PAPER-BASED WEARABLE MOIST-ELECTRIC GENERATORS WITH EFFICIENT ATMOSPHERIC WATER CAPTURE

Yang Gao[1], *Anwar Elhadad*[1], *and Seokheun Choi*[1,2*]
[1]Bioelectronics & Microsystems Laboratory, Department of Electrical & Computer Engineering, State University of New York at Binghamton (SUNY Binghamton), Binghamton, New York, USA
[2]Center for Research in Advanced Sensing Technologies & Environmental Sustainability, SUNY Binghamton, Binghamton, New York, USA

ABSTRACT

This study unveils a pioneering yet straightforward approach to creating a moist-electric generator, using paper as the primary substrate and integrating bacterial endospores within it. The distribution of these endospores is meticulously regulated by the paper's inherent capillary action. The functional groups present on the endospores enhance moisture absorption and facilitate ion dissociation, resulting in a pronounced potential gradient driven by the variation in water content and endospore concentration. To augment water capture efficiency, a paper-based Janus layer combining hydrophobic and hydrophilic properties is applied atop the paper-based moist-electric generator. This dual-sided membrane excels in moisture condensation from the atmosphere and ensures unidirectional water transport to the generator, thus ensuring substantial electrical output even under low relative humidity conditions. This research not only addresses the challenges of power generation in wearable paper-based devices but also heralds new pathways for the development of autonomous, cost-effective, and eco-friendly energy solutions for wearable technologies.

KEYWORDS

Moist-electric generators, paper-based wearable electronics, water harvesting, hygroscopic materials; gradient diffusion

INTRODUCTION

Paper-based technologies offer significant advantages for single-use wearable applications, including their disposability, flexibility, biocompatibility, breathability, and cost efficiency [1]. Nonetheless, the integration of autonomous, self-sustaining power sources within wearable paper-based devices remains a substantial challenge [2]. Recent innovations have led to the development of a new class of energy harvesters that use the moisture-electric effect [3, 4]. This phenomenon exploits the generation of an ion gradient through the ionization of water molecules, with paper's inherent hygroscopic properties making it an ideal medium for such moist-electric generators [5]. These devices establish a moisture gradient through the capillary action of paper, while paper's innate functional groups facilitate the formation of an ion gradient by ionizing water molecules, thus generating an electric potential.

During the IEEE MEMS 2024 conference [6], our research team unveiled an innovative paper-based moist-electric generator, demonstrating considerable enhancements in performance. This breakthrough was achieved by fortifying the paper's inherent hygroscopic properties and functional groups through the strategic incorporation of bacterial endospores within the paper matrix. The presence of numerous functional groups on bacterial endospores' surfaces facilitates a unique interaction with moisture [7], leading to ion dissociation. This interaction creates a substantial potential gradient throughout the paper substrate, significantly enhancing its energy conversion capabilities (Figure 1). This innovative methodology not only enhances the paper's moisture absorption and retention capacities but also substantially increases its ionization potential. Consequently, the approach elevates the moist-electric generator's overall efficiency and performance, marking a significant advancement in the technology's development. However, the generator's efficiency markedly decreased at a relative humidity (RH) of 40%, with an output of only 0.2 V, underscoring a critical challenge for their practical use in wearable technologies and emphasizing the necessity for continued research to improve performance across diverse environmental conditions.

This study proposes a groundbreaking method to augment the atmospheric water capture capability of paper-based moist-electric generators by incorporating a novel Janus membrane with a dual-layer structure: a hydrophobic layer on one side and a hydrophilic layer on the other (Figure 2a). This Janus membrane exhibits exceptional directional water transport and superior atmospheric water capture efficiency (Figure 2b) [8], enabling the moist-electric generator to maintain substantial electrical output even at low RH levels (Figure 2c). This research transcends merely addressing the power limitations inherent in wearable paper-based devices; it pioneers new pathways for the creation of autonomous, cost-effective, and eco-conscious energy solutions tailored for wearable technologies.

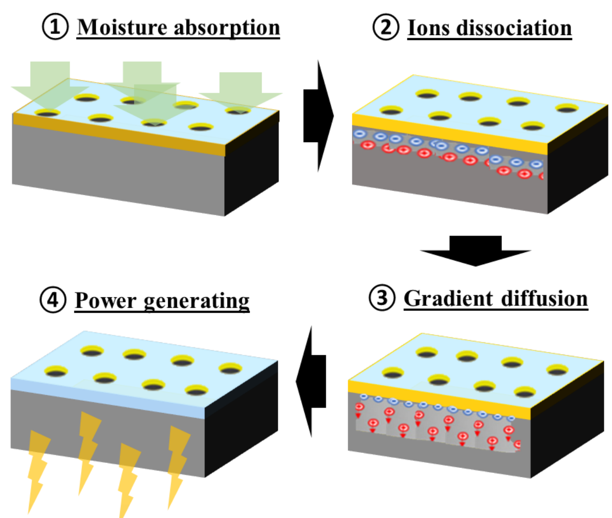

Figure 1: Schematic diagram illustrating the gradient-based moisture-to-electricity generation mechanism. Water molecules are first attracted and absorbed by the material, characterized by its hygroscopic nature and functional attributes, initiating the ionization of these water molecules. This process results in the liberation of a multitude of positively and negatively charged ions. Owing to the material's asymmetric functional structure and the moisture's uneven distribution primarily from the top, an ion concentration gradient is established. This gradient propels the directional migration of ions from areas of higher concentration to those of lower concentration. Such a movement engenders a built-in electrical field, culminating in the generation of electric potential across two electrodes.

978-1-1940470-05-4/HH2024/$25©2024TRF
DOI 10.31438/TRF.HH2024.16

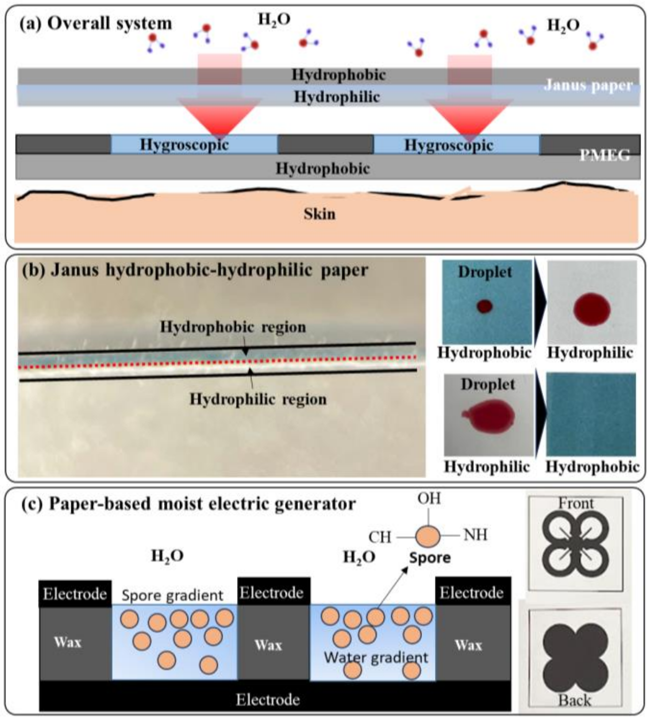

Figure 2: (a) Detailed schematic representation of our proposed system, featuring a synergistic integration of a Janus hydrophobic-hydrophilic paper membrane with a paper-based moisture-electric generator for enhanced performance. (b) High-resolution cross-sectional microscopic imagery of the Janus membrane, accompanied by visual demonstrations of its unidirectional water transport capability. (c) Comprehensive schematic and photographic depictions of the paper-based moist-electric generator, uniquely functionalized with bacterial endospores to optimize its operational efficiency.

EXPERIMENTAL PROCEDURE

Materials

The study employed a selection of specialized materials, including Grade 1 Whatman™ Filter Paper, sourced from Sigma-Aldrich; graphite ink, identified by the product code E3449, obtained from Ercon Inc.; and the Bacillus subtilis strain 168, courtesy of the American Type Culture Collection (ATCC).

Cultivation and sporulation of *B. subtilis*

We initiated the cultivation of bacterial cultures in Luria Broth (LB), maintaining a gentle agitation at 50 rpm and incubating at 37°C for a duration of 24 hours. Subsequent to this initial phase, sporulation was triggered on nutrient-deficient agar plates, adhering to well-established methodologies [9, 10]. Upon reaching maturity, the spores were meticulously harvested, subjected to centrifugation at 4000 rpm for four minutes, and subsequently resuspended in sterilized distilled water. To eliminate any cells that had not undergone sporulation, a heat treatment was applied at 80°C for 30 minutes. The ensuing purified spores were then carefully stored in hermetically sealed 15 mL tubes at 4°C, earmarked for use in future experiments.

Device fabrication

A detailed electrode configuration was designed using AutoCAD software, and this blueprint was then accurately imprinted onto paper using a wax printer. The design specified that the dimensions of the bottom electrode should measure 4 cm by 4 cm, establishing a solid foundation for the device. For the top electrode, graphite ink was employed to create a smaller footprint of 1 cm by 2 cm, strategically chosen to enhance moisture gradient absorption (Figure 2c). The precise application of conductive graphite ink on both electrodes was crucial to ensure consistent electrical conductivity throughout the device. The fabrication of the electrodes involved a screen-printing technique, utilizing a sacrificial mask to preserve the device's structural integrity and ensure precise alignment. The device's architecture was devised to facilitate moisture penetration from the top downward, thereby boosting the operational efficiency of the moist-electric generator. Bacterial endospores were embedded within the paper to enhance its hygroscopic properties and ion-dissociation capabilities. For uniform distribution across each device, 20 µL aliquots of the spore suspension were carefully dispensed using a pipette. A subsequent layer of wax, serving as a Janus membrane, was printed atop the device to optimize moisture absorption (Figure 2b). To enhance the manufacturability and wetting characteristics of Janus paper, a prototype Janus substrate was created and underwent a melting process at 150°C for 40 seconds, following methodologies described in previous research [8, 11]. This methodical approach highlighted the innovative design of the device and its capacity for efficient moisture-to-electricity conversion.

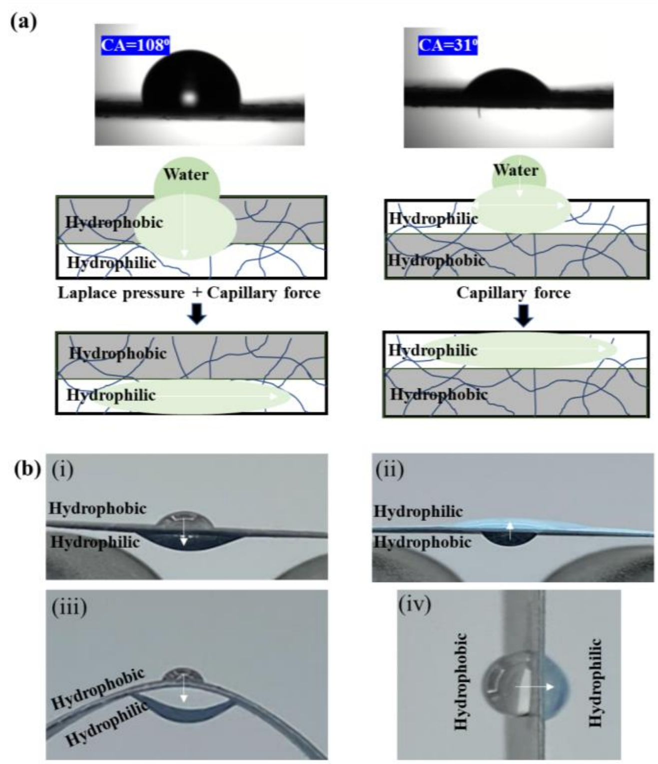

Figure 3: Dynamics of water interaction on a Janus membrane. (a) Photographs of a water droplet on both the hydrophobic and hydrophilic sides of the membrane, illustrating the contrasting wettability properties. Also, it Includes diagrams to further clarify the concepts of water wettability and directional transport across the membrane in these scenarios. (b) Photos of water transport through Janus membrane; (i) horizontal placement with hydrophobic side up, (ii) inverted with hydrophilic side up, (iii) curved shape with hydrophobic side exposed, and (iv) vertical orientation with hydrophobic side forward.

RESULTS AND DISCUSSION

Extensive research has demonstrated that surfaces with hydrophobic properties facilitate a significantly enhanced rate of moisture condensation in stagnant air environments, compared to their hydrophilic counterparts [12]. This improvement is attributed to the reduced contact angle hysteresis associated with hydrophobic surfaces [13]. Furthermore, the strategic incorporation of a hydrophilic interface beneath the hydrophobic layer (i.e., Janus membrane) enables a mechanism for unidirectional water movement, thereby augmenting the efficiency of moisture capture [14, 15]. The process of water droplet penetration through the hydrophobic layer is initiated when the downward exerted Laplace pressure surpasses the opposing hydrophobic force. Upon breaching the hydrophobic barrier and making contact with the underlying hydrophilic region, the droplet experiences a significant enhancement in driving force due to the capillary action intrinsic to the hydrophilic layer. This results in a directed flow of liquid from the hydrophobic surface to the hydrophilic interface, substantially optimizing moisture harvesting efficiency (Figure 3a). Contrastingly, droplets that land on the hydrophilic surface tend to spread across it without infiltrating the underlying layer. Droplets introduced to the hydrophobic side navigate through to the hydrophilic interface, effectively demonstrating wicking behavior (Figure 3b(i)). In scenarios where the membrane is inverted, thus exposing the hydrophobic layer downward, water droplets are capable of defying gravity to permeate the hydrophobic region and moisten the hydrophilic side (Figure 3b(ii)). This liquid transport mechanism persists even under conditions of mechanical deformation (Figure 3b(iii)). Additionally, the unidirectional liquid movement feature of the Janus paper is evidenced when the paper is positioned vertically (Figure 3b(iv)).

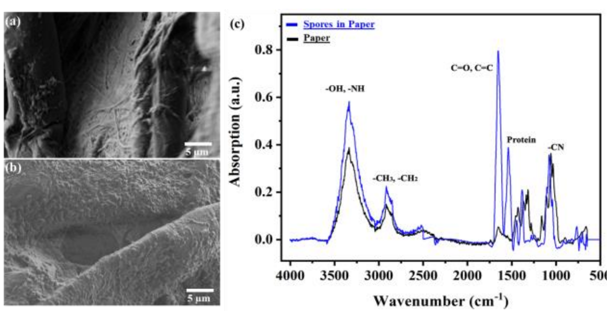

Figure 4: Scanning Electron Microscope (SEM) images depicting (a) bare paper (Whatman Grade 1) and (b) paper infused with spores. Subsequently, (c) showcases their corresponding Fourier-Transform Infrared Spectroscopy (FTIR) profiles.

Figures 4a and 4b reveal that bacterial endospores have been successfully integrated into the three-dimensional fiber networks of the paper. Although the native paper possesses a variety of functional groups, the introduction of spores significantly enriches its composition with an even broader spectrum of functional entities (Figure 4b). This diversification of functional groups is anticipated to enhance the ion dissociation capabilities of water molecules, thereby augmenting the efficacy of power generation [16, 17].

Because of the incorporation of endospores into the paper via capillary action from the top surface, there is a discernible concentration gradient, with a higher density of spores present at the top compared to the bottom (Figure 5). This deliberate gradation in spore concentration facilitates a moisture gradient absorbed from the surrounding air and an ion gradient induced by the functional groups of the spores. Such gradients collectively contribute to a significantly enhanced power generation capability.

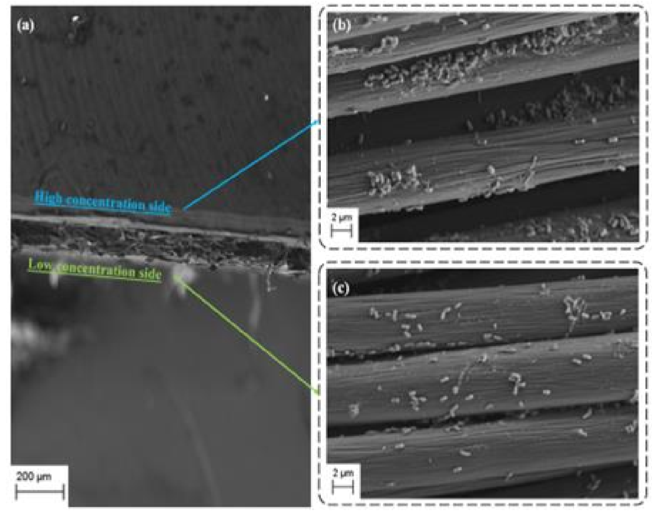

Figure 5: (a) Cross-sectional SEM image of the spore-infused paper, highlighting (b) the top and (b) the bottom regions of the paper.

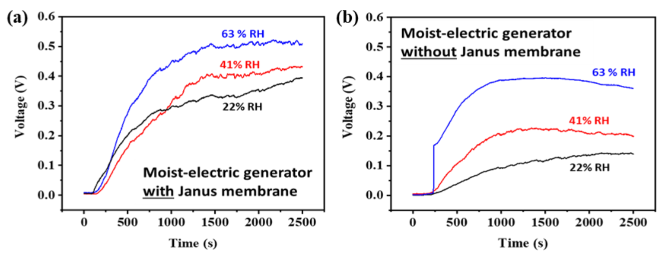

Figure 6: The open-circuit voltages produced by the paper-based moisture-electric generator are presented for two configurations: (a) equipped with the Janus membrane and (b) lacking the Janus membrane, under a range of relative humidity (RH) conditions. The configuration incorporating the Janus membrane demonstrated superior performance across all levels of RH, attributed to its enhanced capability to absorb and retain moisture in comparison to the unmodified paper-based moisture-electric generator

The enhanced design of our system integrates the Janus membrane with a paper-based moisture-electric generator. This innovative combination results in a significant performance improvement over configurations absent of the Janus membrane (Figure 6). The Janus membrane exhibits exceptional directional water transport capabilities and outstanding efficiency in capturing atmospheric water, thereby facilitating the moisture-electric generator to produce a markedly higher electrical output, even under conditions of low relative humidity (RH). Specifically, our device achieved an output voltage of approximately 0.4 V at a relatively low RH of 22%, a substantial increase compared to the 0.1 V generated by a system lacking the Janus membrane. Moreover, at elevated RH levels (41% and 63%), the electrical performance of our device significantly surpassed that of the non-Janus membrane configuration. This observation suggests that the moisture harvesting capacity of the Janus membrane could be a pivotal factor in enhancing the efficacy of moisture-electric generators.

Furthermore, our proposed system exhibited excellent scalability. By interconnecting individual units of the system in series, we observed a notable enhancement in voltage output (Figure 7a). Specifically, when five units were connected in series, the system was capable of generating approximately 1.8 V, which is sufficient to power a light-emitting diode (LED) (Figure 7b). Additionally, the system showcased remarkable potential for applications in wearable technologies (Figure 7c) and disposability (Figure 7d), underscoring its versatility and practical utility in a range of contexts.

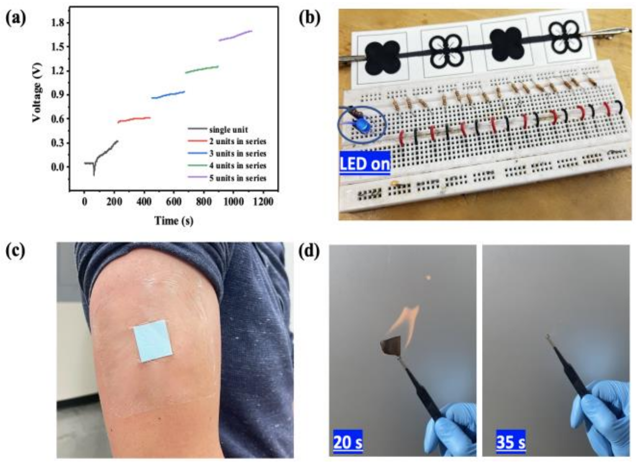

Figure 7: (a) The voltage output from a series of our device units, each with a different serial number, is presented. The electrical output of the moist-electric generator with the Janus membrane can be scaled up by integrating and connecting multiple units in series. (b) An LED can be lit through the serial connection of multiple units. (c) A photo image shows the device applied on skin. (d) The device's disposal by incineration is demonstrated.

CONCLUSION

This study introduces a groundbreaking Janus paper-based moist-electric generator that represents a significant advancement in harnessing atmospheric moisture for energy generation. The innovative integration of *Bacillus subtilis* endospores into a paper matrix, combined with the employment of a Janus membrane, has led to the creation of a hygroelectric device that operates efficiently across a broad spectrum of RH levels. Notably, the device achieves a voltage output of approximately 0.4V at an RH of 22%, markedly outperforming traditional models lacking the Janus membrane. The Janus membrane's unique ability for unidirectional liquid transport, paired with the hygroscopic properties of the bacterial endospores, constitutes a synergistic mechanism that significantly enhances the device's capacity to capture and convert atmospheric moisture into electrical energy. This strategic combination boosts the device's performance and provides a stable and augmented moisture source, facilitating continuous energy generation.

ACKNOWLEDGEMENTS

This research was supported by the SUNY ADL facility through its fee support program, the National Science Foundation under grant number ECCS #2246975, and in part by the Office of Naval Research under award number N00014-21-1-2412.

REFERENCES

[1] Y. Xu, Q. Fei, M. Page, G. Zhao, Y. Ling, S.B. Stoll, Z. Yan, Paper-based wearable electronics. *iScience*, 24, 102736, 2021.
[2] Y. Gao, M. Rezaie, S. Choi., A wearable, disposable paper-based self-charging power system integrating sweat-driven microbial energy harvesting and energy storage devices. *Nano Energy*, 104, 107923, 2022.
[3] H. Lim, M.S. Kim, Y. Cho, J. Ahn, S. Ahn, J.S. Nam, J. Bae, T.G. Yun, I. Kim, Hydrovoltaic electricity generator with hygroscopic materials: a review and new perspective. *Advanced Materials*, 36, 2301080, 2024.
[4] Y. Cao, B. Xu, Z. Li, H. Fu, Advanced design of high-performance moist-electric generators. *Advanced Functional Materials*, 33, 2301420, 2023.
[5] X. Gao, T. Xu, C. Shao, Y. Han, B. Lu, Z. Zhang, L. Qu, Electric power generation using paper materials. *Journal of Materials Chemistry A*, 7, 20574, 2019.
[6] Y. Gao, S. Choi, Paper-based moist-electric generators for scalable, disposable, and green power generation. *Proceedings of IEEE 37th International Conference on Micro Electro Mechanical Systems (MEMS)*. 2024. Pp. 741-744.
[7] A.B. Ammann, H. Brandl, Detection and differentiation of bacterial spores in a mineral matrix by Fourier transform infrared spectroscopy (FTIR) and chemometrical data treatment. *BMC Biophysics*, 4, 14, 2011.
[8] Y. Gao, S. Choi, Micropatternable Janus paper as a wearable skin patch for sweat collection and analysis. *Advanced Materials Technologies*, 8, 2300396, 2023.
[9] J. Ryu, M. Landers, S. Choi, A sweat-activated, wearable microbial fuel cell for long-term, on-demand power generation. *Biosensors and Bioelectronics*, 205, 114128, 2022.
[10] M. Landers, S. Choi, Small-scale, storable paper biobatteries activated via human bodily fluids. *Nano Energy*, 97, 107227, 2022.
[11] Y. Gao, A. Elhadad, S. Choi, "Janus paper-based wound dressings for effective exudate absorption and antibiotic delivery. *Advanced Engineering Materials*, 26, 2301422, 2024.
[12] Y. Wu, J. Zheng, M. Muneeshwaran, K. Yang, C. Wang, Moist air condensation heat transfer enhancement via superhydrophobicity. *International Journal of Heat and Mass Transfer*, 182, 121973, 2022.
[13] D. Song, B. Bhushan, Water condensation and transport on bioinspired triangular patterns with heterogeneous wettability at a low temperature. *Philos. Trans. A Math. Phys. Eng. Sci.*, 377, 20180335, 2019.
[14] J. Wu, H. Zhou, H. Wang, H. Shao, G. Yan, T. Lin, Novel water harvesting fibrous membranes with directional water transport capability. *Advanced Materials Interfaces*, 6, 1801529, 2019.
[15] X. Liu, D. Beysens, T. Bourouina, Water harvesting from air: current passive approaches and outlook. *ACS Materials Letters*, 4, 1003, 2022.
[16] H. Su, A. Nilghaz, D. Liu, L. Dai, J. Tian, J.M. Razal, K. Tang, J. Li, Harnessing the power of water: a review of hydroelectric nanogenerators. *Nano Energy*, 116, 108819, 2023.
[17] P. Guan, R. Zhu, G. Hu, R. Patterson, F. Chen, C. Liu, S. Zhang, Z. Reng, Y. Jiang, T. Wan, L. Hu, M. Li, Z. Xu, H. Xu, Z. Han, D. Chu, Recent development of moisture-enabled-electric nanogenerators. *Small*, 18, 2204603, 2022.

CONTACT

*Prof. S. Choi, tel: +1-607-777-5913; sechoi@binghamton.edu