has been transferred (electrons, ions, or radicals). Please correct this issue, either by completing this experiment, or by drawing the proper conclusions.

Response: We designed more detailed and accurate experiments based on the referenced citations, demonstrating that electron transfer is the dominant process. The testing methods and results are as follows:

Using KPFM to distinguish between electron transfer and ion transfer mechanisms at the solid-liquid interface: According to the literature (Nat. Commun. 11, 399 (2020)), at high temperatures (513 K), electrons are thermally excited and emitted from the surface (Fig. R24a), while ions remain on the surface. This means that under high-temperature heating treatment, by characterizing the changes in the FEP surface potential or charge density after solid-liquid friction, we can determine whether the surface charge of FEP is predominantly due to electrons or ions.

Experimental Design: A 25 μm thick FEP film was selected for the experiments. Before testing, all samples were heated at 513 K for 15 minutes to remove surface charges. During the experiment, the FEP film was continuously flushed with water

droplets for 10 min until the surface charge of the film was saturated. The samples were then heated at 353 K for 5 minutes to remove moisture and ensure the surface remained dry. The film was fixed onto a silicon wafer, and the surface potential was measured using a KPFM probe. After heating the samples again at 513 K for 30 minutes, the surface potential was tested with the KPFM probe (Fig. R24b).

As shown in Fig. R25b and R25d, the surface potential drops from -1.06 V to -4.61 V before and after solid-liquid friction, indicating charge transfer at the solid-liquid interface. When heated to 513 K, electrons are thermally excited and emitted from the surface, returning the surface potential to -1.16 V. During two friction-thermal excitation cycles (Fig. R26), the surface potential remains close to the initial potential, suggesting that electron transfer is dominant in the contact process between FEP and water.

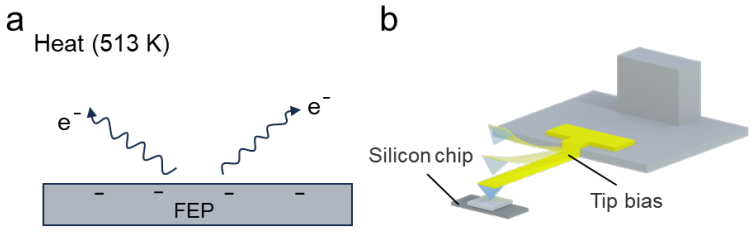


Fig. R24 KPFM test of solid surface potential a Thermal emission of electrons on solid surface, **b** Schematic of the apparatus for KPFM measurement of solid surface potential.

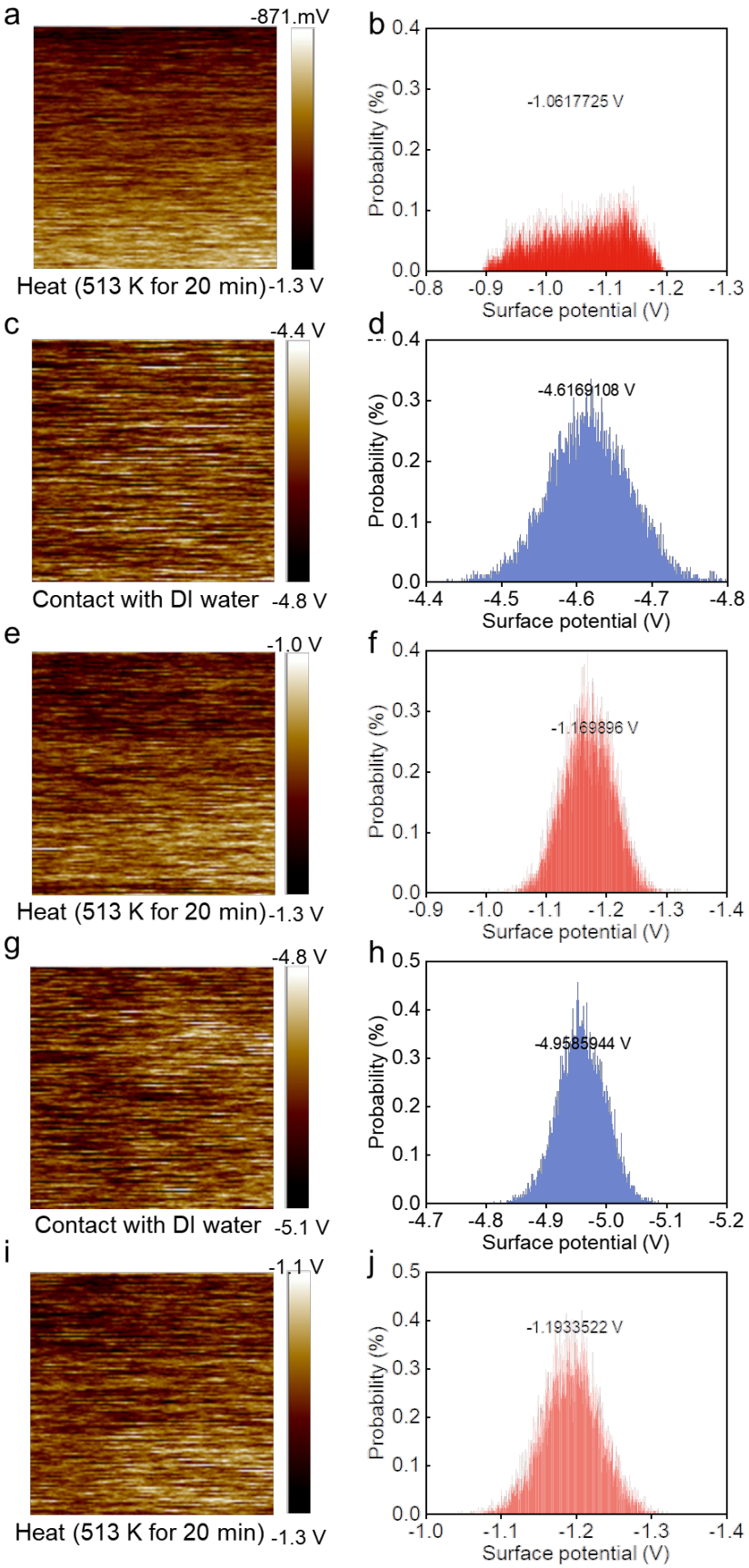


Fig. R25 Friction-thermal excitation cycle surface potential test. a, c, e, g, i Solid KPFM images. **b, d, f, h, j** Surface potential distribution of KPFM results.

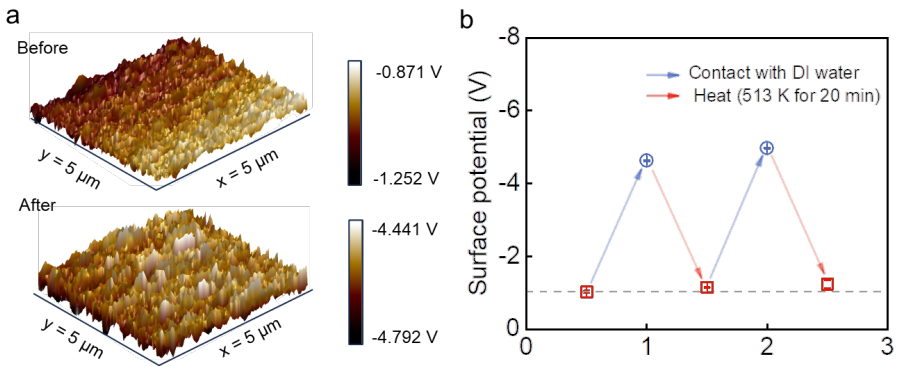


Fig. R26 KPFM potential change diagram before and after solid-liquid friction.

- **Our revision to the manuscript:**

We added Fig. R24 as Fig. S2, added Fig. R25 as Fig. S3 and added Fig. R26 as Fig. S4. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

7. In line 196, you observed a decrease of the electrical output from the generator when the concentration of hydrogen peroxide increases. Could you explain why?

Response: Solid-liquid power generation consists of the charging stage and the saturation stage (Nature, 578, 392-396 (2020)). In the charging stage, periodic contact between the solid and liquid phases causes electrons to transfer from the liquid to the solid phase. During this stage, the electrical signal arises from contact electrification and electrostatic induction. As the solid phase charge density accumulates, the electrical performance gradually increases. When the solid-phase charge density approaches saturation and the solid-liquid electron transfer reaches equilibrium, the system enters the saturation stage (Fig. R27). At this point, the electrical signal, driven by electrostatic induction, reaches its maximum and stabilizes. The solid-phase charge density during the saturation stage is the key factor influencing electrical performance output.

Here, we propose that, unlike ions that directly impact interfacial properties, H_2O_2, as a liquid-phase electron transfer product, affects solid-liquid electron transfer (charging stage) when added in excess to water. This addition results in a decrease in solid surface charge density at equilibrium (saturation stage), thereby reducing electrical transmission. Notably, adding H_2O_2 to a system with a saturated solid-liquid interface charge does not significantly impact electrical performance. Relevant tests are as follows:

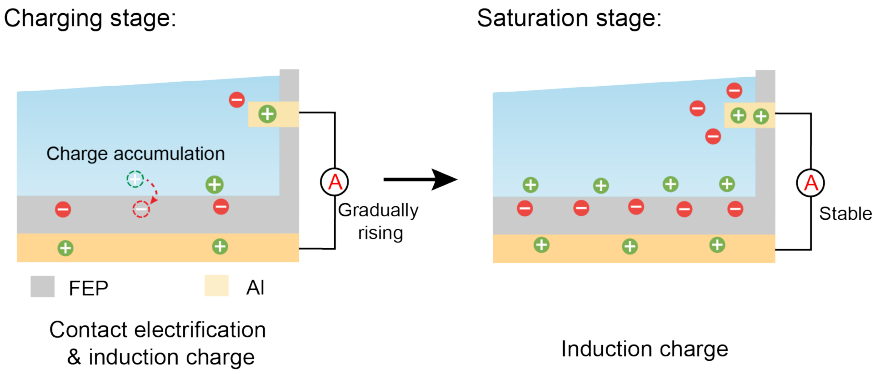


Fig. R27 Solid-liquid power generation consists of the charging stage and the saturation stage.

- **Effect of H_2O_2 on solid-liquid electron transfer (charging stage):**

In the experiment, we tested the electrical performance output of deionized water and 0.1 mM H_2O_2 during the solid-liquid friction process, as well as the change in solid surface potential after friction. During the "charging stage", as solid-phase charge density accumulated, the voltage signal gradually increased to reach equilibrium. However, the addition of H_2O_2 weakened the voltage performance output (Fig. R28a). This effect is due to the presence of H_2O_2, which reduces electron transfer, resulting in a change in solid surface potential from -840 V to -512V (Fig. R28b, c).

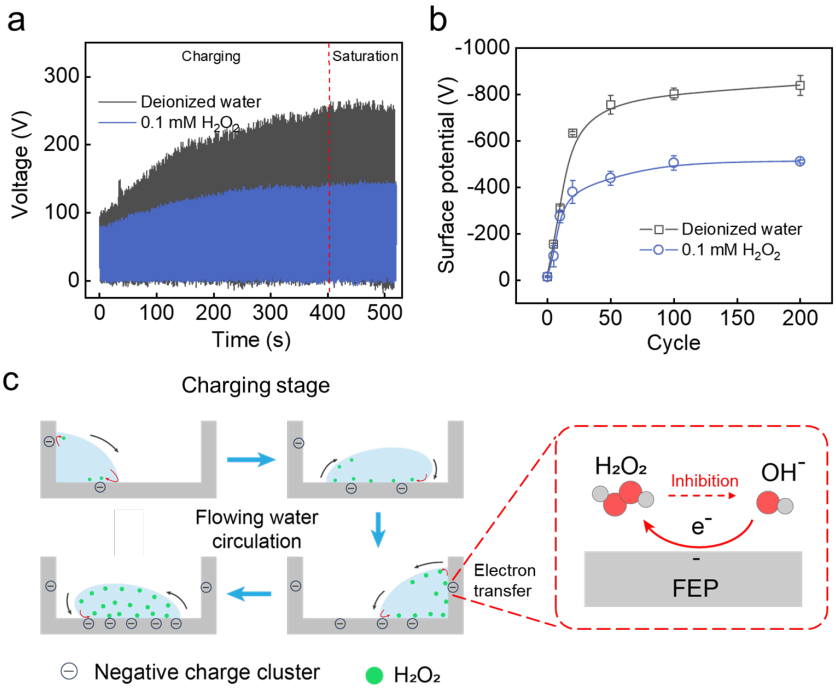


Fig. R28 Effect of H_2O_2 on solid-liquid properties. a Effect of H_2O_2 on voltage performance of solid-liquid power generation (charging stage and saturation stage). **b** Effect of H_2O_2 on solid surface potential. **c** Electron transfer generates H_2O_2, and an

excess amount of H_2O_2 has the potential to inhibit electron transfer.

- **Effect of H_2O_2 on solid-liquid charge balance system (saturation stage):**

It is noteworthy that, unlike ions that directly affect solid-liquid interface performance by intervening in the double electrical layer, H_2O_2 does not impact the electrical properties of the solid-liquid system after surface charge balance is achieved. We designed the following comparative experiments: Experiment I served as the control group, where the voltage reached 255 V (Fig. R29a) after solid-liquid friction charge balance was achieved. Next, we removed the water from the tube, obtaining both the tube with solid-liquid friction charge balance and the water. Experiment II involved adding 0.1 mM H_2O_2 to the friction tube; Experiment III consisted of injecting the friction water into a tube heated to 513 K (thermally excited electrons).

In Experiments I and II, the solid phase was at charge saturation, and the additional H_2O_2 did not significantly affect the electrical performance output, indicating that H_2O_2 does not impact the electrical properties during the "saturation stage" (Fig. R29b). However, in Experiment III, there was a noticeable decrease in electrical performance. This decline is attributed to the presence of a small amount of H_2O_2 in the water after solid-liquid friction, which affects the solid-liquid electron transfer during the "charging stage", leading to a reduction in electrical performance.

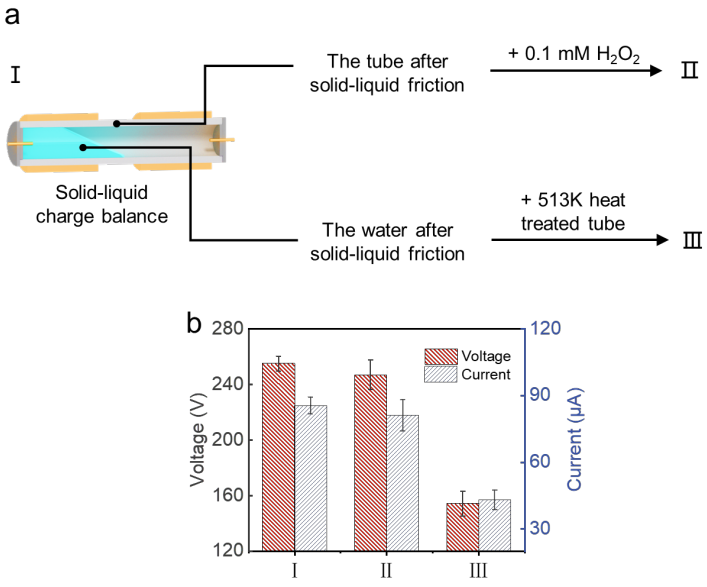


Fig. R29 Effect of H_2O_2 on the solid-liquid electrical properties in the charging and saturation stages. a Experiment I Control group; Experiment II 0.1 mM H2O2 was added to the tube after solid-liquid friction; Experiment III Electron thermal excitation tube was added with water after solid-liquid friction. **b** Experiment I, II and III voltage

and current performance.

- **Our revision to the manuscript:**

We added Fig. R27 as Fig. S24, added Fig. R28 as Fig. S28 and added Fig. R29 as Fig. S29. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

8. Line 232, it would be preferable to replace "H_2O_2 preparation" by "H_2O_2 production" or "H_2O_2 generation".

Response: Thank you very much for your careful review. We have changed "H_2O_2 preparation" to "H_2O_2 generation" and marked these changes in red in the manuscript.

9. Concerning the results of fig. 4b, it would be interesting to conduct a capture experiment, i.e., comparing the rate of the original degradation reaction with the same experiment conducted in presence of radical scavengers (EDTA, p-Benzoquinone, $AgNO_3$, ter-butanol, hindering the effects of holes, superoxide anions, electrons, and hydroxyle radicals, respectively). Thus, you could compare the results from your experiments and those previously presented in ref 16. I expect the results could be different, and could help you distinguishing your paper from previous publications on contact electro catalysis. Same could be done concerning H_2O_2 production.

Response: We added 0.1 mM of each of the four free radical scavengers or H_2O_2 to a 0.5 ppm aqueous solution of methyl orange to test changes in methyl orange concentration. Next, we added the four free radical scavengers into the solid-liquid system and measured the H_2O_2 concentration following solid-liquid friction. The experimental results are as follows:

- **Methyl orange degradation test:**

EDTA has almost no effect on the degradation of methyl orange (Fig. R30). However, in the $AgNO_3$ solution, the freely moving anions and cations influence interfacial charge transfer, slightly reducing the degradation rate of methyl orange from 93.5% to 84.5%.

In Fig. R31, p-benzoquinone as a superoxide anion scavenger and tert-butanol as a hydroxyl radical scavenger both had significant adverse effects on the degradation experiments. Our results are generally consistent with those in Ref. 16, with the

exception that, in our tests, tert-butyl alcohol showed a slightly greater impact on degradation than p-benzoquinone. This suggests that hydroxyl radicals play a primary role in the degradation of methyl orange. This difference may be due to our pre-treatment of the tube with electron thermal excitation, which transferred electrons from the liquid phase to the solid phase, generating more hydroxyl radicals.

Notably, the addition of H_2O_2 also impacts the methyl orange degradation experiment, indicating that excess H_2O_2 affects free radical generation. This finding further supports the view in question 8 that H_2O_2 influences solid-liquid electron transfer.

- **H_2O_2 concentration test:**

During the formation of H_2O_2 at the solid-liquid interface, current research widely agrees that O_2 participates in the reduction reaction and is accompanied by the generation of superoxide radicals (Angew. Chem. Int. Edit., 62, e202300604 (2023)). This is due to the oxidative properties of O_2, enabling it to gain electrons from the solid surface, thereby reducing the surface electrical properties of the material (ACS Nano. 14, 17354-17364 (2020)).

In Fig. R32, EDTA and $AgNO_3$ had minimal impact on the H_2O_2 yield. The addition of p-benzoquinone reduced the H_2O_2 yield to 9.87 μM, while the introduction of tert-butanol lowered the liquid-phase H_2O_2 concentration to 1.16 μM. This indicates that hydroxyl radicals play a dominant role in H_2O_2 formation.

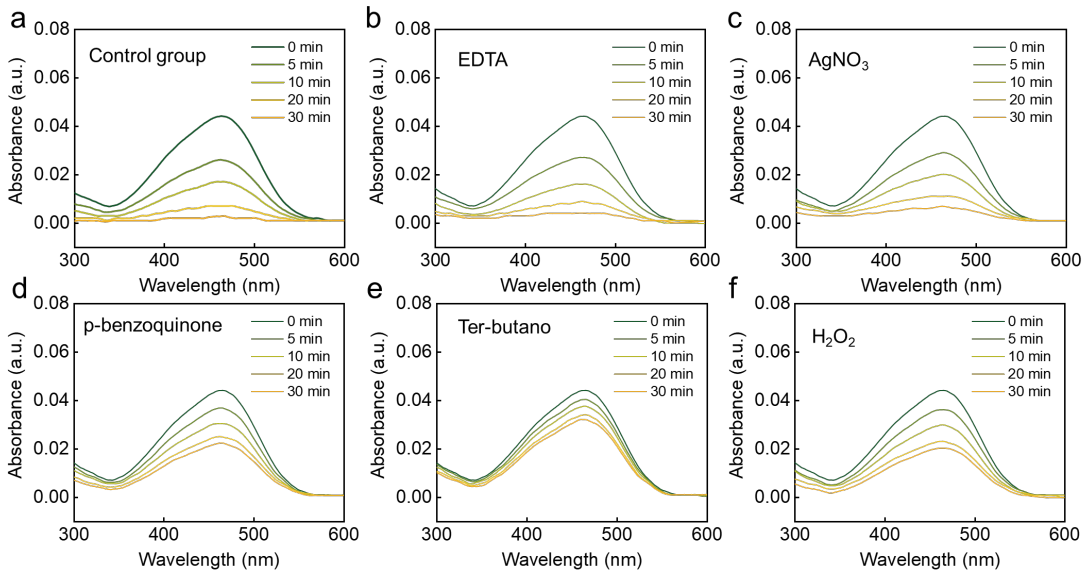


Fig. R30 Effect of adding free radical scavengers or H_2O_2 to water on the degradation of methyl orange. a Control group. **b** 1 mM EDTA. **c** 1 mM $AgNO_3$. **d** 1 mM Ter-butano. **e** 1 mM p-benzoquinone. **f** 1 mM H_2O_2.

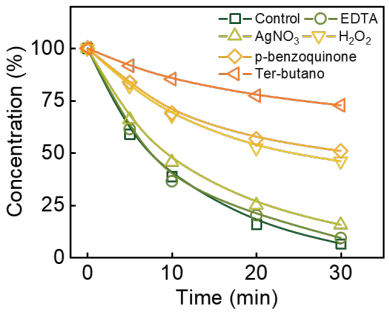


Fig. R31 Changes in methyl orange concentration under free radical scavengers and H_2O_2.

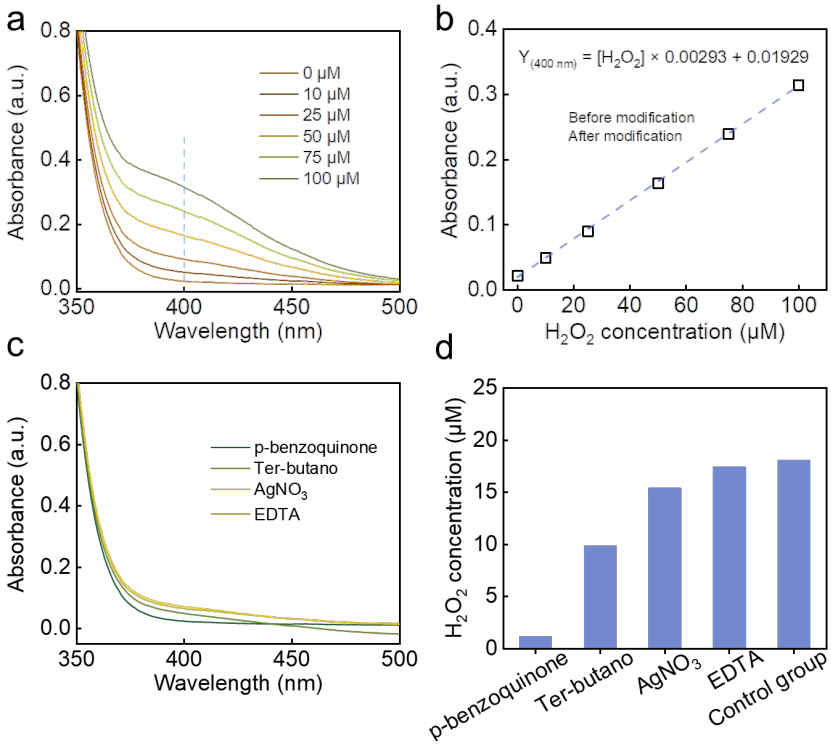


Fig. R32 Effect of free radical scavengers on H_2O_2 production. a The absorption spectrum of an aqueous PTO solution with added H_2O_2. **b** Calibration curve of absorption at 400 nm acquired from the UV absorption spectrum. **c** The absorption spectrum of an aqueous PTO solution with added free radical scavengers. **d** H_2O_2 production under different free radical scavengers.

- **Our revision to the manuscript:**

We added Fig. R30 as Fig. S33, added Fig. R31 as Fig. S34 and added Fig. R32c, d as Fig. S21. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

10. For the power generation application, you employed a rectifier bridge rather than more advanced and power efficient solutions, such as power management systems designed by Harmon W. et al. that caters specifically to the needs of TENGs (Nano Energy 71, 104642 (2020), https://doi.org/10.1016/j.nanoen.2020.104642). Why did you make this choice ?

Response: For the power generation application in Fig. 4f, we use a simple rectifier bridge and a mechanical switch to obtain instantaneous high current for driving the wireless energy module (about 10 mA). While the power management system is well-suited for building stable and efficient circuits, it is less ideal for handling this type of instantaneous high current output. On the other hand, inspired by the electronic switch in this power management system of the above literature (Nano Energy 71, 104642 (2020)), we constructed an electronic switch using Zener diode, silicon-controlled rectifiers (SCR), and resistor (Fig. R33a).

We use discrete semiconductor devices (Fig. R33b) to enable true wireless, unmanned monitoring. When the voltage stored in the capacitor exceeds the breakdown voltage of the Zener diode, current flows into the SCR gate, triggering it to turn on. The capacitor then provides an instantaneous high current supply to the wireless module. This switch design eliminates the need for mechanical switches. After the capacitor is discharged, the SCR disconnects the wireless module from the energy module circuit, and the capacitor continues to accumulate electrical energy (Fig. R33c, d).

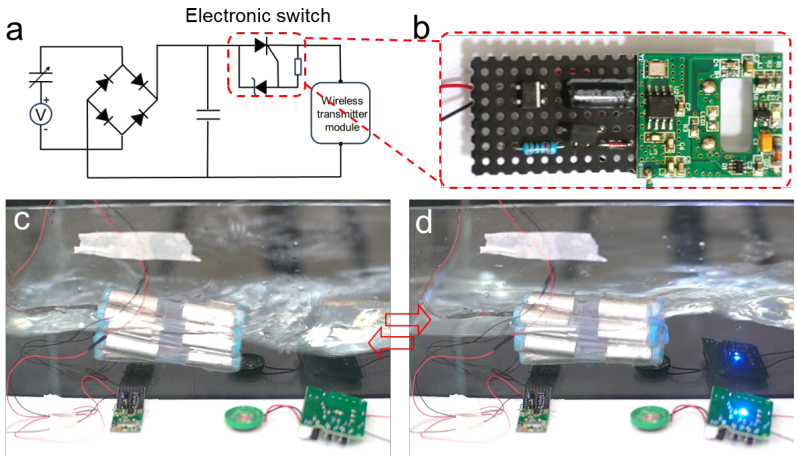


Figure R33 Wireless Monitoring System: **a** Electronic switch circuit diagram. **b** Electronic switch and wireless module device. c, d Wave-driven wireless signal transmission.

- **Our revision to the manuscript:**

We added Fig. R33 as Fig. S41. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

11. This is only a suggestion, but have you though about use your device as water purifier, not for dye contamination, but for bacterial (such as e.coli) ? The fact the dye can be degraded quickly, and that you can generate H_2O_2, indicate that it may have a good potential for decontamination of water from this type of organism.

Response: We agree with your point of view on antibacterial applications. As water flows through the tube, H_2O_2 and hydroxyl radicals are generated, which have antibacterial effects. Additionally, our structural design, which immerses a portion of the electrode in water, not only enhances the electrical signal but also generates a localized electric field on the electrode surface with potential for microbial inactivation (Nature Water, 1-10 (2024)). The following is our experiment.

Escherichia coli (E. coli, BNCC269342) was cultured on LB agar medium at 37 °C for 24 hours. The bacterial culture was then divided into three groups: Group I was injected into a modified sealed FEP tube, kept stationary, and incubated at 37 °C for 3 hours. In contrast, Groups II and III were injected into sealed FEP tubes (without electrodes) and HEG devices (with electrodes), respectively, and shaken in a shaker for 3 hours. 50 μL of bacterial suspension from each group were then transferred onto LB agar plates, spread evenly using a bacterial spreader, and incubated at 37 °C for 24 hours (Fig. R34b-d). After incubation, the plates were gently rinsed with 1X PBS and centrifuged to collect the bacterial pellet, as shown in Fig. R35a.

We characterized the antibacterial activity using the SpectraMax Paradigm Multi-Mode Detection Platform (J. Nanobiotechnol. 10, 1-9 (2012)). The wavelength of the incident light was set to 600 nm, and the optical density (OD_{600}) of the bacterial solution was measured after a tenfold dilution. As shown in the Fig. R35b, under the influence of H_2O_2 free radicals, and the localized electric field, HEG exhibits antibacterial properties.

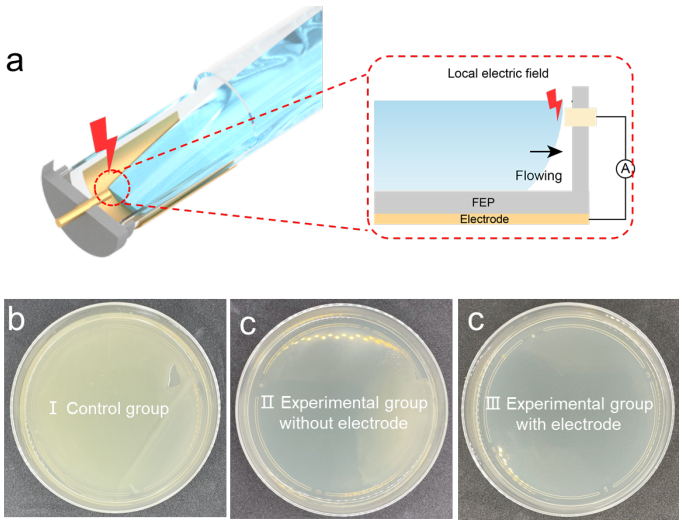


Fig. R34 The antibacterial mechanism of the HEG device. a Local electric fields for antibacterial effects. **b, c, d** Plating photographs showing antibacterial experiment.

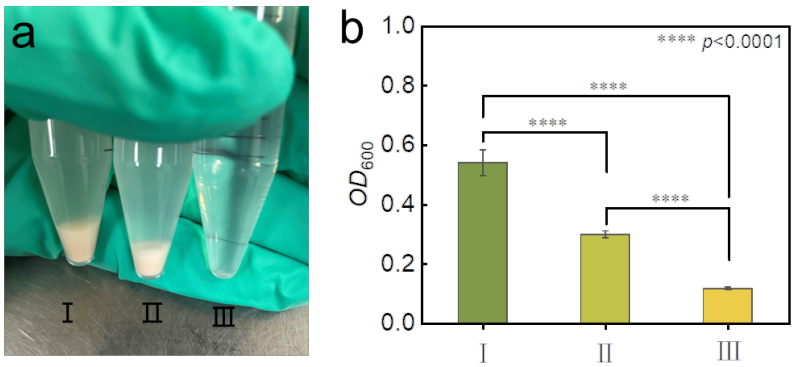


Fig. R35 Antibacterial properties of HEG devices.

- **Our revision to the manuscript:**

We added Fig. R34 as Fig. S35 and Fig. R35 as Fig. S36. Corresponding changes have been marked in red in the revised manuscript and supplementary materials.

Response to Reviewer #4

General comment: *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.*

Response: Thank you for your review and we appreciate your feedback. We have carefully revised the manuscript according to your comments.

Solid-liquid interface charge transfer for generation of H_2O_2 and energy

We sincerely thank the reviewers for their careful and thorough review, which are indeed very helpful to make the paper more solid and smooth. We have revised our manuscript very carefully in the light of their suggestions and comments.

The following responses have been prepared to address all of the reviewers' comments in a point-by-point fashion. (Comments in black, responses in blue):

Response to Reviewer #1

General comment: *All my comments have been fully addressed. This paper can now be published in the current version.*

Response: We thank the reviewer for the effort in reviewing our manuscript and the recommendation of acceptance.

Response to Reviewer #2

General comment: *All my previous considerations have been resolved. The level of this work has been greatly improved and can be accepted by Nature Communications.*

Response: We thank the reviewer for the effort in reviewing our manuscript and the recommendation of acceptance.

Response to Reviewer #3

General comment: *The authors have addressed all the questions I was concerned. I recommend its publication in NC as it is.*

Response: We thank the reviewer for the effort in reviewing our manuscript and the recommendation of acceptance.

Response to Reviewer #4

General comment: *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.*

Response: We thank the reviewer for the effort in reviewing our manuscript and the recommendation of acceptance.