nature portfolio

Peer Review File

Moisture-based green energy harvesting over 600 hours via photocatalysis-enhanced hydrovoltaic effect

Corresponding Author: Professor Tingting Yang

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)
Moisture-enabled electric generator (MEG) technology converts the energy from the gas-liquid phase change of moisture into electrical energy, providing green and clean advantages with broad applicability. Key performance indicators for MEGs are power density and lifespan. Recent advancements have significantly improved power density from 18.4 nW/cm² to ~12 μW/cm². However, lifespan remains a challenge, with many MEGs operating only for seconds to hours, limiting large-scale application. Efforts to improve MEG lifespan focus on continuous moisture absorption-desorption and maintaining ion concentration gradients. New materials (e.g., protein nanowires, graphene oxide) and structures (e.g., PN junctions) have extended continuous output voltage times but maintaining current output is still problematic due to ion migration dynamics. This study proposes using photocatalysis to rebuild the ion concentration gradient, restoring current output. The device, comprising a hydrogel moisture-enabled electricity generation layer, a photocatalytic layer, and inert electrodes, achieves an output VOC of 0.28 V and a peak ISC of 1.8 μA in high humidity without light. Light stimulation rebuilds the ion gradient, extending current output to 650 hours, advancing the sustainable development of MEGs.
While the impressive short circuit current and long-term stable electrical output are noteworthy, the use of photocatalysis is innovative. However, the authors have not provided sufficient evidence to convincingly support the exact mechanism behind this. Therefore, major revisions are necessary, and the following concerns must be addressed before this manuscript can be published in Nature Communications. Moreover, this cannot be considered a new finding, as several studies with a similar concept have already been published. (Yang, S., Zhang, L., Mao, J. et al. Green moisture-electric generator based on supramolecular hydrogel with tens of milliamp electricity toward practical applications. Nat Commun 15, 3329 (2024). Fu, Chunqiao, et al. A Long Life Moisture-Enabled Electric Generator Based on Ionic Diode Rectification and Electrode Chemistry Regulation. Advanced Science 11.15 (2024): 2305530.).

Here, there are several crucial issues that need to be addressed:
1. I would like to inquire whether the MEG in this study, which consists of multiple layers, has been optimized for each individual layer, and whether any comparisons have been conducted. If so, could the authors please provide detailed optimization procedures and results?
2. Can the author provide more detailed evidence and explanation for the mechanism by which photocatalysis rebuilds the ion concentration gradient and restores current output?
3. Can the author elaborate on the choice of materials (e.g., protein nanowires, graphene oxide) and structures (e.g., PN junctions) used in their MEG? How do these contribute specifically to performance improvements?
4. Can the author check the durability of this device and perform recycling tests? On page 7, line 139, they mentioned that 'Moreover, after the photocatalytic reconstruction of the ion concentration gradient, the device power generation is restored, and the current output time can be extended to 650 hours, while the voltage can remain stable for a long time (Supplementary Fig. 1).' However, if the current output is continuously decreasing, can we truly say that it is stable?
5. How about modifying Fig. 5 to improve its quality? It is not easily visible at a glance, especially Fig. 5a to 5f.
6. The power output of advanced MEGs primarily depends on their water capture capability and the established water gradient. In terms of material design, how can the materials balance high moisture absorption with maintaining a sustainable moisture gradient? What specific characteristics are necessary for these materials? Please summarize a general strategy.
7. While the author mention the addition of a photocatalytic layer to address ion concentration gradient issues, the exact effect of photocatalysis on device performance could be elaborated further. What specific improvements are observed with the inclusion of photocatalysis, and how does it compare to the performance without it?
8. On page 10, line 200, they mentioned that 'At the same time, the impedance test shows that the device has good

conductivity, which is conducive to the migration of hydrogen ions inside the device (Supplementary Fig. 6). However, there is insufficient relevant analysis to support the above conclusion. Additional explanation or evidence is required.
9. The manuscript describes the process of photogenerated electron-hole separation and recombination with hydrogen ions. Could the authors provide a more detailed explanation of these mechanisms, perhaps with a diagram to illustrate the process more clearly?

Reviewer #2

(Remarks to the Author)
The manuscript entitled by “Moisture based green energy harvesting over 600 hours via photocatalysis-enhanced hydrovoltaic effect” introduces an interesting design of coupling photocatalysis and hydrovoltaics to synergistically improve power generation. Authors clearly show the superiorities of using photocatalysis to consume H+ and rebuild the ion concentration gradient. I recommend to publish this work after some revisions:
Major
1. The authors clearly explained the promoting effect of photocatalysis on power generation. Conversely, power generation also provides additional H+ for photocatalysis. Can this additional H+ effectively enhance the performance of photocatalysis?
2. Currently, the duration of the hydrovoltaic power generation device can exceed one month. Please conduct a thorough literature review.
3. The authors mentioned that the redox reactions of the electrodes can significantly increase energy input, but the energy source is not green. In this work, the authors used a more complex multi-component carbon bottom electrode. Could this lead to potential redox reactions at the bottom?
4. Why didn't the authors place the PCL layer above the MEL layer to reduce the loss of sunlight transmission? Also, I suggest improving Figure 1a to clearly illustrate the transmission of sunlight.
5. Authors clearly show the synergetic effects by using pH value testing. I suggest considering some theoretical calculations such as MD or first-principle to solid this important mechanism.
6. I suggest evaluating continuous experimental results for over 600 hours with many intermittent illumination. Specify how many times the illumination is applied over 600 hours and report the overall water production and the highest performance in power generation and hydrogen production.
7. In fig. 4d, the device without PCL layer also shows an obvious electrical output recovery. Please explain this phenomenon.
8. In fig. 5h, authors show that the developed device has good harsh condition adaptability. Please show more evidence.
Minor
9. In the abstract, the device is described as being divided into two parts, while in the Introduction, it is said to be divided into three parts. Please make them consistent
10. The phrasing of this sentence on the third page is not precise enough: “the voltage depends on the separation degree of opposite charge carriers, and the current depends on the continuous 61 migration of opposite charge carriers.”. Many factors can influence the voltage and current. Please provide a more precise statement and include references.
11. The PAM/AMPS/LiCl hydrogel was not a new material, please provide the reference.
12. Many sentences need necessary references such as: “releasing the negatively charged sulfonic acid groups fixed in the network and the free positively charged hydrogen ions.” “At the same time, e- will also be excited from the VB to the CB of CN, thereby generating active photogenerated electrons in the CB and photogenerated holes in the VB”. Also, I suggest adding experimental results to better support these discussions.
13. Equations 1, 2, and 4 are simplistic and do not satisfy material balance. It needs to be reviewed and revised. These equations also need references.
14. Why is the pH value in Figure 4b negative?
15. Fig. 5g is not clear enough to show the day-night continuous operation. More words should be added in the main text to explain Fig. 5g.

Reviewer #3

(Remarks to the Author)
In this manuscript, the author propose a design for reconstructing the ion concentration gradient by coupling photocatalytic hydrogen evolution reaction with hydrovoltaic effect, to report a moisture-enabled electric generator (MEG) with continuous current output. Further analysis is conducted on the generation mechanism and various performance aspects, with detailed data characteristics. However, the following issues remain:

1.When comparing Figure 4(d) with (e), it is observed that the presence of the PCL layer significantly promotes current recovery under illumination, while some degree of current enhancement is still triggered by light in the absence of PCL. Thus, it begs the question whether this is achieved through the synergy of photothermal and photocatalytic effects.
2.The device's bottom electrode employed by the author is a CNT:PEDOT:PSS composite material. It is recommended to clearly elaborate on the role of PEDOT:PSS within this system.
3.Figure 1(b) demonstrates a long-term current stability of 650 hours, yet the voltage plot in the supplementary information covers only 7 days (168 hours). To ensure data consistency and completeness, the author is advised to supplement voltage data spanning the same duration as the current tests, allowing for a comprehensive assessment of the device's long-term stability.
4.To gain a deeper understanding of the impact of illumination on device performance, the author should provide voltage-

time images under illumination conditions.
5.Claiming long device lifespan, the author is encouraged to present current and voltage response graphs encompassing at least five illumination cycles, adequately demonstrating the device's stability and durability under repeated illumination.
6.The author asserts that the reticulated structure in P-CN constitutes nanopores; however, the fifth SEM image in Figure 2(a) does not clearly show nanopore diameters, and merely relying on the negative zeta potential of P-CN (Figure 3(b)) does not fully substantiate its cation selectivity. It is recommended to design cation selectivity experiments and couple them with theoretical calculations or molecular simulations to thoroughly elaborate on the selectivity mechanism.
7.In the saturated state image of Figure 4(a), ion distribution gradients should be taken into account.
8.As observed in Figure 5(e), the voltage at an RH of approximately 97 is lower than that at an RH of approximately 75. A reasonable explanation for this phenomenon should be provided in the main text.
9.Mark the peak positions in Figure 3(f).
10.The SEM image of the bottom electrode in the last panel of Figure 2(a) is unclear.

Version 1:

Reviewer comments:

Reviewer #1

(Remarks to the Author)
The authors have well addressed most of the comments and enhanced the overall quality of the manuscript. I think that the revised manuscript is now appropriate to be published in this journal without further revisions.

Reviewer #2

(Remarks to the Author)
The authors have revised and improved the manuscript according to the suggestions, and the manuscript is recommended for publication.

Reviewer #3

(Remarks to the Author)
The revised manuscript has been well polished according to the reviewer's comments, and it is recommended to accept and publish it.

NCOMMS-24-35789A

Point-to-point response to the Reviewers' comments on the manuscript

"Moisture based green energy harvesting over 600 hours via photocatalysis-enhanced hydrovoltaic effect"

We wish to thank the three Reviewers for their comments. First, we have carefully studied all these comments. Then, we have made a major revision of our initial manuscript by accounting for the comments of the three Reviewers as much as possible and in a constructive way. We believe that this revision leads to a substantial improvement of our initial manuscript.

Below, we explain how all the comments of the three Reviewers have been taken into account in our revision. Since a good few comments of the three Reviewers turn out to be quite similar, our answers to such comments are inevitably similar. **To facilitate the reading and understanding of our response to the comments of the three Reviewers, we have chosen to render each response self-contained by taking the risk of making our response appear somewhat repetitive**.

All the changes made with respect to the initial manuscript are highlighted in color in the revised manuscript.

Reviewer #1 :

[General comment] *Moisture-enabled electric generator (MEG) technology converts the energy from the gas-liquid phase change of moisture into electrical energy, providing green and clean advantages with broad applicability. Key performance indicators for MEGs are power density and lifespan. Recent advancements have significantly improved power density from 18.4 nW/cm² to ~12 μW/cm². However, lifespan remains a challenge, with many MEGs operating only for seconds to hours, limiting large-scale application. Efforts to improve MEG lifespan focus on continuous moisture absorption-desorption and maintaining ion concentration gradients. New materials (e.g., protein nanowires, graphene oxide) and structures (e.g., PN junctions) have extended continuous output voltage times but maintaining current output is still problematic due to ion migration dynamics. This study proposes using photocatalysis to rebuild the ion concentration gradient, restoring current output. The device, comprising a hydrogel moisture-enabled electricity generation layer, a photocatalytic layer, and inert electrodes, achieves an output VOC of 0.28 V and a peak ISC of 1.8 μA in high humidity without illumination. Illumination stimulation rebuilds the ion gradient, extending current output to 650 hours, advancing the sustainable development of MEGs.*

While the impressive short circuit current and long-term stable electrical output are

noteworthy, the use of photocatalysis is innovative. However, the authors have not provided sufficient evidence to convincingly support the exact mechanism behind this. Therefore, major revisions are necessary, and the following concerns must be addressed before this manuscript can be published in Nature Communications. Moreover, this cannot be considered a new finding, as several studies with a similar concept have already been published. (Yang, S., Zhang, L., Mao, J. et al. Green moisture-electric generator based on supramolecular hydrogel with tens of milliamp electricity toward practical applications. Nat Commun 15, 3329 (2024). Fu, Chunqiao, et al. A Long Life Moisture-Enabled Electric Generator Based on Ionic Diode Rectification and Electrode Chemistry Regulation. Advanced Science 11.15 (2024): 2305530.).

[Response] Thank you very much for your valuable comments above. We have added experiments and analyses to address these comments. We look forward to giving you satisfactory answers.

Green and clean energy can be generated by collecting the energy from the interaction between hygroscopic materials and atmospheric water. However, the ion diffusion process of moisture-induced dissociation causes the ion concentration gradient to gradually disappear, and there is still a lack of truly continuously operating moisture-enabled power generators(MEGs), especially the duration of current output still needs to be extended. Previously, some researchers have proposed new methods to extend the life of MEGs. The uniqueness and innovation of our work are reflected in the followings:

Tao's group introduced polyvinyl alcohol-sodium alginate-based supramolecular hydrogel as an active material to prepare a MEG [Nature Communications, 2024; 15: 3329]. The hydrogel has the characteristics of rapid absorption of water while the ionic water clusters inside the gel slowly diffuse, and the power generation time can reach one month. The main innovation of this work is that sodium alginate (AlgNa) provides abundant hydrophilic sites for the gel, which enhances the hygroscopicity of the gel and is conducive to the dissociation of ions. The asymmetric rapid moisture absorption enables the device to quickly build a concentration gradient in a humid environment. At the same time, the strong attraction of the AlgNa network causes the water clusters to be captured around the Na^+ ions to form ionic water clusters, which will slowly diffuse until they absorb enough water to release ions. This slow diffusion ensures that the device can maintain the concentration gradient for a long time and generate electrical output. This work uses the slow diffusion of water clusters to extend the life of the device. The ion concentration gradient inside the device will decay over time until it disappears. Our work uses the photocatalytic effect to rebuild the original ion concentration gradient and continuously restore the already balanced concentration gradient. This will hopefully extend the life of the device further on the basis of the above work. Although reverse transport of cations can be observed in the work of Tao's group, this transport requires the device to remain in a charged state, and the device cannot generate electrical output at this time. In addition, our device can continue to generate electricity while consuming hydrogen ions to rebuild the concentration gradient, without the need for an additional charging process.

Yang's group used PN junctions to prepare nanofluid diode devices [Nature Communications, 2022; 13: 3484]. However, this device introduced active metal electrodes, which continuously consumed the ions accumulated at both ends of the device through redox reactions, converted the ion transport inside the device into electronic current, and extended the device life to one month. However, the active metal will inevitably passivate during the redox process, hindering ion transport, so the current output of the device will continue to decay. In order to solve the passivation problem of active metal electrodes, Fu *et al.* introduced a small amount of calcium chloride into the nanofluid diode to extend the life of the device [Advanced Science 2024; 11. 15: 2305530]. The main principle is that chloride ions adsorb on oxygen atoms, destroying the generated passivation layer. In addition, chloride ions can also promote the reduction of the electrode passivation layer, so that the passivation layer of the device can be eliminated by itself when the device is charged by an external power supply. Its main innovation is to use chloride ions to inhibit partial passivation of metal electrodes, and at the same time, use the charging of an external power supply to achieve the reduction of the passivation layer of the metal electrode. The innovation of this work is to use the photocatalytic effect to reconstruct the ion concentration gradient inside the device, which is different from the innovation of the above work. The work of Fu *et al.* cannot completely suppress the passivation of metal electrodes, and its performance degradation will continue and be irreversible. The device in this work can achieve the reconstruction of the ion concentration gradient that has been diffused and balanced, and achieve reversible recovery of performance. In addition, our MEG does not require external access to other power equipment, and can reconstruct the ion concentration gradient only under sunlight, while the above devices require external power sources such as solar cells or voltage sources to remove the passivation layer. In addition, our device does not introduce active metal electrodes and is a pure green and sustainable energy source.

[Comment 1] *I would like to inquire whether the MEG in this study, which consists of multiple layers, has been optimized for each individual layer, and whether any comparisons have been conducted. If so, could the authors please provide detailed optimization procedures and results?*

[Response] Thank you for your constructive comments. The MEG device in this work is a multilayer device, including electrode layers, a hydrogel moisture-enabled electricity generation layer (MEL), and a photocatalytic layer (PCL).

For MEL, we explored the effects of AMPS and LiCl on device performance. The purpose of adding AMPS is to provide hydrolyzable hydrogen ions for power generation, and the purpose of adding LiCl is to increase the hygroscopic sites of MEL and enhance its hygroscopic capacity. The test results are shown in Figure R1, Figure 5c and Figure 5d. The device containing both AMPS and LiCl exhibited the highest voltage and current. AMPS increases the current output of the device by hydrolyzing H+, but since its large-scale dissociation will reduce the internal resistance of the device, excessive addition will decrease the voltage of the device. LiCl gives MEL good

hygroscopic and moisturizing capabilities, and the device can form a humidity gradient in a humid environment to generate electrical energy output. However, excessive addition of LiCl will affect the internal nanopore double electric layer, causing the Debye length to drop sharply, which is not conducive to the spatial separation of anions and cations, and reduces the electrical output performance.

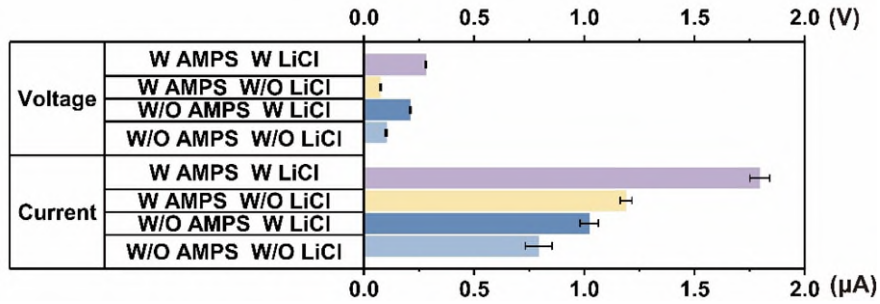


Fig. R1 Effect of adding AMPS and LiCl to the MEL on device performance

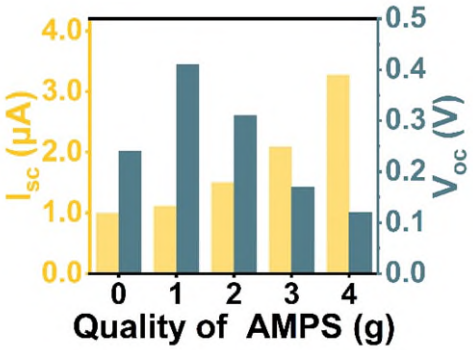


Fig. 5c Influence of AMPS addition on device performance

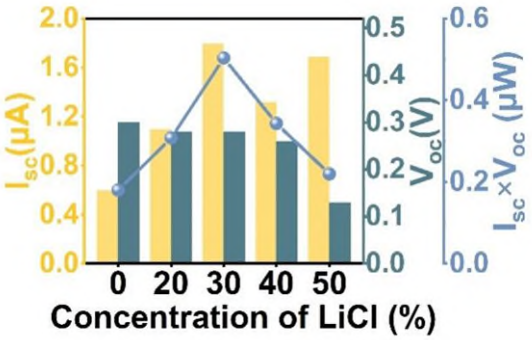


Fig. 5d Influence of LiCl addition on device performance

For the photocatalytic layer PCL, we first photosensitized the photocatalytic material CN, that is, modified g-C_3N_4 with sodium copper chlorophyllin to obtain P-CN. Then we explored (Figure 5a) the effect of the composition ratio of P-CN to PVDF on the pure hydropower generation performance. When P-CN content is relatively low, the surface charge of the PVDF membrane is weak and the pores are large, the Debye screening effect is weakened, which reduces the spatial separation of anions and cations, resulting in poor electrical output performance. When PVDF-HFP content is relatively low, since P-CN particles are difficult to effectively connect to form a self-supporting membrane, excessive agglomeration of particles and collapse of pores will also weaken the electrical output. Therefore, the optimal composition ratio of P-CN to PVDF-HFP

is 1:1.

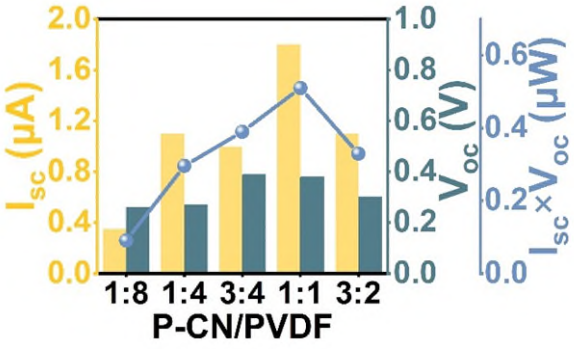


Fig. 5a Influence of PCN/PVDF-HFP ratio on device performance

For the electrode layer, we added SDBS to help CNTs disperse evenly in the solution. In addition, we added PEDOT:PSS to fill the gaps in the carbon nanotube network, reduce the defects inside the membrane, and provide additional conductive channels, so that the charge transfer in the electrode will be more uniform and efficient. The PEDOT:PSS layer can ensure the stability of the CNT electrode and prevent CNTs from agglomerating in a humid environment. The optimization results are shown in Figure R2.

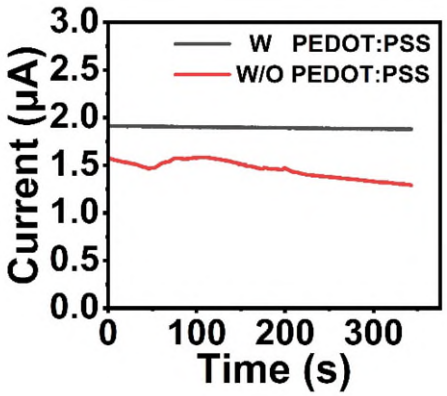


Fig. R2 Effect of PEDOT: PSS on device current performance

[Comment 2] *Can the author provide more detailed evidence and explanation for the mechanism by which photocatalysis rebuilds the ion concentration gradient and restores current output?*

[Response] Thank you for your kind comments. In our article, we use multiple experiments and characterizations to demonstrate the existence of the photocatalytic effect and to prove that photocatalysis reconstructs the ion concentration gradient and restores the current output.

(1) As shown in Figure 4b, the pH value test of PCL and MEL before and after illumination showed that the pH value increased significantly after illumination, indicating that the photocatalytic effect consumed hydrogen ions. In addition, the pH value difference between the upper and lower surfaces of MEL was 0.2 before illumination, while the pH value difference after illumination was 0.7, which

effectively demonstrated that the photocatalytic effect rebuilt the ion concentration gradient.

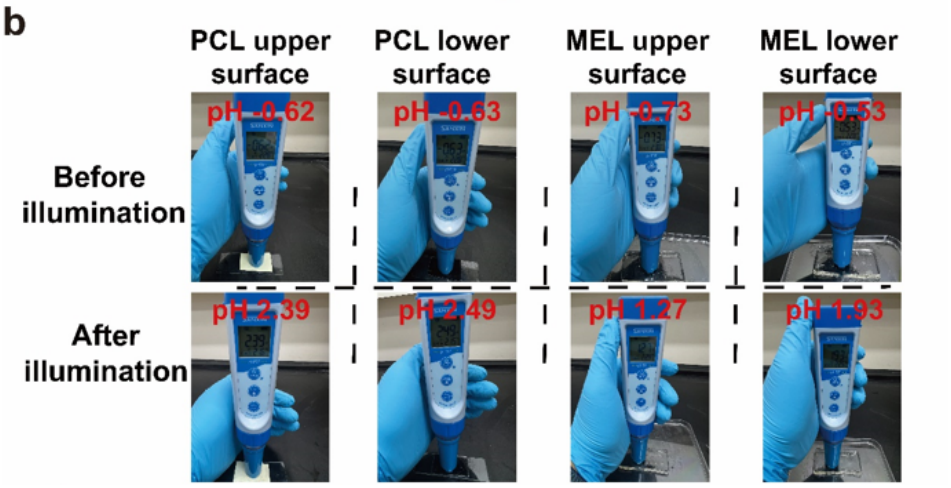


Fig.4 b pH value of PCL and MEL surface before and after illumination

(2) The photocatalytic hydrogen evolution test in Supplementary Table 2 can show that the device has a photocatalytic effect under illumination, consuming hydrogen ions and producing hydrogen.

Supplementary Table 2 | Photocatalytic hydrogen production data of our devices

Time (h)	Peak area (uV*s)	H_2 evolution (μmol)
0	0	0
1	4538.6	2.64722
2	5871.3	3.424541
3	6215.6	3.62536
4	11599.3	6.7655

(3) As shown in Figure 4, we designed a comparative experiment with and without PCL. The device without PCL did not show current output recovery after illumination, while the device with PCL showed recovery in electrical output after illumination for the same period of time.

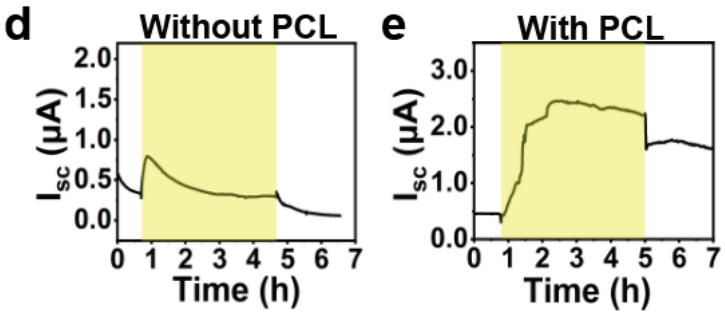
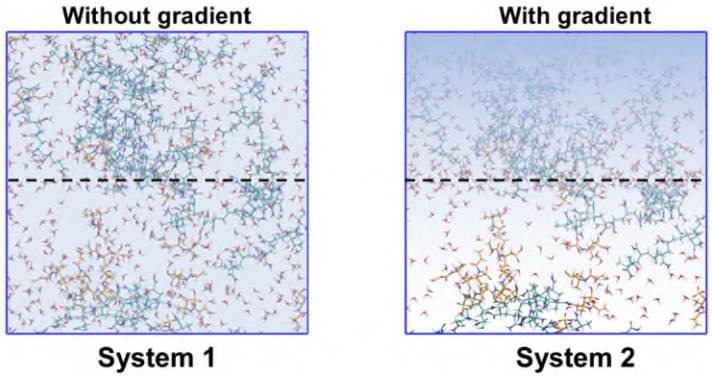


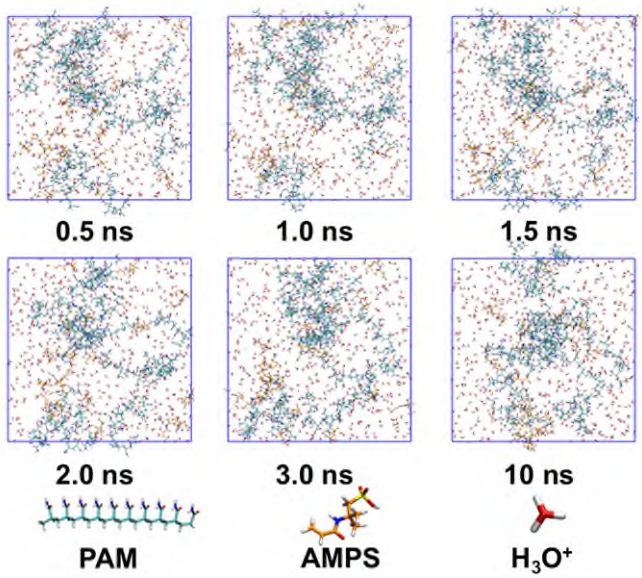
Fig.4 d, e Effect of the PCL on electrical output recovery (yellow is the part with illumination applied)

(4) To demonstrate the continued diffusion of the hydrogen ion concentration gradient after photocatalysis, we used molecular simulation to calculate this process. Supplementary Figure 10 shows the initial conformation of the simulated system before and after illumination. Before illumination, the H_3O^+ inside the system was evenly distributed due to moisture saturation. After illumination, the H_3O^+ concentration at the bottom decreased, and the simulated hydrogen ions were consumed by the photocatalytic effect.

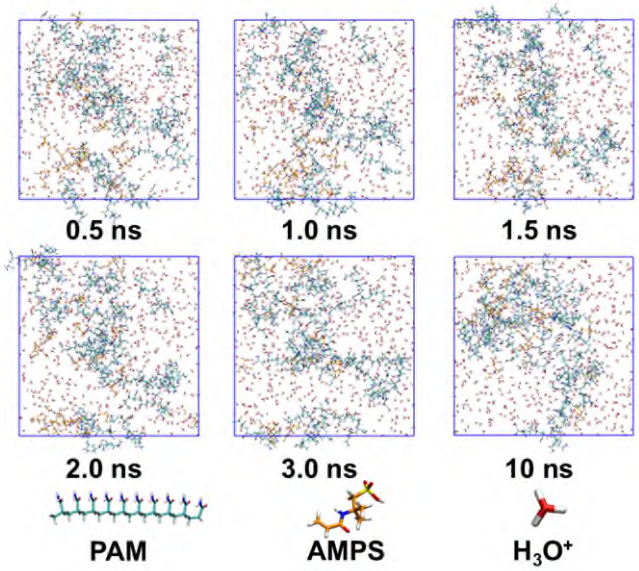


Supplementary Fig. 10 Initial conformation of the simulation system before and after illumination

The changes in the H_3O^+ density distribution are shown in Supplementary Figures 10 and 11. In the homogeneous system (system 1), only the microscopic movement of the gel skeleton can be observed. Since there is no concentration gradient inside it, the density distribution of H_3O^+ in the system has not changed significantly (Supplementary Fig. 11). In other words, in a system without a concentration gradient, H_3O^+ does not have a directional diffusion phenomenon. In a non-homogeneous system (system 2), the density changes of the gel skeleton and H_3O^+ can be observed. As shown in Supplementary Figure 12, the H_3O^+ density distribution in the upper half of the initial state system is significantly higher than that in the lower half. As the simulation time goes on, the H_3O^+ density in the upper and lower parts becomes uniform, that is, H_3O^+ will migrate from the high concentration side to the low concentration side along the concentration gradient direction, which is consistent with the experimental results.



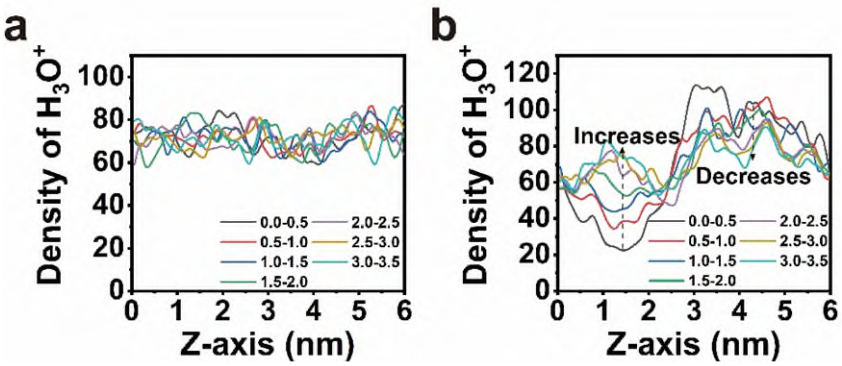
Supplementary Fig. 11. H_3O^+ density distribution change of system 1



Supplementary Fig. 12. H_3O^+ density distribution change of system 2

In addition, the density changes of H_3O^+ in the vertical direction in the two systems were calculated. As shown in Supplementary Figure 13a, the density of H_3O^+ in system 1 did not change significantly over time in the Z-axis direction. This shows that in an environment without a concentration gradient, H_3O^+ will not move in a directional manner, which will cause the electrical output of the device to drop to a very low level. However, as shown in Supplementary Figure 13b, the density of H_3O^+ in system 2 changed significantly over time in the z-axis direction (the left side of the horizontal axis in the figure is the low concentration side, and the right side of the horizontal axis is the high concentration side). As the ions migrate with the concentration gradient as the driving force, the density of H_3O^+ on the low concentration side gradually increases, while the density of H_3O^+ on the high concentration side gradually decreases, and the two reach a state of density distribution equilibrium after the migration is completed. The simulated density changes of H_3O^+ in the two states are consistent with the actual

experimental phenomena.



Supplementary Fig. 13 a Density change of H_3O^+ in the absence of concentration gradient **b** Density change of H_3O^+ when there is a concentration gradient. Different colors mark the average density of the system along the Z axis (concentration gradient direction) in each time period (ns).

In summary, the photocatalytic effect can produce hydrogen by consuming hydrogen ions inside the device, and then rebuild the hydrogen ion concentration gradient inside the device to achieve the recovery of current output.

In addition, we added the following statement on page 15 of the revised manuscript: "In addition, we used molecular simulation to calculate the hydrogen ion transport before and after the reconstruction of the concentration gradient (Supplementary Fig. S10). In the system without concentration gradient, the density distribution of H_3O^+ did not change significantly. In other words, in the system without concentration gradient, H_3O^+ did not diffuse in a directional manner (Supplementary Fig. 11). In the system with concentration gradient, there was an obvious migration of H_3O^+ from the high concentration side to the low concentration side along the concentration gradient, which is consistent with the experimental results (Supplementary Fig. 12). In addition, the change of H_3O^+ along the z-axis direction also fully proves that the concentration gradient will act as a power source to drive the transport of H_3O^+ along the concentration gradient direction (Supplementary Fig. 13)."

[Comment 3] *Can the author elaborate on the choice of materials (e.g., protein nanowires, graphene oxide) and structures (e.g., PN junctions) used in their MEG? How do these contribute specifically to performance improvements?*

[Response] Thank you for your constructive comments. Material improvement: In moisture power generation devices, the nanopores of the device and the hydrophilic properties of the material will be related to the electrical output performance of the device. Materials such as protein nanowires, graphene oxide and cellulose mentioned in the article can form nanopores inside the device to a greater extent, while ensuring better hydrophilicity. Water molecules in the air can be absorbed and captured by these materials, and the dissociated ions can migrate in the abundant nanopores to achieve efficient electrical output. At the same time, the presence of cellulose can strengthen the moisture-sensitive layer in MEG, improve its mechanical properties, and promote the application of MEG in the field of flexible electronics. In this work, we used PAM/AMPS/LiCl hydrogel as the moisture power generation layer. The addition of

LiCl not only provides a large number of hydrophilic sites for the gel and enhances its hygroscopicity, but also provides the gel with good antifreeze properties, allowing it to maintain a stable morphology at low temperatures.

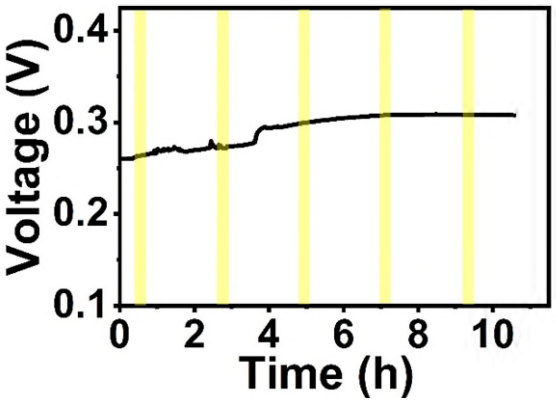
Structural improvement: The stable directional migration of ions dissociated by moisture absorption in MEG is the key and difficulty to improve the performance of MEG. Structural improvement is one of the solutions to achieve directional migration of protons. The PN junction can form a built-in electric field inside the nanopore. This built-in potential promotes the ionization of adsorbed water molecules and the unidirectional transfer of ionic charges, reducing the power loss during energy transfer. The asymmetric structure can provide a gradient for ion transport to a greater extent, enhance the directional migration of ions and inhibit charge recombination. In addition, the asymmetric moisture absorption-desorption structure can construct a stronger humidity gradient, promoting the continuous directional migration of ions dissociated by moisture absorption along the direction of the humidity gradient. In this work, both MEL and PCL are porous structures. The abundant nanopores of MEL effectively increase the surface area, provide sufficient sites for moisture absorption, and improve the moisture absorption capacity of MEL; its directional pore structure reduces the resistance to water and ion migration and improves the energy conversion efficiency. The porous structure of PCL can ensure the rapid transport of ions. In addition, the PCL structure can also avoid the rapid disappearance of the ion concentration gradient caused by the excessive migration of ions, effectively extending the life of the device.

Due to space limitations in the article, this section has been added to page 3 of the revised manuscript and the content is as follows: “Current efforts to improve lifespan include the development of new materials (protein nanowires[19,20], graphene oxide[21-23], conductive polymer[24,25], cellulose[26-28]) to form nanopores inside the device while ensuring better hydrophilicity, as well as the development of new structures (PN junctions[29-33], antisymmetric moisture absorption-desorption[34-36], etc.) to provide a gradient for ion transport. Asymmetric structures can create stronger concentration gradients and enhance the directional migration of ions.”

[Comment 4] *Can the author check the durability of this device and perform recycling tests? On page 7, line 139, they mentioned that 'Moreover, after the photocatalytic reconstruction of the ion concentration gradient, the device power generation is restored, and the current output time can be extended to 650 hours, while the voltage can remain stable for a long time (Supplementary Fig. 1). However, if the current output is continuously decreasing, can we truly say that it is stable?*

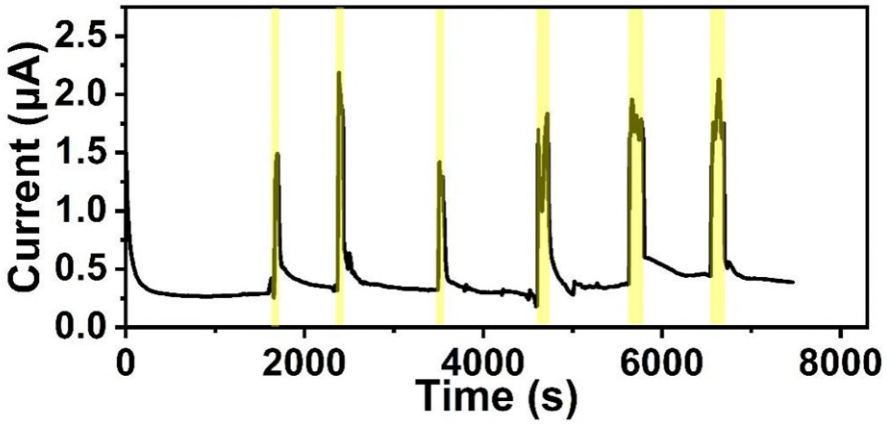
[Response] Thank you for your above comments. To verify the durability and repeatability of MEG, we conducted multiple illumination experiments on the device (Supplementary Fig.17). For voltage, we applied illumination for 0.3 h at 0.4 h, 2.6 h, 4.8 h, 7 h, and 9.2 h, respectively. The experimental results show that illumination has no significant effect on the device voltage. This is because the voltage is greatly affected by the degree of separation of anions and cations. Although photocatalysis consumes cations and rebuilds the cation concentration gradient, it does not change the nature of

anion-cation separation. Therefore, illumination has little effect on voltage.



Supplementary Fig. 17. Voltage responses during five illumination cycles

In addition, we also subjected the device to 6 cycles of illumination (100 s, 100 s, 100 s, 180 s, 180 s, 180 s) to test its current response under the illumination cycle (Supplementary Figure S18). In the 6 illumination cycles, the device had a good current response. In addition, after the illumination was turned off, the device had a performance recovery phenomenon (due to the relatively short illumination time, the current output recovery ability was slightly lower than that of 4h long-term illumination), proving that the device has a stable performance recovery phenomenon under multi-cycle illumination.



Supplementary Fig. 18. Current responses during six illumination cycles

In general, the device can maintain a stable response under multiple illumination cycles, which demonstrates that the device can maintain stability under repeated illumination, can withstand multiple cycles, and has good durability.

Regarding the second comment: The continuous migration of ions or protons is the basis of MEG output current, and the ion concentration gradient is the main factor driving most MEGs to produce electrical output. In actual tests, the current output of MEG will inevitably show a phenomenon of first stabilizing and then decaying. This is because the device will dissociate a large number of ions or protons due to asymmetric moisture absorption at the beginning, which will build a relatively stable concentration gradient inside the device. However, as the initial ion concentration gradient drives ion diffusion, the migration of the preceding ions will produce a reverse built-in potential

and weaken the ion concentration gradient, which will cause the electrical output of the device to inevitably decay. Our work can reconstruct the weakened ion concentration gradient so that it can drive ions to produce directional transport again and restore the device life.

In addition, we added relevant discussion on page 20 of the revised manuscript as follows: “In addition, we tested the repeatability and durability of MEG, and tested the voltage (Supplementary Fig. 17) and current (Supplementary Fig. 18) response images of MEG under multiple illumination cycles. The experimental results show that the device can maintain a stable response under multiple illumination cycles, which demonstrates that the device can maintain stability under repeated illumination, can withstand multiple cycles, and has good durability.”

[Comment 5] *How about modifying Fig. 5 to improve its quality? It is not easily visible at a glance, especially Fig. 5a to 5f.*

[Response] Thank you for your kind suggestion! We have adjusted the color and font size of Figure 5, and improved the clarity of the image to improve its quality. The corrected image is as follows:

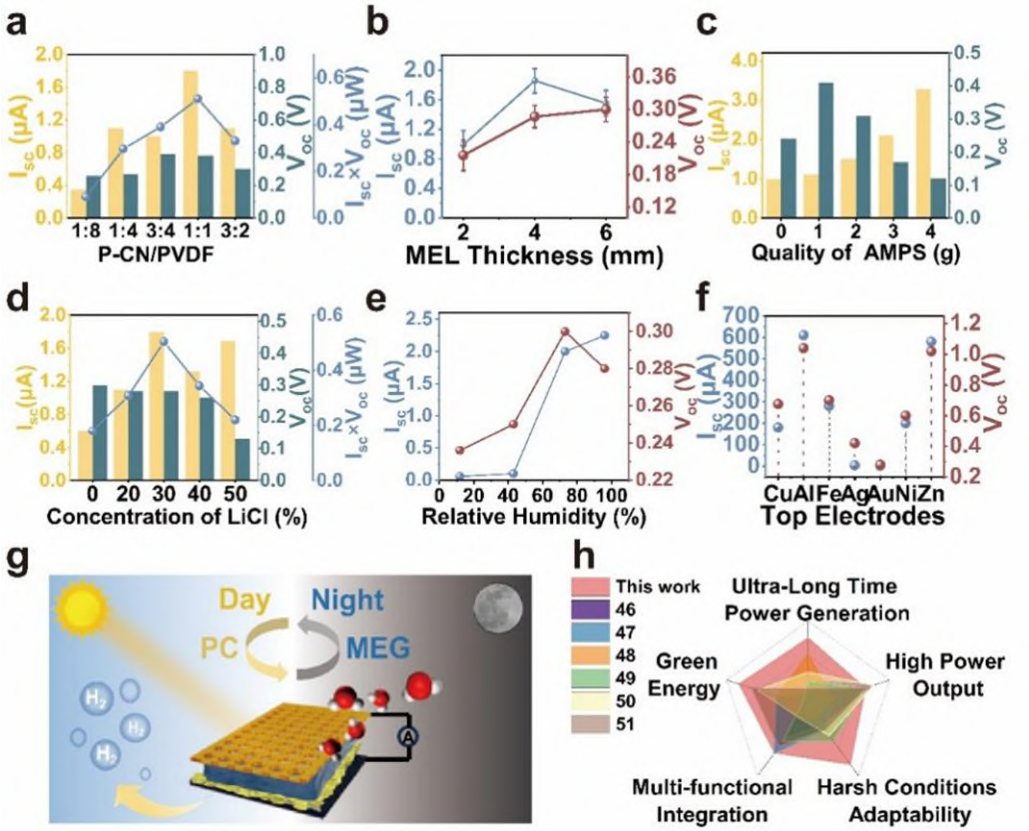


Fig. 5 Factors affecting the electrical output performance of MEG and application outlook. **a** Influence of PCN/PVDF-HFP ratio on device performance **b** Influence of MEL thickness on device performance **c** Influence of AMPS addition on device performance d Influence of LiCl addition on device performance **e** Influence of humidity on device performance **f** Performance graphs of different metallic materials as top electrodes **g** Schematic diagram of the device for day-

night cycle power generation **h** Advantages of the device for practical application[54-59].

[Comment 6] *The power output of advanced MEGs primarily depends on their water capture capability and the established water gradient. In terms of material design, how can the materials balance high moisture absorption with maintaining a sustainable moisture gradient? What specific characteristics are necessary for these materials? Please summarize a general strategy.*

[Response] Thank you for your kind suggestion. This question is very worth exploring. Water plays a vital role in MEG devices. Water is a good solvent that can dissolve a variety of ions and carriers. Good moisture absorption capacity can improve the power generation performance of MEGs [Energy Environ. Sci., 2022;15, 123-135]. In addition, the water gradient or ion concentration gradient inside MEG is a key driving factor for power generation. Weak moisture absorption capacity of the material will prevent the functional groups or ions from fully dissociating. Excessive moisture absorption capacity will cause the inside of the device to quickly reach a saturated state and fail to maintain the internal concentration gradient. Therefore, the water capture ability of the hygroscopic material in MEG and the maintenance of the concentration gradient inside the device are decisive for the device performance.

Developing new materials to improve the device's moisture capture ability is one of the mainstream strategies. At present, hygroscopic materials such as protein nanowires[19], modified graphite oxide[24], and polymer electrolytes[37] have been developed. By increasing the hygroscopic sites of hygroscopic materials[38] and adding functional groups[23], the hygroscopic capacity and moisture retention ability of devices can also be effectively improved.

The asymmetric material surface modification and the construction of asymmetric device structures are two main methods to maintain ion gradient. Currently, surface modification methods such as moisture-electric annealing[21], laser reduction and plasma treatment[39], directionally-induced thermal reduction[40] have been used to enhance and maintain concentration gradients. In addition, ion diode structures[13], double-layer membrane structures[32], asymmetric moisture absorption-desorption structures[41], heterojunctions[42], *etc.* have been applied.

Combining the above schemes can achieve stable moisture absorption and concentration gradient maintenance. The double-layer membrane structure of polyanion electrolyte membrane and polycation electrolyte membrane effectively realizes the spontaneous adsorption of water and the induced diffusion of oppositely charged ions[41]. Integrating the moisture absorption and dehumidification processes into a closed-loop process can also achieve a balance between moisture absorption and gradient maintenance[11].

We have added a discussion of the overall strategy on page 3 of the revised manuscript as follows: “ Current efforts to improve lifespan include the development of new materials (protein nanowires[19,20], graphene oxide[21-23], conductive polymer[24,25], cellulose[26-28]) to form nanopores inside the device while ensuring better hydrophilicity, as well as the development of new structures (PN junctions[29-33], antisymmetric moisture

absorption-desorption[34-36], *etc*.) to provide a gradient for ion transport. Asymmetric structures can create stronger concentration gradients and enhance the directional migration of ions. Combining the two can achieve a benign coupling of material hygroscopicity and gradient maintenance[11,37-42], realize ion continuous migration inside the device, and thus extend the electrical output of the device."

[Comment 7] *While the author mention the addition of a photocatalytic layer to address ion concentration gradient issues, the exact effect of photocatalysis on device performance could be elaborated further. What specific improvements are observed with the inclusion of photocatalysis, and how does it compare to the performance without it?*

[Response] Thanks a lot for your nice suggestions. The introduction of PCL, on the one hand, provides a one-way flow channel for the ion transport of the device, and on the other hand, PCL can produce a photocatalytic effect under illumination to consume hydrogen ions to rebuild the hydrogen ion concentration gradient, thereby extending the life of the MEG. As shown in Figure 4d, the current output of the device without the photocatalytic layer will decay to a lower level in a short time. At the same time, when illumination is applied to the device without the photocatalytic layer, the device output only shows weak fluctuations due to the temperature response caused by the illumination. After the illumination is withdrawn, the output quickly decays to a lower level.

In addition, as shown in Figure 4e, after a period of ion diffusion, the electrical output of the device will gradually decrease due to the disappearance of the concentration gradient. The presence of PCL can produce a photocatalytic effect, which can recover the current output after the light source is turned off. However, the output of the device without PCL decays rapidly after the light source is turned off.

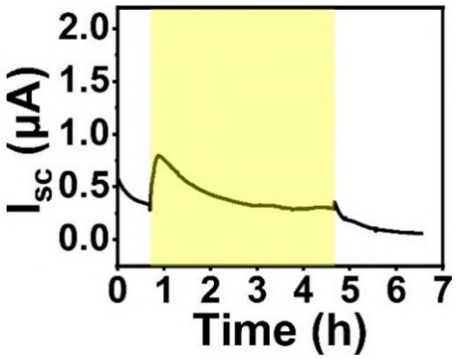


Fig.4 d No electrical output recovery without PCL (yellow is the part with illumination applied)

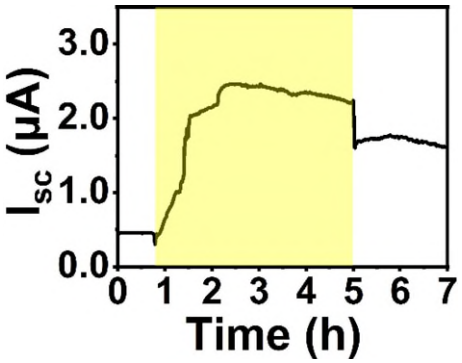
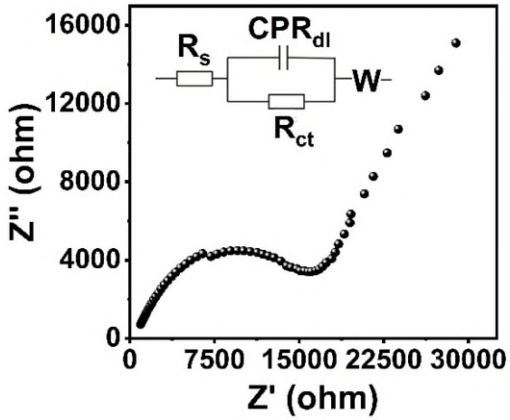


Fig.4 e Effect of the PCL on electrical output recovery (yellow is the part with illumination applied)

[Comment 8] *On page 10, line 200, they mentioned that 'At the same time, the impedance test shows that the device has good conductivity, which is conducive to the migration of hydrogen ions inside the device (Supplementary Fig. 6). However, there is insufficient relevant analysis to support the above conclusion. Additional explanation or evidence is required.*

[Response] Thanks a lot for your comments. We further fitted and analyzed the impedance picture in the article and obtained the corresponding equivalent circuit diagram, as shown in the inset of Supplementary Figure 9. After circuit analysis and calculation, the results of various device parameters can be obtained (Supplementary Table 3).



Supplementary Figure 9. Impedance analysis of the device

Supplementary Table 3 | Electrochemical impedance spectroscopy results of MEG

R_s (Ω)	C_d (uF/cm^2)	n	R_{ct} (Ω)	W
408.9	5.036	0.594	14610	$2.233*10^{-5}$

Using the formula $\sigma = \frac{L}{R \times S}$ [Advanced Materials. 2022; 34: 2103897], it can be calculated that the conductivity of this device is 0.1711μS/cm.

Moreover, we added the relevant description on page 11 of the revised manuscript as follows: “In addition, we conducted an impedance test and the equivalent circuit diagram is shown in the inset of Supplementary Figure 9. The conductivity of the device can be calculated to be 0.1711 μS/cm through the equivalent circuit.”

[Comment 9] *The manuscript describes the process of photogenerated electron-hole separation and recombination with hydrogen ions. Could the authors provide a more detailed explanation of these mechanisms, perhaps with a diagram to illustrate the process more clearly?*

[Response] Thanks a lot for your pertinent comments. Graphitic carbon nitride (CN) has a specific energy band structure (Fig. 3a), which includes a conduction band (CB) and a valence band (VB). Under illumination, CN absorbs photons, thereby exciting the generation of photogenerated electrons and holes, and electrons can jump from the valence band to the conduction band. In addition, the photosensitive material contained in the photosensitized carbon nitride (P-CN) can also help to separate the hole-electron pairs and prevent them from recombination. The separated photogenerated electrons will contact the ions in the water on the surface of the photocatalyst, and can reduce the H^+ in the water to generate hydrogen[52, 53]. In the case of MEG, the photocatalytic film contacts the moisture-enabled electricity generation layer(MEL) to form a solid-liquid interface. When light penetrates the MEL and irradiates the photocatalytic film, P-CN will be excited to generate photogenerated electrons. The photogenerated electrons and the hydrogen ions in the MEL can effectively contact and transfer at the interface, thereby realizing the reaction and generating hydrogen.

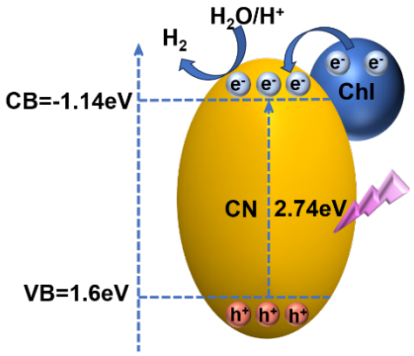


Fig. 3 a Band structure of the P-CN

Reviewer #2 :

[General comment] *The manuscript entitled by "Moisture based green energy harvesting over 600 hours via photocatalysis-enhanced hydrovoltaic effect" introduces an interesting design of coupling photocatalysis and hydrovoltaics to synergistically improve power generation. Authors clearly show the superiorities of using photocatalysis to consume H+ and rebuild the ion concentration gradient. I recommend to publish this work after some revisions:*

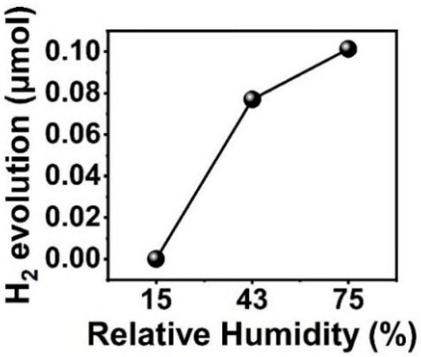
[Response] Thank you very much for providing constructive comments on our work. We hope our response will satisfy you.

Major

[Comment 1] *The authors clearly explained the promoting effect of photocatalysis on power generation. Conversely, power generation also provides additional H+ for photocatalysis. Can this additional H+ effectively enhance the performance of photocatalysis?*

[Response] Your above comments are very constructive. The experimental results show that the photocatalytic effect prolongs the life of the MEG device. At the same time, the transport of H^+ along the concentration gradient also provides additional H^+ for photocatalysis. Since the hydrogen ions in the device mainly come from the dissociation of AMPS in water, the H^+ that acts in power generation is closely related to the ambient humidity. Therefore, we explored the effect of humidity on the photocatalytic performance of the device. In the experiment, we placed the device in three different humidity environments (15% RH, 43% RH, 75% RH) for 1 hour to absorb moisture. Subsequently, the device was taken out for photocatalytic hydrogen production experiments.

Supplementary Figure 15 shows the hydrogen production of the device under different humidity conditions. As the humidity increases, the hydrogen production of the device shows an upward trend. This is because the device absorbs moisture faster at higher humidity, so more H^+ is generated by dissociation inside the device. In addition, we added the relevant description on page 19 of the revised manuscript as follows: "In addition, the ambient humidity also affects the photocatalytic effect of the device (Supplementary Fig. 15). The photocatalytic effect will increase with the increase of humidity, that is, more dissociated hydrogen ions will promote the photocatalytic process." Therefore, we can conclude that power generation can also provide more H^+ for photocatalysis, which in turn has a certain promoting effect on the performance of photocatalysis.



Supplementary Fig. 15. Hydrogen production of the device at different humidity levels for 4 hours

[Comment 2] *Currently, the duration of the hydrovoltaic power generation device can exceed one month. Please conduct a thorough literature review.*

[Response] Thank you for your kind suggestion. At present, some of the reported devices can generate electricity for more than one month. Yang's group introduced the ion diode effect into the MEG device and constructed a PN junction in the nanopore. The built-in electric field formed by this structure promotes selective ion separation and stable unidirectional ion charge migration. In addition, active metals are added to the system to convert ion current into electron current through redox reaction, thereby generating continuous current and voltage output, and the output time can reach 750h [Nature Communications. 2022; 13: 3484]. Qu's group used the moisture absorption-dehumidification cycle process inside the device to achieve continuous power generation for more than one month. The power generation process is moisture absorption power generation driven by ion concentration gradient in high humidity environment and desorption power generation dominated by ion hydration energy in low humidity. This power generation method can realize cyclic power generation according to the humidity changes in the actual environment [Nature Communications. 2022; 13: 2524]. Yao's group prepared protein nanowires to achieve long-term moisture absorption power generation. This work uses the asymmetric moisture absorption of nanowire films to construct a water gradient to induce ionization gradient power generation. In addition, water molecules at the interface can be dynamically adsorbed and desorbed, providing continuous output [Nature, 2020, 578: 550]. Tao's research group introduced polyvinyl alcohol-sodium alginate-based supramolecular hydrogel as an active material to prepare a moisture power generation device. This work combines rapid moisture absorption with slow diffusion of water clusters to achieve rapid construction of concentration gradients and continuous ion migration inside the device, and the power generation time can reach more than one month [Nature Communications, 2024; 15: 3329]. Guo's group integrated water adsorption and water evaporation to prepare a long-duration power generation device that can continuously generate considerable current and voltage. The LiCl-containing fiber paper provides the water adsorption sites and the carbon black-containing fiber paper provides the evaporation sites, achieving a complete water cycle in the device. [Nature

Communications. 2022; 13: 3643].
However, many current works basically use the established chemical or humidity gradient to extend the time of ion diffusion to achieve long-term power generation, or further enhance the migration of ions by introducing redox reactions. Devices using these strategies will inevitably fail to continuously generate electrical output due to the gradual disappearance of the ion concentration gradient. In addition, devices that use the moisture absorption-dehumidification cycle process have high requirements for moisture changes, and continuous humidity changes are required to maintain the long-term operation of the device, which has certain disadvantages in practical applications. This work introduces photocatalysis into MEGs, using the photocatalytic effect to consume hydrogen ions to rebuild the ion concentration gradient and restore the device's electrical output. This method is expected to extend its power generation time of other devices, achieving longer power output.
We have described the above part on page 4 of the revised manuscript. The original text is as follows: “In the work published so far, some devices have achieved electrical output for more than one month. However, redox reactions[44] or moisture absorption-dehumidification cycles that depend on humidity changes[11, 19] will limit the application of the devices. In addition, Tao et al. combined rapid moisture absorption with slow movement of water clusters to provide a new idea for long-term power generation[1]. Guo et al. combined hygroscopicity and evaporation to achieve water circulation inside the device[15]. However, these devices will inevitably fail to continuously generate electrical output due to the gradual disappearance of the ion concentration gradient.”

[Comment 3] *The authors mentioned that the redox reactions of the electrodes can significantly increase energy input, but the energy source is not green. In this work, the authors used a more complex multi-component carbon bottom electrode. Could this lead to potential redox reactions at the bottom?*

[Response] Thanks a lot for your useful suggestions. The bottom electrode uses a carbon nanotube electrode, in which two substances, SDBS and PEDOT: PSS, are added. Among them, SDBS, as a surfactant, is used to improve the dispersibility of CNT in the solution, so that CNT is easier to form a film and will not aggregate when sprayed. PEDOT: PSS is a hole transport layer. When added to the bottom electrode, it can provide the electrode with better conductivity. At the same time, it can serve as a hole transport layer to effectively realize the hole-electron separation during photocatalysis. After actual current testing (Fig. R2), we found that the current performance of the device with PEDOT: PSS added is slightly higher than that of the device without PEDOT: PSS. This is because the addition of this material can improve the conductivity of the electrode and promote the migration of ions inside the device. The device without this material also has a high electrical output performance, which shows that the complex multi-component carbon electrode does not have potential redox reactions.

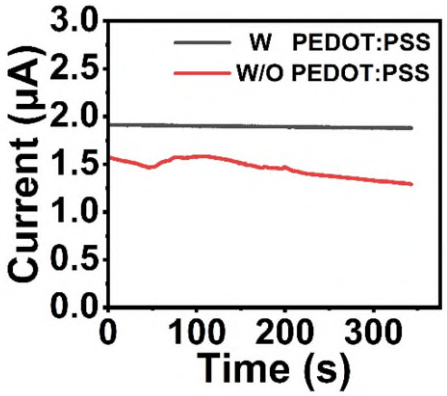


Fig. R2 Effect of PEDOT: PSS on device current performance

[Comment 4] *Why didn't the authors place the PCL layer above the MEL layer to reduce the loss of sunlight transmission? Also, I suggest improving Figure 1a to clearly illustrate the transmission of sunlight.*

[Response] Thank you for your pertinent opinion. Direct illumination of PCL can indeed directly reduce the loss of sunlight projection, but the photocatalytic effect in this device mainly occurs at the solid-liquid interface between PCL and MEL. If PCL is placed directly on the MEL layer, due to the poor light transmittance of PCL (Fig. R3), only a small part of the light can reach the solid-liquid interface between PCL and MEL (Fig. R4), so that the photocatalytic effect is weakened or even disappears at the interface due to insufficient light, which in turn affects the device life recovery. When MEL is placed on the upper layer of PCL, light can effectively reach the interface between the two (Fig. R4, Supplementary Fig. 3), and the photocatalytic effect occurs, which reconstructs the hydrogen ion concentration gradient at this position and restores the device life. Therefore, MEL needs to be placed on top of PCL to allow light to reach the solid-liquid interface smoothly, thereby achieving the photocatalytic effect to consume hydrogen ions.

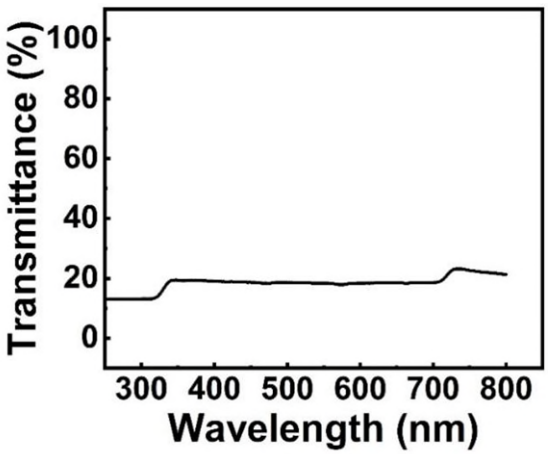


Fig. R3 Light transmittance test of the PCL

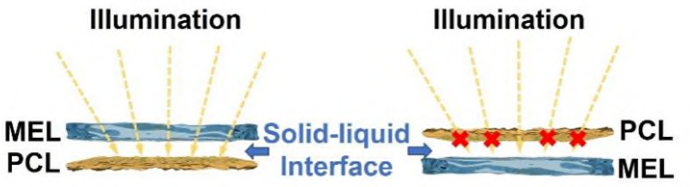
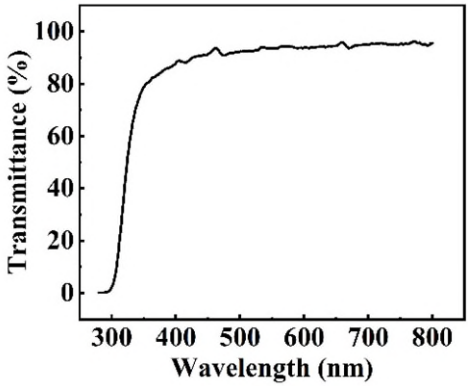


Fig. R4 Schematic diagram of MEL and PCL light transmission

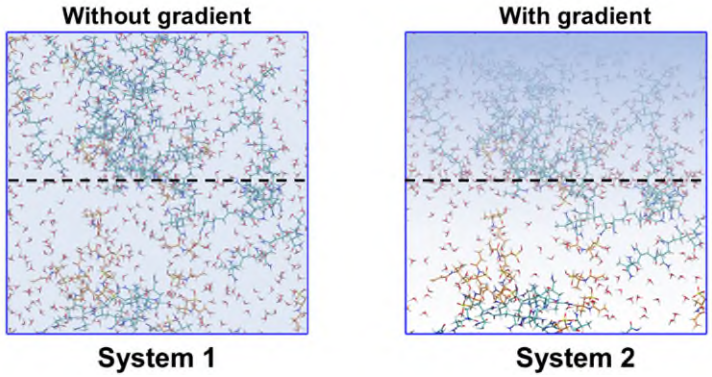


Supplementary Fig 3. Light transmittance rate of the MEL

[Comment 5] *Authors clearly show the synergetic effects by using pH value testing. I suggest considering some theoretical calculations such as MD or first-principle to solid this important mechanism.*

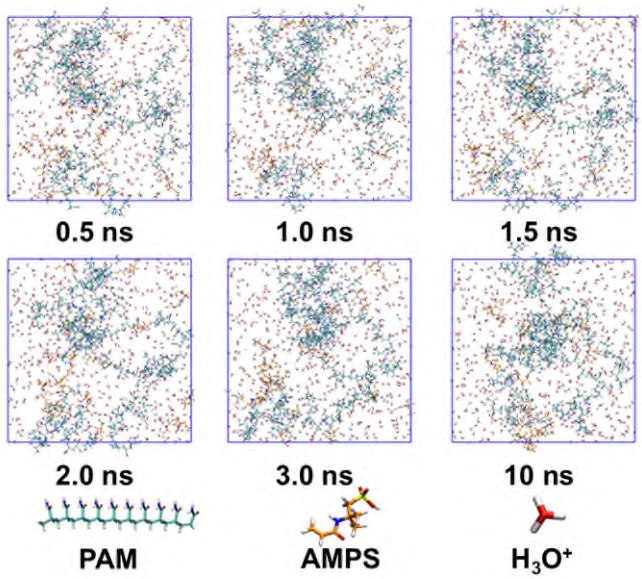
[Response] Thank you for your comment. To demonstrate the continued diffusion of the hydrogen ions after photocatalysis, we used molecular simulation to calculate this process.

Supplementary Figure 10 shows the initial conformation of the simulated system before and after illumination. Before illumination, the H_3O^+ inside the system was evenly distributed due to moisture saturation(system 1). After illumination, the H_3O^+ concentration at the bottom decreased, and the simulated hydrogen ions were consumed by the photocatalytic effect(system 2).

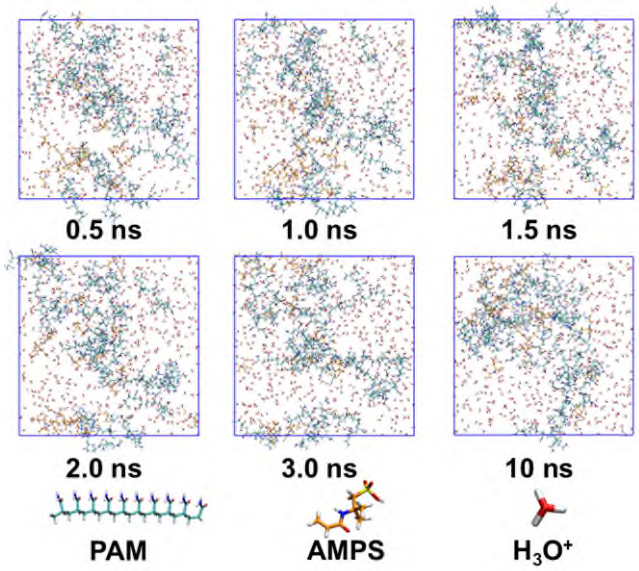


Supplementary Fig. 10 Initial conformation of the simulation system before and after illumination

The changes in the H_3O^+ density distribution are shown in Supplementary Figures 11 and 12. In the homogeneous system (system 1), only the microscopic movement of the gel skeleton can be observed. Since there is no concentration gradient inside it, the density distribution of H_3O^+ in the system has not changed significantly (Supplementary Fig. 11). In other words, in a system without a concentration gradient, H_3O^+ does not have a directional diffusion phenomenon. In a non-homogeneous system (system 2), the density changes of the gel skeleton and H_3O^+ can be observed. As shown in Supplementary Figure 12, the H_3O^+ density distribution in the upper half of the initial state system is significantly higher than that in the lower half. As the simulation time goes on, the H_3O^+ density in the upper and lower parts becomes uniform, that is, H_3O^+ will migrate from the high concentration side to the low concentration side along the concentration gradient direction, which is consistent with the experimental results.



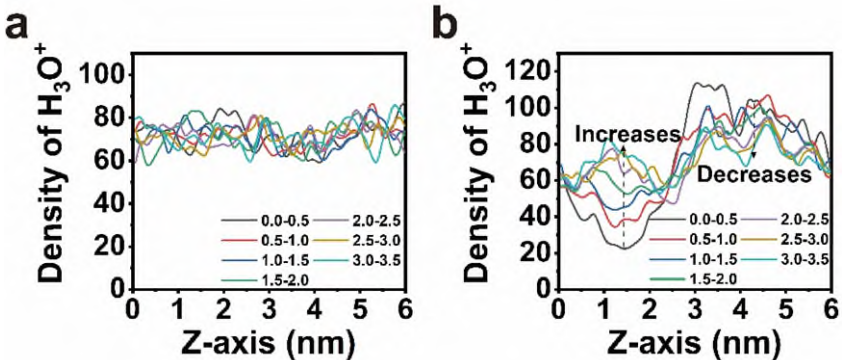
Supplementary Fig. 11. H_3O^+ density distribution change of system 1



Supplementary Fig. 12. H_3O^+ density distribution change of system 2

In addition, the density changes of H_3O^+ in the vertical direction in the two systems

were calculated. As shown in Supplementary Figure 13a, the density of H_3O^+ in system 1 did not change significantly over time in the Z-axis direction. This shows that in an environment without a concentration gradient, H_3O^+ will not move in a directional manner, which will cause the electrical output of the device to drop to a very low level. However, as shown in Supplementary Figure 13b, the density of H_3O^+ in system 2 changed significantly over time in the z-axis direction (the left side of the horizontal axis in the figure is the low concentration side, and the right side of the horizontal axis is the high concentration side). As the ions migrate with the concentration gradient as the driving force, the density of H_3O^+ on the low concentration side gradually increases, while the density of H_3O^+ on the high concentration side gradually decreases, and the two reach a state of density distribution equilibrium after the migration is completed. The simulated density changes of H_3O^+ in the two states are consistent with the actual experimental phenomena.



Supplementary Fig. 13 a Density change of H_3O^+ in the absence of concentration gradient **b** Density change of H_3O^+ when there is a concentration gradient. Different colors mark the average density of the system along the Z axis (concentration gradient direction) in each time period (ns).

In summary, the photocatalytic effect can produce hydrogen by consuming hydrogen ions inside the device, and then rebuild the hydrogen ion concentration gradient inside the device to achieve the recovery of current output. In addition, we added the following statement on page 15 of the revised manuscript: "In addition, we used molecular simulation to calculate the hydrogen ion transport before and after the reconstruction of the concentration gradient (Supplementary Fig. S10). In the system without concentration gradient, the density distribution of H_3O^+ did not change significantly. In other words, in the system without concentration gradient, H_3O^+ did not diffuse in a directional manner (Supplementary Fig. 11). In the system with concentration gradient, there was an obvious migration of H_3O^+ from the high concentration side to the low concentration side along the concentration gradient, which is consistent with the experimental results (Supplementary Fig. 12). In addition, the change of H_3O^+ along the z-axis direction also proves that the concentration gradient will act as a power source to drive the transport of H_3O^+ along the concentration gradient direction (Supplementary Fig. 13)."

[Comment 6] *I suggest evaluating continuous experimental results for over 600 hours with many intermittent illumination. Specify how many times the illumination is applied*

over 600 hours and report the overall water production and the highest performance in power generation and hydrogen production.

[Response] Thank you for your kind comment. To confirm the actual performance of the device, we re-evaluated the experimental data of the device for more than 600 hours. First, we tested the current and voltage of the device within one month (Figure 1b, Supplementary Fig. S2). Only when the device current decays to a lower level can the applied light promote its performance to recover greatly. Therefore, light was applied twice within 650 hours (the yellow part in the figure). During this period, the maximum current output of the device was 2.5 μA, the stable average was about 1.8 μA, and the maximum voltage output was 0.3 V, with an average of 0.28V.

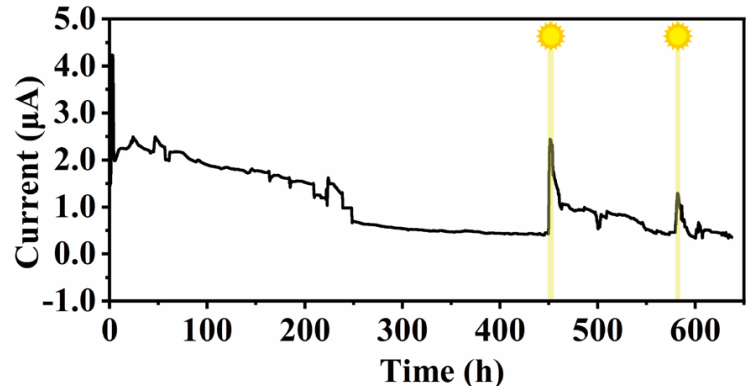
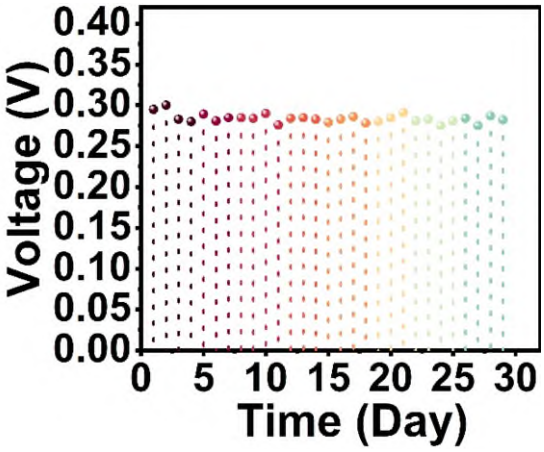


Fig. 1b Schematic diagram of long-time I_{SC} (yellow area is the part of illumination)



Supplementary Fig. 2 Long-term voltage test of MEG under a humid environment (98% RH, 25 ℃)

Since the device has good hygroscopicity, we also recorded its water absorption within 27 days (Fig. R5). During this period, we carried out 6 illuminations, each for 3 hours. Afterwards, the device continued to absorb moisture in a high humidity environment (98% RH, 25 ℃). After calculation, the total water absorption of the device within 27 days was 21.49 g.

In addition, we also evaluated the device's maximum hydrogen production performance. Since our laboratory does not have experimental equipment and gas phase testing instruments for photocatalytic hydrogen production, the photocatalytic hydrogen production test was conducted by an external testing agency

(https://www.eceshi.com/). Due to the large number of orders, the agency was unable to provide us with a photocatalytic hydrogen production test for up to 650 hours. Therefore, we conducted a 4-hour photocatalytic hydrogen production test on the device and measured the device's maximum hydrogen production of 3.1404 μmol·h^{-1}.

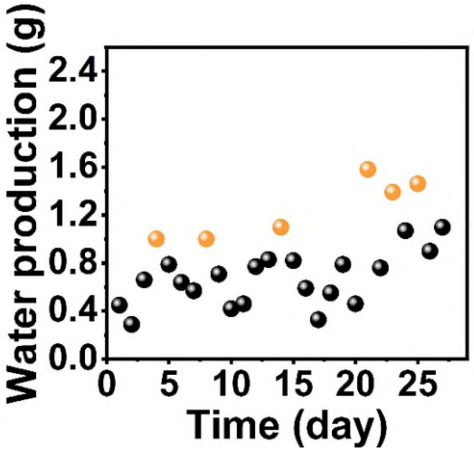


Figure R5. Water production of the device in 27 days (The yellow ball is the amount of water absorbed by the device after illumination)

[Comment 7] *In fig. 4d, the device without PCL layer also shows an obvious electrical output recovery. Please explain this phenomenon.*

[Response] Thanks for your comment. In Figure 4d, after the application of light, the device without PCL also showed a process of current increase. However, the reason for this process is not photocatalysis, we guess the heat generated by the application of light accelerates the ion transport speed inside the device, which in turn leads to an increase in the current output. But after turning off the light (5-7h), the current data of the device with PCL is higher than that before the light. This is the result of the photocatalytic effect consuming some hydrogen ions and reconstructing the concentration gradient. After the light is turned off, the device without PCL has no external energy input, and the electrical output rapidly decays to a very low level. Therefore, the role of PCL in the device is very important.

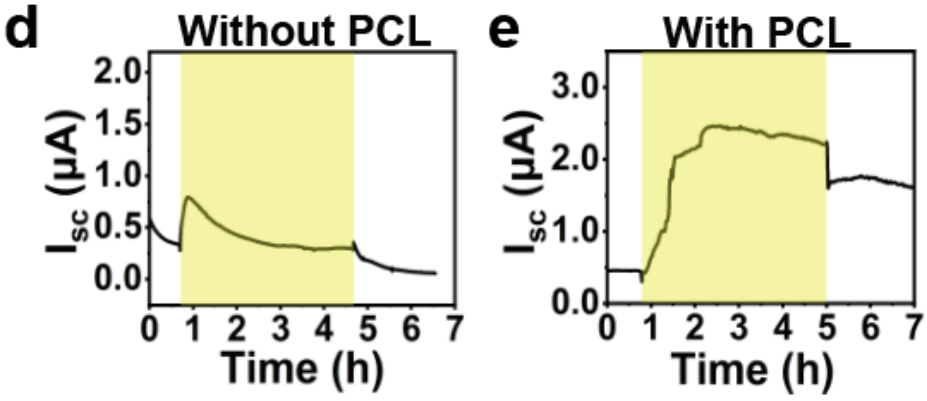
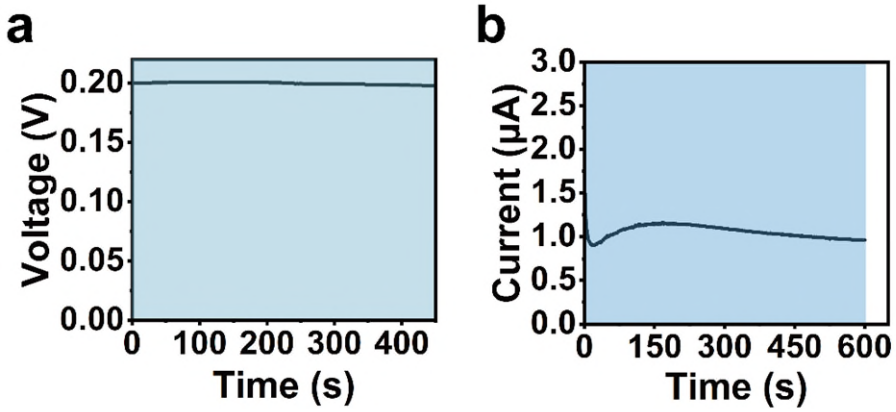


Fig.4 d, e Effect of the PCL on electrical output recovery (yellow is the part with illumination applied)

[Comment 8] *In fig. 5h, authors show that the developed device has good harsh condition adaptability. Please show more evidence.*

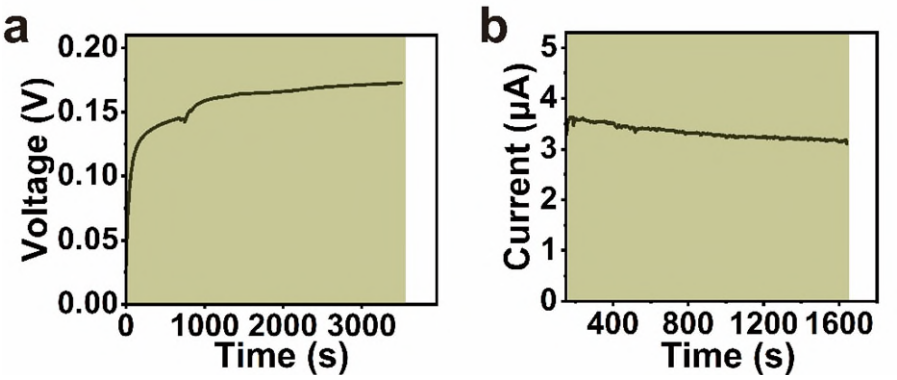
[Response] Thanks for your kind comments. We should indeed provide more evidence to prove the device's adaptability to harsh environments.

To prove that the device can still generate electrical output under harsh conditions, we simulated two environments in the laboratory, low temperature and dust burial, and tested the electrical output of the device under these two conditions. In a low temperature environment (-20 ℃), the nanopore structure of traditional MEG will be affected by ice, which will have a significant impact on the internal ion transport. However, the good antifreeze performance of MEL prevents our device from being greatly affected. Although the internal ions are transported more slowly in a low temperature environment, the device can still maintain an open circuit voltage of 0.2 V and a short-circuit current output of ~1 μA (Supplementary Fig. 19).



Supplementary Fig. 19. a Voltage output of the device at -20° C (the blue part is a low temperature environment) **b** Current output of the device at -20° C (the blue part is a low temperature environment)

We also tested the device's anti-pollution ability (Supplementary Fig. 20). We covered the device with soil, and the ions in the soil entered the device. The influx of a large number of ions reduced the device's internal resistance and also had an adverse effect on the separation of anions and cations, so the voltage of MEG would decrease. In addition, MEL can absorb moisture from the parts that are not completely covered by the soil and the gaps in the soil, thereby providing an internal ion concentration gradient, which in turn causes the ions to move and generate current output. Interestingly, when the ions in the soil enter the device, they will enhance the ion concentration gradient and increase the current output of the device.



Supplementary Fig. 20. a Voltage output of the device when it is covered with soil (the brown part is the soil-covered environment) **b** Current output of the device when it is covered with soil (the brown part is the soil-covered environment)

Experimental data show that the device can have good electrical output under two conditions: low temperature and dust burial, which indicates that the device has good adaptability to harsh conditions.

Minor

[Comment 9] *In the abstract, the device is described as being divided into two parts, while in the Introduction, it is said to be divided into three parts. Please make them consistent*

[Response] Thank you very much for your careful reading. In the abstract, we described the two most important parts of the device, namely MEL and PCL, while in the introduction, we described the entire structure of the device, that is, the device includes three parts: MEL, PCL and electrodes. The two different descriptions are indeed easy to cause misunderstanding. We have kept the two consistent in the original text. The modified part is on the first page of the revised manuscript, as follows: The MEG contains three types of functional layers: a hydrogel moisture-enabled electricity generation layer (MEL), a photocatalytic layer (PCL) that generates hydrogen under illumination and electrode layers.

[Comment 10] *The phrasing of this sentence on the third page is not precise enough: "the voltage depends on the separation degree of opposite charge carriers, and the current depends on the continuous 61 migration of opposite charge carriers.". Many factors can influence the voltage and current. Please provide a more precise statement and include references.*

[Response] Thank you very much for your suggestion. Current and voltage are the two most intuitive parameters to characterize the electrical output performance of MEGs. The current and voltage output are affected by factors such as the properties of ions inside the device, the movement speed of ions or protons, and the wetting behavior of the material. Besides, the ion amount in the solution will affect the structure of the double electric layer. Within a certain range, the increase in ion concentration will lead

to a higher concentration gradient, the ion transport speed and transport volume will increase, and the power generation will increase. However, when the ion concentration exceeds the critical value, the excess ions will produce a shielding effect near the nanopores, resulting in a decrease in the power generation capacity of the device [*Chem. Soc. Rev.*, 2022,51, 4902-4927].

In addition, the surface properties and nanopore structure of the material will also affect the electrical output of MEG. Analogous to the ion concentration gradient transport across the membrane and the ion diffusion of the nanofluid osmotic energy, the voltage formula (V) for the ion transport process from the high concentration side to the low concentration side can be calculated by the following formula [Nature Nanotechnology. 2008; 3: 666] [Nano Energy. 2022; 92:106709]:

$$V = (2t^{+} - 1)\frac{RT}{zF}\ln\left(\frac{\gamma_{C_H} C_H}{\gamma_{C_L} C_L}\right) \quad (1)$$

Where t^{+}, γ, C_H, C_Lrepresent the number of ion transfers, diffusion coefficient, high concentration and low concentration respectively. The diffusion coefficient will be affected by the surface properties of the material and the nanopore structure. In addition, the temperature, pressure, viscosity, etc. of the fluid will also affect the diffusion coefficient. Strategies such as maintaining good hydrophilic wettability of the material surface [Joule. 2022; 6: 690], introducing functional groups inside the nanopores [Nature Nanotechnology. 2017; 12: 317] [Nature Communications. 2021; 12: 1573] [National Science Review. 2020; 7: 1349], and constructing porous structures [Advanced Functional Materials. 2022; 12: 2202634] can improve energy conversion efficiency and obtain higher electrical output.

Therefore, we have adjusted this section on pages 3 and 4 of the revised manuscript, and the revised text is as follows: “Current and voltage are the two most intuitive parameters that characterize the electrical output performance of MEG devices, and the current and voltage output are affected by factors such as the properties of ions inside the device, the movement speed of ions, and the wetting behavior of the material. In addition, the number of ion transfers, diffusion coefficients, and concentration gradients in the nanopores will also affect the electric output. Among them, the transport speed and migration amount of ions are closely related to the current output of MEG, and the degree of separation of ions on both sides of the electrodes is closely related to the voltage output of MEG. ”

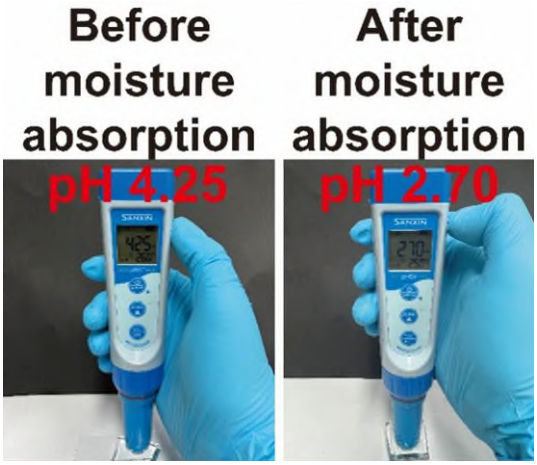
[Comment 11] *The PAM/AMPS/LiCl hydrogel was not a new material, please provide the reference.*

[Response] Thank you for your comment. The PAM/AMPS/LiCl hydrogel has been widely used in various fields. In this work, we use them as the functional layer for moisture-enabled power generation. We have provided the relevant references on page 6 of the revised manuscript, and the revised text is as follows: “We chose the polyacrylamide/2-acrylamido-2-methylpropane sulfonic acid/lithium chloride (PAM/AMPS/LiCl) hydrogel enriched with a large number of hydrophilic functional groups to construct the MEL (Fig. 1a)[38].”

[Comment 12] *Many sentences need necessary references such as: "releasing the negatively charged sulfonic acid groups fixed in the network and the free positively charged hydrogen ions." "At the same time, e- will also be excited from the VB to the CB of CN, thereby generating active photogenerated electrons in the CB and photogenerated holes in the VB". Also, I suggest adding experimental results to better support these discussions.*

[Response] Thank you for your suggestion. We have provided the relevant references on pages 6 and 11 of the revised manuscript. The revised content is as follows: "releasing the negatively charged sulfonic acid groups fixed in the network and the free positively charged hydrogen ions[24, 38](Supplementary Fig. 1)." "At the same time, e^- will also be excited from the VB to the CB of CN, thereby generating active photogenerated electrons in the CB and photogenerated holes in the VB (Eq. 1). The electrons generated by Chl are transferred to the CB of CN to saturate the CB of CN[51]."

To prove the above description, we designed relevant experiments to prove it. First, we compared the pH value of the gel before and after moisture absorption, as shown in Figure R8. When the gel is dry, AMPS will not dissociate, and the pH value of the gel is 4.25. However, after placing the gel in a humid environment (98% RH, 25 ℃), the gel absorbs water molecules from the humid air and the pH value drops to 2.7. This is because the AMPS with sulfonic acid groups interacts with water molecules and the free H+ ions at the dissociation site will reduce the pH value of the gel.



Supplementary Fig. 1 Comparison of pH value of gel before and after moisture absorption

In addition, to prove that holes and electrons are generated under the action of light, we measured their products according to their reaction paths. For electrons, they react with hydrogen ions to generate hydrogen, and some electrons react with oxygen to generate superoxide radicals, while holes can react to generate hydroxyl radicals and be captured by DMPO [Chemical Engineering Journal. 2022; 442:136115]. We collected and detected hydrogen (Supplementary Table 2), superoxide radicals (Figure 3c) and hydroxyl radicals (Figure 3d) respectively. The test results prove that the device generates these three substances during the reaction process, which can support the description in the article.

Supplementary Table 2 | Photocatalytic hydrogen production data of our devices

Time (h)	Peak area (uV*s)	H_2 evolution (μmol)
0	0	0
1	4538.6	2.64722
2	5871.3	3.424541
3	6215.6	3.62536
4	11599.3	6.7655

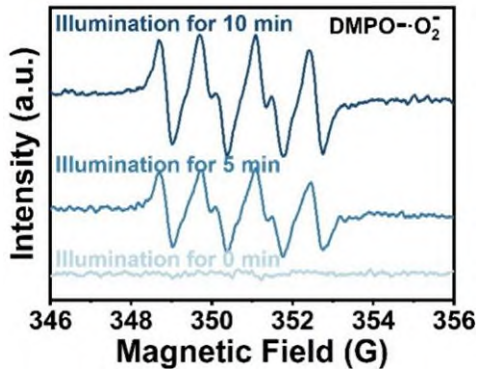


Fig. 3c Electron paramagnetic resonance (EPR) spectra of superoxide radicals

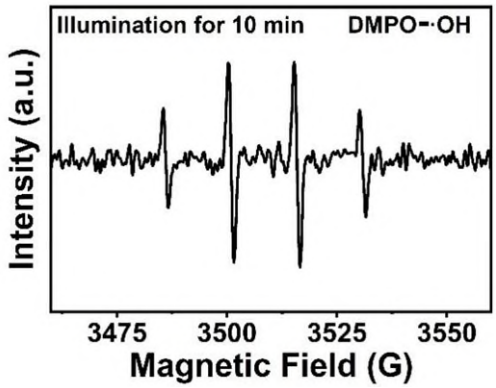


Fig. 3d Electron paramagnetic resonance (EPR) spectra of hydroxyl radicals

[Comment 13] *Equations 1, 2, and 4 are simplistic and do not satisfy material balance. It needs to be reviewed and revised. These equations also need references.*

[Response] Thank you for your pertinent advice. We have revised equation 1, 2, 4. In addition, we have reviewed and added the conservation of matter and references to the equation. In addition, equation 1 is the equation for the generation of holes and electrons by photocatalysis[52, 53]. The content of page 11 of the revised manuscript is as follows:

$$CN + Chl + hv \rightarrow e^- + h^+ \quad (1)$$

$$e^- + 2H^+ \rightarrow H_2 \quad (2)$$

$$e^- + O_2 \rightarrow \cdot O_2^- \quad (3)$$

$$h^+ + H_2O \rightarrow \cdot OH + H^+ \quad (4)$$

[Comment 14] *Why is the pH value in Figure 4b negative?*

[Response] Thank you for your comment. The pH value is defined as the negative logarithm of the hydrogen ion concentration in the solution, that is, $pH=-\log_{10}[H^+]$. Therefore, when the hydrogen ion concentration is very high, that is, when the acid is strong, the pH value will be negative.

In addition, we also contacted the equipment manufacturer as soon as possible. The relevant staff gave an explanation: It is normal for the equipment used in the experiment to measure a negative pH value. The range of the equipment is -2 to 16. The values measured in the experiment are within the range of the equipment, so the values in the figure are reasonable.

[Comment 15] *Fig. 5g is not clear enough to show the day-night continuous operation. More words should be added in the main text to explain Fig. 5g.*

[Response] Thank you for your suggestion. We have used more language in the text to explain Figure 5g. The content on page 21 of the revised manuscript is as follows: "Figure 5g shows the schematic diagram of the device day and night cycle power generation. Through reasonable modification and regulation of the material, the device's power generation mode can be switched between night and day. That is to say, in the absence of sunlight at night, MEG can use the ion concentration gradient inside the device to continuously generate electricity. Due to the diffusion of ions, the concentration gradient inside the device will gradually tend to equilibrium. After reaching equilibrium, when there is sunlight during the day, the device consumes the already balanced hydrogen ions through the photocatalytic effect, thereby rebuilding the ion concentration gradient inside the device and restoring the life of the device. Therefore, the device can theoretically achieve continuous power generation in a day and night cycle."

Reviewer #3 :

[General comment] *In this manuscript, the author propose a design for reconstructing the ion concentration gradient by coupling photocatalytic hydrogen evolution reaction with hydrovoltaic effect, to report a moisture-enabled electric generator (MEG) with continuous current output. Further analysis is conducted on the generation mechanism and various performance aspects, with detailed data characteristics. However, the following issues remain:*

[Response] Thank you very much for your insightful comments. Your opinions make our work more rigorous and meticulous.

[Comment 1] *When comparing Figure 4(d) with (e), it is observed that the presence of the PCL layer significantly promotes current recovery under illumination, while some degree of current enhancement is still triggered by light in the absence of PCL. Thus, it begs the question whether this is achieved through the synergy of photothermal and photocatalytic effects.*

[Response] Thank you for your thoughtful comments. When comparing Figure 4 (d) and (e), it can indeed be found that in the absence of PCL, a certain current enhancement will occur when the device is illuminated. This phenomenon is caused by the heat generated during the application of light. Light provides additional energy input to the device, causing the device temperature to rise to a certain extent, which in turn causes the internal ion migration of the device to accelerate. However, by comparing the current data after turning off the light (5-7h), it can be seen that the electrical output of the device with PCL has a significant current recovery compared to that before the application of light, while the electrical output of the device without PCL gradually decays and there is no current recovery. Therefore, the photocatalytic effect of PCL plays a very important role in life recovery.

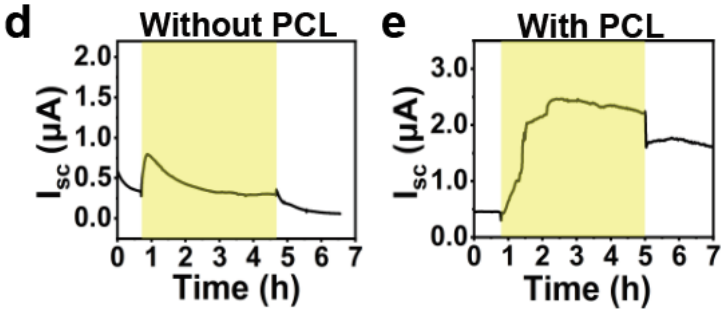


Fig.4 d, e Effect of the PCL on electrical output recovery (yellow is the part with illumination applied)

[Comment 2] *The device's bottom electrode employed by the author is a CNT: PEDOT: PSS composite material. It is recommended to clearly elaborate on the role of PEDOT: PSS within this system.*

[Response] Thank you for your comment. Generally, the conductivity, hygroscopicity and interface properties of electrode materials will have an important impact on their power generation performance. PEDOT: PSS is a polymer material with good conductivity. Adding this material to the CNT electrode can effectively promote the conduction of charge, reduce resistance loss, and thus improve the efficiency of power generation(Fig. R2). Compared with a single CNT network, the addition of PEDOT: PSS can effectively fill the gaps in the carbon nanotube network, reduce the defects inside the film, provide additional conductive channels, and the transfer of charge in the electrode will be more uniform and efficient. In addition, the PEDOT: PSS layer can ensure the stability of the CNT electrode and prevent CNT from agglomerating in a humid environment, thereby extending the working life of the electrode [Energy Environ. Sci., 2022,15, 3086-3096].

On the other hand, for our MEG, the bottom electrode not only needs to have good conductivity, but hole-electron separation is also a very important influencing factor. Adding PEDOT: PSS to the bottom electrode is expected to promote the separation and transmission of photogenerated holes and electrons, reduce the probability of holes and electrons matching, allow more electrons to react, accelerate the consumption of hydrogen ions, and then promote the reconstruction of hydrogen ion concentration gradients, thereby extending the life of MEG devices.

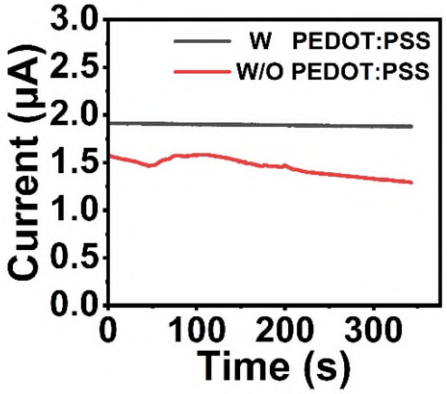
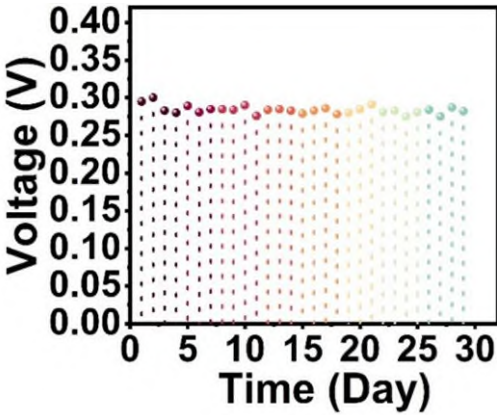


Fig. R2 Effect of PEDOT: PSS on device current performance

[Comment 3] *Figure 1(b) demonstrates a long-term current stability of 650 hours, yet the voltage plot in the supplementary information covers only 7 days (168 hours). To ensure data consistency and completeness, the author is advised to supplement voltage data spanning the same duration as the current tests, allowing for a comprehensive assessment of the device's long-term stability.*

[Response] Thank you for your valuable comments. We show the long-term current image of 650h in Figure 1b. To ensure the consistency and completeness of the experiment, we added a long-term voltage test experiment and changed the voltage image in the supplementary material. The modified image is shown in Supplementary Figure 2. The voltage test results show that the device can maintain a stable voltage output value within the test time (29 days/700 hours) and has long-term stability.



Supplementary Figure 2. Long-term voltage test of MEG under a humid environment (98% RH, 25 ℃)

[Comment 4] *To gain a deeper understanding of the impact of illumination on device performance, the author should provide voltage-time images under illumination conditions.*

[Response] Your comment helps us to study the photo-response of the device more comprehensively. The article shows the significant effect of light on current, and the photocatalytic effect effectively restores the current output. We supplemented the voltage-time image under light conditions. As shown in Figure R6, the experimental data show that the effect of light on voltage is not obvious. This is because the main site of light action is the interface between the gel and the photocatalytic film, where the photocatalytic effect consumes hydrogen ions. Although photocatalysis consumes cations and rebuilds the cation concentration gradient, the voltage is greatly affected by the degree of separation of anions and cations, photocatalysis does not change the nature of anion-cation separation, so light has little effect on voltage.

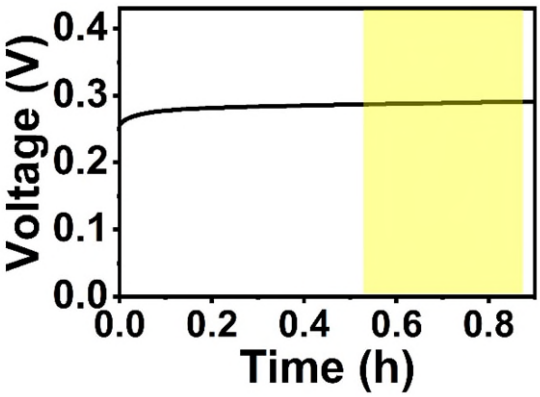
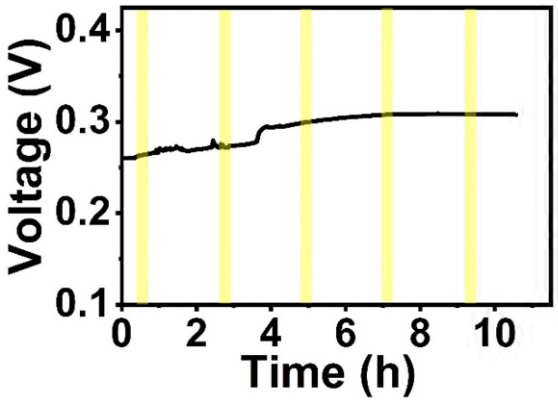


Figure R6 Voltage-time image of the device under illumination (the yellow part is the part with illumination)

[Comment 5] *Claiming long device lifespan, the author is encouraged to present current and voltage response graphs encompassing at least five illumination cycles, adequately demonstrating the device's stability and durability under repeated*

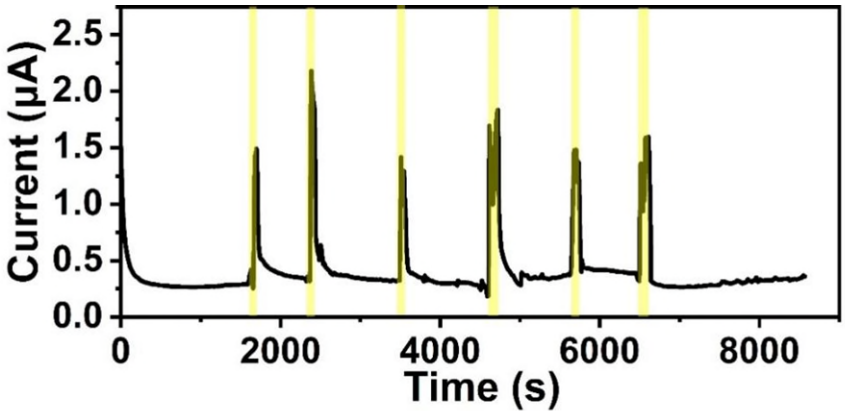
illumination.

[Response] Thanks for you valuable comments. To verify the durability and repeatability of MEG, we conducted multiple illumination experiments on the device (Supplementary Fig. 17). For voltage, we applied illumination for 0.3 h at 0.4 h, 2.6 h, 4.8 h, 7 h, and 9.2 h, respectively. The experimental results show that illumination has no significant effect on the device voltage. This is because the voltage is greatly affected by the degree of separation of anions and cations. Although photocatalysis consumes cations and rebuilds the cation concentration gradient, it does not change the nature of anion-cation separation, so illumination has little effect on voltage.



Supplementary Figure 17. Voltage responses during five illumination cycles

In addition, we also subjected the device to 6 cycles of illumination (100 s, 100 s, 100 s, 180 s, 180 s, 180 s) to test its current response under the illumination cycle (Supplementary Fig. 18). In the 6 illumination cycles, the device had a good current response. In addition, after the illumination was turned off, the device showed performance recovery phenomenon (due to the relatively short illumination time, the current output recovery ability was slightly lower than that of 4h long-term illumination), proving that the device has a stable performance recovery phenomenon under multi-cycle illumination.



Supplementary Figure 18. Current responses during six illumination cycles

In general, the device can maintain a stable performance recovery response under multiple light cycles, indicating that the device can withstand multi-cycle cycles and has good durability. In addition, we added relevant discussion on page 20 of the revised

manuscript as follows: “In addition, we tested the repeatability and durability of MEG, and tested the voltage (Supplementary Fig. 17) and current (Supplementary Fig. 18) response images of MEG under multiple illumination cycles. The experimental results show that the device can maintain a stable response under multiple illumination cycles with good durability.”

[Comment 6] *The author asserts that the reticulated structure in P-CN constitutes nanopores; however, the fifth SEM image in Figure 2(a) does not clearly show nanopore diameters, and merely relying on the negative zeta potential of P-CN (Figure 3(b)) does not fully substantiate its cation selectivity. It is recommended to design cation selectivity experiments and couple them with theoretical calculations or molecular simulations to thoroughly elaborate on the selectivity mechanism.*

[Response] Thanks for your constructive comment. We took more detailed electron microscope photos of the nanopores (Figure R7) and marked the diameters of the nanopores. The diameters of the nanopores are all in the hundreds of nanometers or tens of nanometers, which meets the size requirements for the Debye effect to screen monopolar ions.

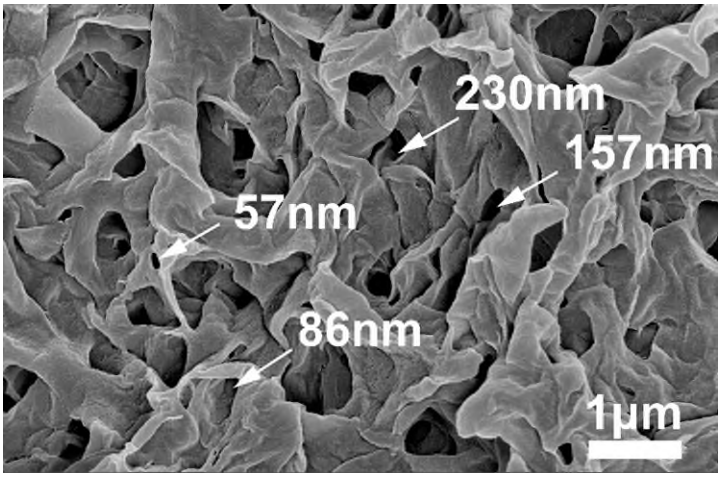
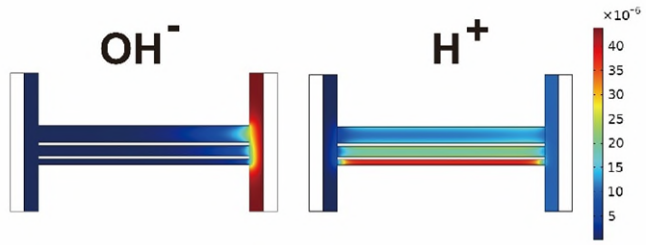


Fig. R7 Nanopores and pore diameters

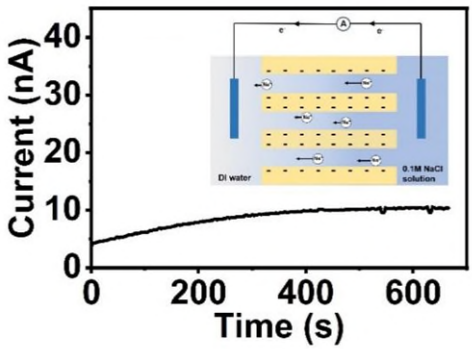
Moreover, we used COMSOL software to simulate the cation selectivity of the nanopores. The COMSOL simulation results also show (Supplementary Fig.7) that the nanopores obtained by SEM can only selectively pass cations.



Supplementary Fig. 7 Simulation of cation selectivity

In addition, we conducted a cation selectivity experiment to verify the cation

selectivity of PCL (Supplementary Fig. S8). In the system, the liquid on the left is deionized water, the right is a 0.1 mol/L NaCl solution, and the membrane in the middle is PCL. The unidirectional conductivity of ions passing through the membrane can be determined by the direction of the current. The experimental results show that the left side of the system is the positive electrode of the current, that is, the membrane can selectively pass cations, allowing them to move from the right to the left. Therefore, both the cation selectivity experiment and simulation analysis can prove that the membrane has cation selectivity.



Supplementary Fig. 8 Experiment of cation selectivity

[Comment 7] *In the saturated state image of Figure 4(a), ion distribution gradients should be taken into account.*

[Response] According to your comments, we further analyzed the experimental results. We found that when the gel was in a saturated state (as shown in Figure 4a), there was also a slight difference in pH between the upper and lower surfaces of the gel, with the pH of the upper surface being -0.73 and the pH of the lower surface being -0.53, indicating a weaker hydrogen ion distribution gradient. Therefore, we modified the saturated state object in Figure 4a and added some hydrogen ions in the upper half to indicate that there is still an ion distribution gradient in the saturated state. The modified picture is as follows:

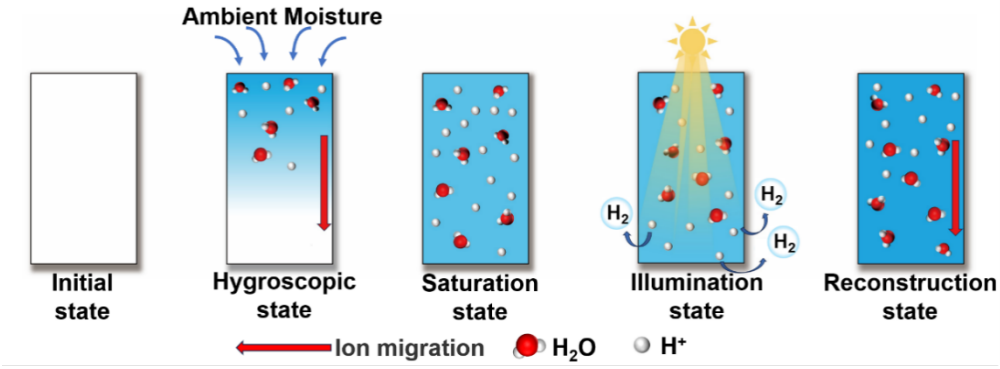


Fig. 4a Schematic diagram of moisture absorption and ion transport inside the MEL

[Comment 8] *As observed in Figure 5(e), the voltage at an RH of approximately 97 is lower than that at an RH of approximately 75. A reasonable explanation for this*

phenomenon should be provided in the main text.

[Response] Thank you for your patience and care. At 75% RH and 98% RH, the gel can effectively absorb moisture. However, at 98%RH, the device absorbs moisture at a high rate, and a large number of ions dissociate in the same period of time. The dissociation of ions will reduce the internal resistance of the device, resulting in an increase in current and a decrease in voltage in a 98% RH environment. We have modified the original text, and the content of page 19 of the revised manuscript is as follows: "However, at high humidity, supersaturated moisture absorption leads to a decrease in the internal resistance of the device, which in turn leads to a decrease in voltage output and an enhancement in current output."

[Comment 9] *Mark the peak positions in Figure 3(f).*

[Response] Thank you for your suggestion. We have marked the peak position and the modified image is shown in Figure 3f:

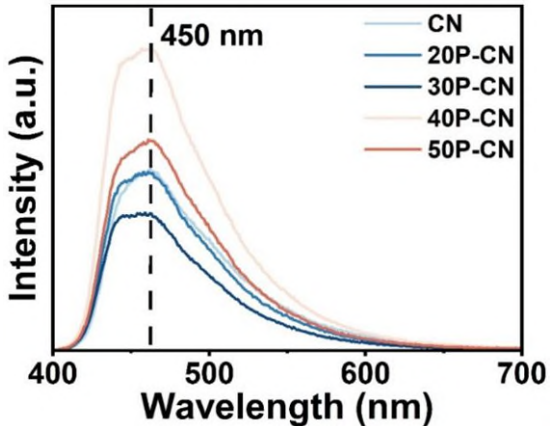


Fig. 3f Photoluminescence (PL) spectra of the CN and the P-CN with excitation wavelength of 380 nm.

[Comment 10] *The SEM image of the bottom electrode in the last panel of Figure 2(a) is unclear.*

[Response] We have re-photographed the bottom electrode and the modified image is shown below. In the re-photographed electrode, the morphology and structure of the CNT in the bottom electrode can be clearly seen.

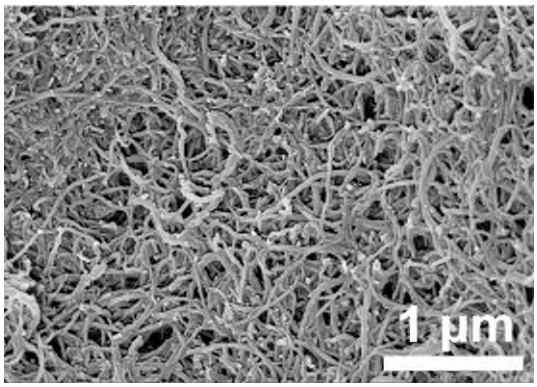


Fig. 2a SEM image of the bottom electrode

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Point-to-point response to the Reviewers' comments on the manuscript

"Moisture based green energy harvesting over 600 hours via photocatalysis-enhanced hydrovoltaic effect"

Reviewer #1 :

[General comment] *The authors have well addressed most of the comments and enhanced the overall quality of the manuscript. I think that the revised manuscript is now appropriate to be published in this journal without further revisions.*

[Response] Thank you very much for your suggestions. Your suggestions make our article more scientific.

Reviewer #2 :

[General comment] *The authors have revised and improved the manuscript according to the suggestions, and the manuscript is recommended for publication.*

[Response] Your suggestions make our article more perfect, thank you very much for your contribution.

Reviewer #3 :

[General comment] *The revised manuscript has been well polished according to the reviewer's comments, and it is recommended to accept and publish it.*

[Response] Thank you very much for your comments, which have made our article more rigorous and complete.