Contents lists available at ScienceDirect

Nano Energy

journal homepage: www.elsevier.com/locate/nanoen

Anion-cation heterostructured hydrogels for all-weather responsive electricity and water harvesting from atmospheric air

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ABSTRACT

Despite the recent boom in moisture-enabled electricity generation (MEG), it suffers from fabrication intricacy and materials inadequacy for water and energy harvesting purposes. Moreover, conventional MEGs face challenges in restricted operating humidity, inertness to subtle humidity fluctuations and inability to sustain longlasting power output under high humidity due to limitations in hydrophilicity and hydration. Here, we exploit a unique oppositely-charged hydrogel heterojunction for electricity and fresh water harvesting from atmospheric air without trade-offs in process simplicity and humidity limits. This anion-cation heterostructure engages two oppositely polarized ions and features a self-regulating ionic gradient for MEG in a dynamically fluctuating ambient, making it not only capable of responding to sluggish and subtle humidity fluctuations but delivering undisrupted power even under extremely wet conditions. Different from other MEGs, moisture can be captured and largely stored in the hydrogel and then released as fresh water. This moisture absorption/desorption, interestingly, is accompanied by electricity generation, indicating a two-in-one strategy to address the waterenergy nexus. In such a hydrogel heterojunction, multiple environmental elements like moisture, light, temperature, wind, etc., are feasibly mobilized for energy harvesting. This work provides a promising autonomous and continuous operation of an energy-water system for sustainable and decentralized purposes.

1. Introduction

ARTICLE INFO

Distributed energy generation

Low-grade energy harvestings

Atmospheric water harvestings

Light-heat conversions

Keywords:

Hydrogel diodes

Fueled by the urgency to address global warming and energy crisis along with the development of nanostructured materials, moistureenabled electricity generation (MEG), a nascent technology to produce electricity via the moisture-nanomaterials interactions, has burgeoned in recent years, [1–4] bringing about many MEGs crafted with a variety of materials including carbon materials, [5–8] graphene oxides, [9–13] polymers, [14–17] proteins, [18–20] transition metal oxides/dichalcogenides, [21–23] and others. [24–27] However, it is still a challenge to assemble MEGs in a simple approach and ensure the MEGs can effectively work without limitations from the external environment. For example, MEGs based on the mechanism of streaming potential necessitate sophisticated pumps or special settings for maintaining an uninterrupted hydrodynamic flow within MEG active materials, and the electrical output halts immediately once the water flow is interrupted. [4–7] Whilst MEGs based on the ionic gradient diffusion require complicated pretreatments or specific structure designs to ensure an ionic gradient that survive for a given time scale. Besides, the electricity output tends to be either transient in response to brief and dramatic humidity changes, [9,12,13,16] or continuous within strictly defined humidity limits. [10,11,19,27,28].

Exceeding the specific range, most materials will lose their MEG function due to the inadequate moisture-material interactions at low humidity and the quick collapse of the ionic gradient at high humidity. This, to a large extent, is because most active MEG materials have poor hydrophilicity at low RH, and possess very limited water storage capacity, hence becoming water-saturated rapidly at high RH. Once in contact with water, ions attributable to electricity generation (e.g. H⁺) would quickly be transferred, leading to the collapse of the ionic gradient and impairment of the generated potential. [3] Moreover, these generators are inactive or dormant to humidity variations, especially those in a real environment featuring low-frequency and low-amplitude changes. As such, they lose the agility to detect humidity fluctuations in

https://doi.org/10.1016/j.nanoen.2022.107892

Received 29 July 2022; Received in revised form 26 September 2022; Accepted 10 October 2022 Available online 14 October 2022 2211-2855/© 2022 Elsevier Ltd. All rights reserved.







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the real environment, and also the ability to restore energy generation function by exploiting humidity fluctuations to rebuild the ionic gradient. Also, the limited moisture and water storage within most MEG materials tarnishes the prospect of solving the interlaced water-energy challenges, where fresh water and electricity can be simultaneously harvested, e.g., from the atmospheric air.

Known for their superior hydrophilicity and hydration, charged hydrogels have become one of the advanced functional materials [29] and have shown promising potentials in e.g., osmotic energy harvesting [30–32] and bio-potential generation, [33] together with other exceptional merits such as soft, biocompatible, as well as ionic conductive and selectivity. Bringing together two oppositely charged hydrogels creates a hydrogel heterojunction (or the hydrogel ionic diode). Such a hydrogel heterojunction does not only inherit the merits of charged hydrogels, but also delivers unique traits, like enhanced adhesion and ionic transport control at the interface, and diode-like behavior, embracing the era of ionotronics [34] as applications like the ion-to-ion amplification, [35] soft diode, transistor, and electromechanical transducer, [36,37] wearable batteries, [38] and mechanical energy harvester. [39].

In this work, we demonstrate a soft and compliant moisture-enabled electricity and water generator (MEWG) constructed from a hydrogel heterojunction consisting of two oppositely charged hydrogels compact planar films without compromised interfacial integrity and process simplicity. Across the heterojunction, amplified and longstanding ionic gradients established by the oppositely-charged heterojunction, are employed to achieve continuous power generation over a wide humidity range of 20-100% RH. Distinct from other MEGs, particularly heterojunction-based MEGs, [14,25,26] our device inherits hydrogels' unique nature such as facile and diverse functionalization, smart responsiveness, high hydration, etc., making it a fully accessible platform to dynamically engage various environmental sources for autonomous operation. Through amenable functionalization of hydrogel with hygroscopic salts and photothermal light absorbers, the hydrogel heterojunction could engage solar light to deliver sustainable fresh water and electricity from the atmospheric air. Additionally, other environmental elements like solar light, temperature, and wind can also facilitate electricity generation, suggesting that the hydrogel heterojunction can be deployed as a hybrid system to harvest multiple low-grade energy sources from the environment. Hence, our cost-effective and eco-friendly MEG demonstrates the viability of an uninterrupted, decentralized energy harvesting strategy that is less inhibited by environmental factors and geographical distributions compared to other sustainable energy generation methods. [40,41].

2. Materials and methods

In a typical polyanion (PA) hydrogel synthesis, 0.5 g of poly (sodium 4-styrene sulfonate) (PAAS), 0.5 g acrylamide (AM), and 15 mg of N,N'methylenebisacrylamide (mBAm) cross-linker were dissolved in 4 ml of deionized (DI) water and purged with N₂ gas for 5 mins. Then, 5 mg of ammonium persulfate (APS) and 20 µl of N,N,N',N'-tetramethylethylenediamine (TEMED) was added into the purged solution. After that, the solution was transferred into a mold of 6 cm (L) \times 2.5 cm (W) \times 1.5 mm (H) and then the polymerization was initiated by UV irradiation (wavelength of 365 nm and optical power density of 350 mW·cm⁻²). After 20 mins, the polymerization was completed to obtain the PA hydrogel. Polycation (PC) hydrogel was synthesized by a similar method but replacing PAAS with 0.5 g of 3-acrylamidopropyl[trimethylammonium] chloride (DMAPAA-Q) and employing high temperature (70 °C) instead of UV light to initiate the polymerization. The synthesized hydrogels were cut into circles with a diameter of 4 mm. A PA/PC hydrogel heterojunction was attained by bringing PA and PC together, and then, this heterojunction was dried in a vacuum dryer for 3 days. After the vacuum drying, the water content of hydrogel heterojunction was measured to be 5 wt%. The purchased (carboxylic multiwalled carbon nanotubes, diameter < 8 nm, length 10-30 µm, XFNANO) CNTs

were firstly distributed in DI water assisted by ultrasonication. To prepare PA_CNT and PC_CNT, the CNT water solution (4 mg CNT / 1 g H2O) was used to replace the DI water for the synthesis of PA and PC hydrogel, respectively.

The chemical structures of the synthesized hydrogels were determined by a Fourier transform infrared (FTIR) spectrometer (IR Prestige-2, Shimadzu). The optical absorption spectra (300-800 nm) were acquired using a UV-Vis-NIR spectrophotometer (UV-3600, Shimadzu). The infrared (IR) images were captured by an Infrared camera (E50, FLIR). The peel adhesion between two pieces of hydrogels was measured by the 90-degree peel test performed on a force testing system (MultiTest-I, Mecmesin). The moisture harvesting experiments were conducted by placing dry hydrogel samples in a humidity chamber in which the relative humidity was controlled by a humidity generator (HumiSys, InstrQuest Inc.), and recording the weight of samples at certain time intervals. The moisture uptake was calculated according to, weight $gain = (m_t - m_{dry})/m_{dry}$, where m_{dry} and m_t are the weight of dry samples and samples at time t, respectively. To test the light illuminationinduced moisture desorption, saturated samples were exposed to one Sun irradiation (Solar Simulator, CEL-PE300L-3A, CEAu-Light), and the mass change and the temperature were recorded by electronic balance and IR camera, respectively. Kelvin probe force microscopy (KPFM) measurements were conducted on a commercial scanning probe microscopy (SPM) system attached with a humidity controllable cell (MPF-3D, Asylum Research, Oxford Instrument). For KPFM, a double-passing scheme with a lift height of 40 nm was adopted to minimize the topographic crosstalk and conductive Pt-coated silicon tips (AC240 PP, Olympus) were used.

The open-circuit voltage and the short-circuit current of the hydrogel heterojunction were recorded by an electrochemical workstation (CHI660EM, CH Instruments). To measure moisture-enabled electricity generation, the hydrogel heterojunction was placed in a closed chamber where the humidity level can be set as required by connecting to a humidity generator (HumiSys, InstrQuest Inc.). The voltage, the current, as well as the relative humidity inside the closed chamber were recorded (Fig. S11) to show the correlation between electricity generation and environmental humidity. The moisture-enabled electricity generation is quantified by the voltage increase. All the values of the voltages/currents presented in the figures are normalized by subtracting the voltages of the hydrogel cell at the initial state. For example, when testing the continuous power supply under a certain RH, the hydrogel cell is placed in a chamber with an extremely low RH (~10% RH) for one hour before the moisture feeding, and the final voltage presented at this RH is the value after deducting the voltage at 10% RH. Keeping samples under low RH aims to remove the moisture absorption during the sample transfer and keep stable the initial state of samples. Specifically, for the voltage changes as the humidity switching between two RH states, the hydrogel cell is stabilized at the lower RH before the humidity switching starts, and the final voltage is normalized by setting the voltage at the lower RH as zero. The outdoor experiments were carried out using a proof-ofconcept prototype at National University of Singapore on 16 May 2021 from 09:00 a.m. to 09: 00 p.m. The ambient temperature and humidity were recorded using an indoor air quality (IAQ) monitor (TSI Q-TRAK 7575).

3. Results and discussion

3.1. Synthesize charged hydrogels and hydrogel heterojunctions

Charged hydrogels were prepared by copolymerizing the chargeable monomer and acrylamide (AM). Poly (sodium 4-styrene sulfonate) (PAAS) and 3-acrylamidopropyl[trimethylammonium] chloride (DMA-PAA-Q) were used to impart negatively and positively chargeable monomers, respectively (Fig. S1-S2). Fig. 1 shows the conceptual scheme of MEWG that is designed from a hydrogel heterojunction consisting of two oppositely charged hydrogels: positively charged



Fig. 1. a) Schematic representation of moisture-enabled electricity and water generator (MEWG) made up of hydrogel heterojunctions consisting of two oppositely charged hydrogels: Positively charged PC and negatively charged PA hydrogels. Through the interaction between moisture and hydrogel heterojunctions, electricity closely depending on the environmental humidity is delivered from the generator: continuous power is yielded in a stable humidity while synchronously varying electrical signal is output in response to humidity fluctuations. b) Suggested moisture-enabled electricity generation mechanism via hydrogel heterojunction.

polycation (denoted as PC) and negatively charged polyanion (denoted as PA). The two oppositely charged hydrogels were brought together to construct a PA/PC heterojunction. When exposed to moist air, the charged hydrogels, owing to their hygroscopic nature, will quickly seize moisture from ambient and dissociate counter-ions from the polymer chains, making free dual ions with opposite polarity (e.g., positive Na⁺ in PA and negative Cl⁻ in PC) available for energy generation. As the long-range movement of the charged polymer chains is hindered, the diffusion of free counter-ions into the adjoining hydrogel will cause a depletion region of the mobile counter-ions thus forming an ionic double layer in the vicinity of the PA/PC interface. [35,36,38] In turn, this will induce an interfacial electrical field directing from PC to PA. Driven by this interfacial electrical field, counter-ions will drift in a direction opposite to that of the ionic diffusion. Thus, the interfacial electrical field helps to separate oppositely charged counter-ions in each hydrogel, ensuring the long-lasting ionic gradients and the generated potential. Humidity fluctuations prompt the hydration/dehydration process in hydrogels followed by the ionic gradient variations, which eventually are converted into the electrical output.

Notably, for such a hydrogel heterojunction, dual ions with opposite charge signs are involved in the power generation. This differs from the conventional MEGs where ions responsible for electricity generation are of the same polarity [13,15–17]. Engaging dual ions, coupled with the interfacial electrical field-regulated ionic flows, would effectively amplify the ionic gradients of positive or negative ions for an extended time scale. This offers the heterojunction with sufficient moisture sensitivity not only to respond to sluggish and subtle environmental humidity variations but also to work under various humidity levels. The feasible humidity range can span from extremely low humidity where limited free ions are pumped by the minute moisture absorption, to extremely high humidity where concentrations of free ions are diluted by the substantial moisture absorption. Meanwhile, as hydrogels are known to host and confine plenty of mobile ions in their highly hydrated network, the counter-ions attributable to MEG are well-retained in the hydrogel and not leeched at high humidity. Nevertheless, the typical protons (H⁺) active ions in most existing MEG systems are vulnerable to seepage loss of conductive ions.

The established interfacial electrical field endows the PA/PC heterojunction with the current rectification behavior [37,42], analogous to a semiconductor p-n junction. A forward voltage directing from PA to PC will attract the counter-ions into the PA/PC interface, shrinking the ionic double layer and passing the current flow through the junction; while a reverse voltage pointing from PC to PA will pull counter-ions away from the interface, widening the ionic double layer and hindering the current flow (Fig. 2a). This current rectification has been observed in the PA/PC hydrogel heterojunction, where the current at a positive voltage (2.5 V, applied to the PA/PC junction) is much larger than that at the negative voltage of -2.5 V (Fig. 2b), with a current rectification ratio up to 4.5 (Fig. S3). In contrast, this current flow with a preferential direction is not observed for PA/PA and PC/PC junctions. Likewise, static I-V (current-voltage) characteristics reveal the asymmetrical and symmetrical current flow under polarity-altered voltages for PA/PC and PA/PA or PC/PC junctions, respectively (Fig. S4). Additionally, this interfacial electrical field will favorably strengthen the bonding between two hydrogels by providing an additional electrostatic adhesion to the hydrogel interface. This results in the peel adhesion at the PA/PC heterojunction being more than double that of the PA/PA or PC/PC junctions (Fig. 2c). Note that the peel adhesion was measured on as-prepared hydrogels with a water content of around 70 wt%, and the peel force is observed to significantly increase with the decrease of the water content. To assess the structural stability in an extreme condition, we deployed this PA/PC heterojunction in an extremely wet condition (>100% RH) and there was no sign of hydrogel delamination (Fig. S5-S6). This, undoubtedly, testifies that assembling a hydrogel heterojunction-based MEG is viable and the resulting interfacial contact is stable and robust.

The prepared PA and PC hydrogels inherit the hygroscopic nature of polyelectrolyte [43] with moisture uptake of 4 wt% under 10% RH and of 85 wt% under 90% RH (Fig. S7), indicating the extraordinary sensitivity of charged hydrogels to moisture under a full-range humidity. The moisture absorbed by the hydrogel will cause counter-ions to dissociate



Fig. 2. a) Schematic of the formation of ionic double layer (IDL) and interfacial electric field (E) due to the entropic depletion of mobile ions at the PA/PC junction. The presence of IDL and E imparts the current rectification behaviour and the enhanced structural bonding to the hydrogel heterojunction. b) Under polarity-altered voltages, the current flow is asymmetrical for the PA/PC heterojunction, but it is symmetrical for the PA/PA or PC/PC junctions. c) The peel adhesions of the PA/PC heterojunction, the PA/PA, and PC/PC junctions. d) Histograms of the relative surface potentials of PA and PC hydrogels under various humidity levels. The surface potentials were measured by Kelvin Probe Force Microscopy (KPFM) and normalized relative to the surface potential in the dry air. e) The voltage evolution of PA/PC, PA/PA, and PC/PC junctions with the environmental humidity. f) The hydrogel heterojunction can deliver a long-lasting voltage under 90% RH. G) Comparison of the power supply durations of MEGs under high humidity level (90% RH and above).

from the polymer network, altering the localized concentration of counter-ions and correspondingly the surface potentials of hydrogels. To investigate the counter-ion dissociation under various humidity conditions, Kelvin Probe Force Microscopy (KPFM), [44] one of the scanning microscopy techniques, was combined probe with humidity-controllable setup (Fig. S8) for in-situ probing of hydrogels' surface potential under specified RHs. The acquired images and histograms of the surface potentials of PA and PC hydrogels under varied RHs are presented in Fig. S9. To clearly show the potential variation with the humidity, surface potentials are normalized relative to that at the dry state (0% RH). As shown in Fig. 2d, the relative surface potential of PA positively shifts to 0.075 V at 30% RH and 0.462 V at 50% RH with the increase in humidity. In contrast, the relative surface potential of PC negatively shifts to - 0.124 V at 30% RH and - 0.418 V at 50% RH, because of the dissociation and accumulation of counter-ions. The opposite changes in surface potential of PA and PC with humidity effectively amplify the potential difference across the junction (Fig. S10, and Table S1). This suggests the active involvement of dual ions of opposite polarity, instead of ions with single polarity, will greatly augment the MEG performance.

The inbuilt and amplified potential difference, together with the inherited hygroscopic nature as well as the enhanced interfacial integrity, are the competitive advantages of the proposed MEWG. To verify its feasibility, a PA/PC heterojunction with a diameter of 4 mm and thickness of 3 mm, clamped by two silver (Ag) plate electrodes, was placed in a humidity-adjustable closed chamber, and the voltage between the two electrodes was recorded as the humidity varied (Fig. S11). There was no voltage generation observed for the PA/PA and PC/PC junctions, while the voltage of the PA/PC was found to gradually rise to and then stabilize at 10 mV as the humidity increased from 10 to a

constant 60% RH. This demonstrates the capability of the heterostructured hydrogels to yield continuous electricity and also the determinative role of the PA/PC heterojunction for the MEG.

As mentioned, owing to the exceptional hydration level (Fig. S2) of charged hydrogels and also their ability to host many ions within the network, ions responsible for MEG are well-contained within the hydrogel and not leeched at high humidity. This, together with the ability to amplify the voltage, allows for a long-lasting power supply. As such, after nearly 45 h of exposure under 90% RH, the continuous voltage maintains at 10 mV (Fig. 2 f). This long-lasting power supply exceeds the previously reported values of other ionic-gradient-based MEGs of which the durations are often less than 5 h under 90%RH and above [8,25–27] (Fig. 2 g). It is worth noting that the power output duration of the streaming potential-based MEGs is not included here because it depends on how long the hydrodynamic flow within the MEG materials can be maintained by deliberately engaging sophisticated pumps or special settings, for instance.

3.2. MEG performance of the hydrogel heterojunction

Besides the continuous electrical output, the hydrogel heterojunction also displays its sensitivity to humidity fluctuations with various frequencies and amplitudes. Fig. 3a shows the electrical output of a discshaped hydrogel heterojunction with optimized hydrogel/moisture interaction (Fig. S12) in response to rapid switching of humidity (with a frequency of 0.2 Hz). The electrical signals that vary with the humidity can be repeated continuously (hundreds of cycles). Moreover, the electrical output is reproducible even after the hydrogel heterojunction is shelved for 24 h before resuming (Fig. S13). Fig. 3b, c, and Fig. S14 show the electrical signal of the hydrogel heterojunction in response to humidity variations with smaller frequencies (a scenario much closer to humidity changes in an actual environment). Independent of the frequency of the humidity variation, the electrical output of the hydrogel heterojunction is found to closely vary with changes in ambient humidity. Effectively, it works even when the humidity change is of low amplitude (e.g., RH%, Δ RH% < 10 RH%, in Fig. S15). All these results have demonstrated that the hydrogel heterojunction has excellent moisture sensitivity, structural integrity, and performance stability to work in the real environment.

Increasing humidity will boost the hydration degree of the hydrogels, making more free charges available to improve MEG electrical output. The MEG dependence of the hydrogel heterojunction on the humidity is illustrated in Fig. 3d, e, and S16, where the electrical output switches between valley and peak as the humidity ascends and descends between an initial 10% RH and targeted RHs. The peak voltages (currents) are observed to increase as the target RH increases from 20% to 50% RH. Moreover, the output voltage (current) is found to linearly increase with the number of heterojunction cells connected in series (parallel), demonstrating that the electrical output of our heterojunction can be effectively scaled up by increasing the cell number (Fig. 3f). A voltage up to 400 mV can be acquired by connecting 20 cells in series to successfully charge up a capacitor (Fig. 3g and S17).

3.3. Functionalization of hydrogel for water and energy harvesting

Earlier, we have shown that electricity can be generated as the hydrogel heterojunction hydrates in moist air. Beyond energy generation, the hydrogel is known for its high hydration capacity as it can hold copious water in its network, signifying that the captured moisture can be amassed in the hydrogel. To prove this, the electrical output and weight change of a PA/PC hydrogel heterojunction under stepwise humidity change were recorded. Stable voltages of 1.5, 11.7, and 20 mV (and currents of 0.19, 0.48, and 0.9 nA) are measured while keeping the heterojunction under 30%, 60%, and 90% RHs, respectively. In



Fig. 3. The MEG performance of the PA/PC hydrogel heterojunction. a-c) The voltage output of the hydrogel heterojunction in response to humidity variations with frequencies of a) 0.2 Hz, b) 0.016 Hz and c) 1.1×10^{-3} Hz. d-e) The electric output increases with the humidity. f) The linear relationship between voltage (or current) and the number of heterojunction cells connected in series (or in parallel). g) Voltage evolution of a capacitor (15 pF) being charged by 20 heterojunctions in series.

conjunction, during the same period of moisture exposure, weight gain of 7, 9, and 22 wt% are obtained accordingly (Fig. S18). Most reported MEG active materials, like carbon materials, polymers, and celluloses, have limited water storage capacity, making them challenging to concurrently achieve freshwater and electricity generation.

On top of the distinct water storage capacity, the hydrogel network offers an exceptional platform to achieve diverse materials modification or functionalization for varied purposes [29,45–48]. In our case, hygroscopic salts were infused to modify the hydrogel network interaction with the ambient moisture, while light absorbers, CNT were imbued to grant the hydrogel with the light-to-heat conversion feature (Fig. 4a). The capability of PA and PC hydrogels to seize moisture is significantly boosted by loading hygroscopic LiCl salt. As shown in Fig. 4b, the moisture uptake of the LiCl-loaded hydrogels is about five times that of LiCl-free hydrogels. Despite the substantial increase in moisture uptake, adding excessive salts into the hydrogel heterojunction is reported to undermine the ionic double layer and interfacial electric field [38]. This may reduce the ionic gradients across the heterojunction and lower the output voltage of the PA/PC hydrogel.

To determine the permissible amount of salt infusion for concurrent moisture and electricity harvesting, a series of hydrogel heterojunctions with various salt loadings were prepared. When the salt concentration is

less than 5 M, the hydrogel heterojunctions preserve the ability to generate electricity, presenting simultaneous moisture and electricity harvesting potential. Accordingly, the effects of the salt on the moisture uptake, the voltage generation, and the moisture sensitivity of the PA/ PC heterojunction are revealed in Fig. 4c. As the salt content increases, the moisture capture capability rises to a threefold increase at 5 M compared to the hydrogel without salt. As for the voltage generation characteristic, voltages up to more than a dozen millivolts can be acquired when the hydrogel salt loading is less than 10^{-5} M. As the salt loading increases further, the voltage drops to a few millivolts. Since environmental humidity and salt constitution are critical factors affecting the moisture and energy harvesting performance of the hydrogel heterojunction, a data visualization chart (Fig. 4d and Table S2) is provided to guide material design and operating humidity. From the chart, quantitative data clearly shows the evolutions of the moisture and energy generation functions under the influence of environmental humidity and hydrogel salt constitution. Correlations between the two variables will guide the crafting of appropriate hydrogel heterojunctions for specified purposes, whether it is solely for harvesting freshwater or electricity, or both in arid to humid climate environments.

The light-to-heat conversion feature endowed by the CNT-hydrogel hybridization enables solar-driven moisture desorption to release the



Fig. 4. a) Hybridation and functionalization of hydrogels for varied purposes. Imbuing the hydrogel with hygroscopic salt like LiCl will enhance its interaction with moisture and including a light absorber like CNT will enable the light-heat conversion and then the solar-driven moisture release. b) The water uptake of LiCl-free and LiCl (10 M)-loaded hydrogels under 90% RH for 24 h. c) The effect of the LiCl loading on the moisture uptake (under 60% RH for 1 h) and the voltage generation. d) The voltage and moisture uptake (for 1 h) of hydrogel heterojunctions with various LiCl loadings under various humidity levels. e) The light absorption of the CNT-free and CNT-loaded hydrogels. f) The electrical output of a PA_CNT/PC heterojunction in response to the light switching. g) Electricity generation and the concurrent weight loss of a highly hydrated PA_CNT/PC heterojunction under light illumination.

captured moisture from the hydrogel as freshwater [49,50]. As the solar moisture evaporation proceeds, ionic concentrations in a CNT-imbued hydrogel heterojunction will be increased to enhance or reconstruct the ionic gradients. Thus, apart from producing freshwater, light irradiation on a highly hydrated CNT-imbued hydrogel heterojunction also brings about synchronous electricity generation, allowing for the light-to-electricity conversion mediated by light-driven moisture desorption. With the CNT infusion, both the PA and PC hydrogels exhibit excellent light absorption (Fig. 4e). After light irradiation (one Sun) for seven min, the surface temperature of a hydrated hydrogel can be heated to 44 °C and after light heating for 20 min, a mass loss of 50 wt% can be achieved (Fig. S19).

To avoid the short circuit between two CNT-imbued hydrogels, only one of the hydrogels is infused with CNT to construct CNT-modified hydrogel heterojunctions i.e. PA/PC CNT or PA CNT/PC junctions. The light irradiation-induced energy generation is validated as the current and voltage rise/fall correspondingly with the on/off light switching (Fig. 4 f and S20). Fig. 4 g shows the electrical output and mass change of a highly hydrated PA CNT/PC heterojunction with time predominantly under light illumination state. Once the light is switched on, the voltage and current surge and then gradually increase with continuous illumination. After illuminating for half an hour, around 95 wt% of water is effectively desorbed from the hydrogel. Hence, the PA_CNT/PC hydrogel heterojunction demonstrates electricity generation during moisture absorption in the humid air as well as during moisture desorption under light irradiation. Furthermore, the ability of the PA_CNT/PC heterojunction to operate in a continuous absorptiondesorption process is validated in Fig. S21. The voltage increases rapidly at the early stage of moisture absorption and gradually drops as the hydrogel saturates with further moisture absorption. Notably, it immediately reconfigures its ionic gradation once the moisture desorption is activated by light illumination.

3.4. A hybrid system to harvest multiple low-grade energies in a real environment

To examine the feasibility of our hydrogel heterojunction working as a hybrid system to harvest multiple low-grade energies in a real environment, we fabricated a prototype consisting of a 4×7 array of

PA CNT/PC heterojunction cells (Fig. 5a) to perform outdoor testing. When placed in natural light, the PA_CNT surface has a higher temperature due to CNT photothermal effect (Fig. 5b and c). As presented in Fig. 5d, this prototype starts to generate electricity when exposed to moist air (stage I), and it can continuously work under various weather conditions including the humidity fluctuating morning, sunny noon, cloudy afternoon, and night. This suggests the robustness and also the striking feature of the device: its energy generation is continuous regardless of the day/night alternation, solar and wind intermittency, and humidity irregularity. Moreover, the electricity generation of the hydrogel heterojunction stems from the ionic gradient which can be readily initiated, enhanced, and rebuilt by changes in the hydration of hydrogels. As many elements in a real environment can couple with the relative humidity, such as temperature, wind, air pressure, precipitation, etc. the hydration of the hydrogel can be incessantly modulated to power the MEG continuously. For example, solar light illuminating the moisture-saturated hydrogels leads to water loss, which will reform the ionic gradient and boost the electrical output via a so-called solarthermo-electricity conversion (stage II). Temperature shows a similar effect on the electricity generation of the device (stage III). This demonstrates that the resilient electrical output of the hydrogel heterojunction can be modified by different weather elements serving as a hybrid generator system that either directly or indirectly harvests multiple energy sources from the environment. The explicitly or implicitly harvested energy comprises low-grade energy from diffuse or lowintensity sunlight, wind, fog, etc. which otherwise are untapped renewable energy potential.

4. Conclusion

In this work, we have introduced a moisture-enabled electricity and water generator from a hydrogel heterojunction consisting of two oppositely charged hydrogels. The unique features of the hydrogel heterojunction, including hygroscopicity, high hydration, dual ions of opposite polarity, and interfacial electric field are synergic to output electric power across a full humidity range from extremely low < 20% to high 100% RH. Remarkably, the hydrogel heterojunction has been demonstrated to deliver a long-lasting power supply (~50 mV and 0.36 nW·cm⁻², up to 40 h) under extremely wet condition (90% RH and



Fig. 5. a) The photo, b) the infrared photo, c) the temperature profile along the dashed line in b), and d) the electrical output of a MEG prototype including a 4×7 array of PA_CNT/PC heterojunctions in a real environment.

above). This unique capability to survive and to supply power for a long time is rarely reported in other MEGs. Besides, the hydrogel heterojunction has been demonstrated as a versatile platform for diverse functionalization in combating energy and water crises. For instance, incorporating hygroscopic LiCl salt into the hydrogel significantly enhances moisture capturing capability. Strikingly, within a permitted salt loading, atmospheric moisture and electricity harvesting can coexist. Additionally, infusing CNT into the hydrogel has granted the capability of water release from the hydrated gel and present power generation notwithstanding on/off light irradiation conditions. Mediated by the humidity variations, various environmental elements such as temperature, solar and wind are engaged in electrical power generation. To this end, the hydrogel heterojunction is designed as a hybrid system to harvest freshwater and multiple types of low-grade energy from the environment to mutually address the supposedly interlaced water and energy scarcity issues.

CRediT authorship contribution statement

Wanheng Lu: Conceptualization, Methodology, Data curation, Writing – original draft. Tianpeng Ding: Methodology. Xiaoqiao Wang: Methodology, Visualization. Chen Zhang: Conceptualization, Visualization. Tongtao Li: Writing – Review & editing. Kaiyang Zeng: Methodology, Supporting. Ghim Wei Ho: Supervision, Visualization, Writing – review & editing.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data Availability

no shared data/code.

Acknowledgement

The research is supported by National Research Foundation NRF2020NRF-CG001-023, A*STAR under its 2019 AME IRG & YIRG Grant Calls, A2083c0059 and the Advanced Research and Technology Innovation Centre (ARTIC), the National University of Singapore under Grant (project number: R261-518-014-720).

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2022.107892.

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