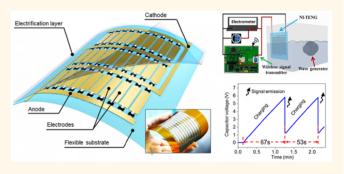


Highly Adaptive Solid-Liquid Interfacing **Triboelectric Nanogenerator for Harvesting Diverse Water Wave Energy**

Xue Jiao Zhao, †,‡ Shuang Yang Kuang, †,‡ Zhong Lin Wang, †,‡,|| and Guang Zhu*,†,‡,§®

Supporting Information

ABSTRACT: Harvesting water wave energy presents a significantly practical route to energy supply for selfpowered wireless sensing networks. Here we report a networked integrated triboelectric nanogenerator (NI-TENG) as a highly adaptive means of harvesting energy from interfacing interactions with various types of water waves. Having an arrayed networking structure, the NI-TENG can accommodate diverse water wave motions and generate stable electric output regardless of how random the water wave is. Nanoscaled surface morphology consisting of dense nanowire arrays is the key for obtaining high electric output. A NI-TENG having an area of 100 X



 70 mm^2 can produce a stable short-circuit current of 13.5 μ A and corresponding electric power of 1.03 mW at a water wave height of 12 cm. This merit promises practical applications of the NI-TENG in real circumstances, where water waves are highly variable and unpredictable. After energy storage, the generated electric energy can drive wireless sensing by autonomously transmitting data at a period less than 1 min. This work proposes a viable solution for powering individual standalone nodes in a wireless sensor network. Potential applications include but are not limited to long-term environment monitoring, marine surveillance, and off-shore navigation.

KEYWORDS: energy harvesting, contact electrification, water wave, self-powered, wireless sensing

mbient water wave motions represent a type of perpetual and sustainable mechanical energy. Exploitation of the water wave energy by power plants has major significance for producing electrical power for public utilities on a large scale.^{2,3} What is more, it also offers a viable solution to fulfilling onsite power needs for standalone systems, especially autonomous sensors in a wireless sensor network.⁴ Various types of marine hydrokinetic generators have been explored and commercialized. 1,5-8 However, those previously developed generators were designed to be bulky and heavy. They usually needed accessories, such as an absorber for capturing the water wave and a turbine to drive the generator. As a result, they could be driven by only violent water waves.^{6,7} This problem was properly addressed by recently developed thin-film structured triboelectric nanogenerators (TENGs), which are based on the combination of triboelectrification and electrostatic induction. $^{9-11}$ Specifically, the solid–liquid inter-

facing TENGs utilize surface triboelectric charges, generated by the interaction with the water wave and polymer, to drive an electric current as a wave repeatedly submerges the TENG. 12 It was proved that the TENG turned out to possess advantages such as high conversion efficiency, low cost, flexibility, and diverse choices of materials. In previously published works, the fundamental principle of the solid-liquid interfacing TENGs was discussed, which proved the effectiveness of the TENG in the conversion of water wave energy. 12-14 However, previous works were only applicable to regular water waves that interacted with the TENG through a linear water level.¹³

Received: December 9, 2017 Accepted: April 5, 2018 Published: April 5, 2018



[†]CAS Center for Excellence in Nanoscience, Beijing Key Laboratory of Micro-nano Energy and Sensor, Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences, Beijing 100083, China

[§]Department of Mechanical, Materials and Manufacturing Engineering, The University of Nottingham Ningbo China, Ningbo 315100, China

^{*}School of Nanoscience and Technology, University of Chinese Academy of Sciences, Beijing 100048, China

School of Materials Science and Engineering, Georgia Institute of Technology, Atlanta, Georgia 30332, United States

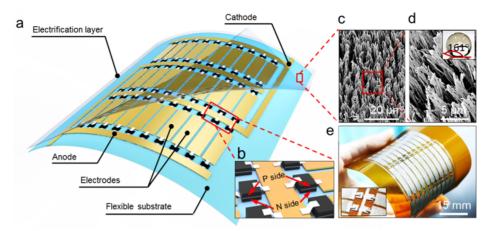


Figure 1. Structure of a networked integrated triboelectric nanogenerator (NI-TENG). (a) Schematic diagram of a NI-TENG. (b) Enlarged sketch of the arrayed bridge rectifiers. (c) SEM image of the PTFE nanowires on the electrification layer. (d) Enlarged view of the nanowires. Inset: Contact angle on the nanostructured surface. (e) Picture of a bendable as-fabricated NI-TENG. Inset: Enlarged view of the rectifying diodes.

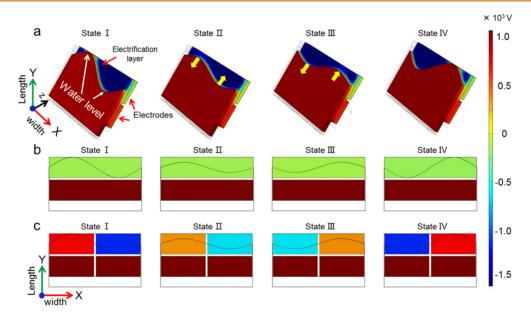


Figure 2. Electric potential distribution via COMSOL simulation as the water level interacts with two rows of electrodes at different states. (a) Top-down view of electric potential distribution on the electrodes that have one column. (b) Top-down view of electric potential distribution on the electrodes that have two columns.

Here, we report a networked integrated triboelectric nanogenerator (NI-TENG) as a highly adaptive means of harvesting energy from interfacing interactions with water waves of various types. Having a two-dimensional networked structure, the NI-TENG can accommodate diverse water wave motions that are either regular or highly random, which generates a stable electric output regardless of the wave type. This feature promises practical applications of the NI-TENG in real circumstances, where water waves are highly random and variable. A nanoscaled surface morphology consisting of dense nanowire arrays is the key to increasing the electric output. 15 A NI-TENG having dimensions of 100 mm by 70 mm can optimally produce a short-circuit current of 13.5 μ A with a corresponding electric power of 1.03 mW when the water interacts with the NI-TENG at a water wave height of 12 cm and at an average velocity of 0.5 m/s. After energy storage, the generated electric energy is adopted as a power supply for wireless sensing by autonomously transmitting data at a period

less than 1 min. This work proposes a viable solution for powering individual standalone nodes of a wireless sensor network. Potential applications include but are not limited to environment monitoring, water quality surveillance, and navigation.

RESULTS AND DISCUSSION

The NI-TENG consists of multiple thin-film layers (Figure 1a). We chose Kapton film as the substrate because of its excellent chemical stability, high temperature resistance, toughness, wear resistance, electric insulation, *etc.* A two-dimensional array of strip-shaped electrode units made of a conductive textile is laminated onto the substrate. Both ends of the electrode units are connected to a rectifying chip based on a p-n junction (Figure 1a). The two chips are in serial connection at the opposite sides of each electrode unit, as shown in the enlarged inset in Figure 1b. The comb-shaped anode bus and cathode bus are positioned between columns of the electrode units,

which are connected to the "P" and "N" side of the rectifying chips, respectively. The chips act as "gates", determining the flow of induced current from the anode to the cathode. The polytetrafluoroethylene (PTFE) film, the outermost layer, acts as an electrification layer as well as a waterproofing membrane. The surface of the PTFE film is covered with vertically aligned PTFE nanowires (Figure 1c,d). Not only do the nanowires make the surface more hydrophobic (with a water contact angle of 161°, shown in the inset of Figure 1d) but they also play a pivotal role in enhancing the electric output of the NI-TENG. ¹⁵ The photograph of a fabricated NI-TENG shown in Figure 1e illustrates the multilayered structure and presents its flexibility.

Extensive studies have been made in previous research showing that water motion on the PTFE surface can make the PTFE negatively charged. 16 Here we established a simplified simulation model, in which the electric potential distribution of two rows of the electrode units is obtained via the finite element method (Figure 2). Given the complexity of the water wave motions, ^{17,18} here we simplified the water level as a steady sinusoidal wave, on which each point performs reciprocating motion in the vertical direction. This assumption represents the interaction between the curved water level and the NI-TENG surface (Figure 2a). The amplitude of the reciprocating motion equals the width of an electrode unit. Four sequential states as the water level interacts with the NI-TENG surface are sorted out, shown in Figure 2a. If the electrode units have only one column (Figure 2b), the electric potential distribution on the electrode units remains unchanged regardless of the water wave motion. Without the change of the electric potential, the induced charge cannot flow between the cathode and the anode. As a result, even when connected to a load, no electric current can be produced, as illustrated in Figure 3a. If the electrode units are split into two columns, the electric potential distribution in accordance with the aforementioned four states experiences significant variation, as plotted in Figure 2c. At a transitional state in Figure 2c, the left-hand electrode column is emerging from the water, so the negative triboelectric charges on the NI-TENG are exposed. Such a water distribution reduces the electric potential on the left-hand electrode column. On the contrary, the right-hand electrode column is being submerged in the water, and the water screens the negative triboelectric charges on the NI-TENG, which raises the electric potential on the right-hand electrode column. The imbalance between the two electrode columns will produce an induced current in the external circuit. Due to the rectifying property of the diode chips, the induced current always has a flow direction from the anode to the cathode, as shown in Figure 3b. As a result, a transient current peak is then generated.

As described in the above analysis, the integration of a two-dimensional electrode network is vitally important to ensure the adaptability of the TENG in harvesting random wave energy. To experimentally elaborate this feature, we prepared five groups of NI-TENGs that have different column numbers from 1 to 5. The NI-TENGs were attached to the side wall of a water tank. A water wave that repeatedly submerged the NI-TENGs was generated by a wave generator (Figure 4a). To ensure that the height of the water wave affected the electric output, 13 the height was kept constant at 12 cm. As the area density of the electrode units increases due to the increase of the column number, the average amplitude of the short-circuit current is enhanced by over 73% from 7.9 μ A to 13.7 μ A. It is noticed that the enhancement is much more apparent when the

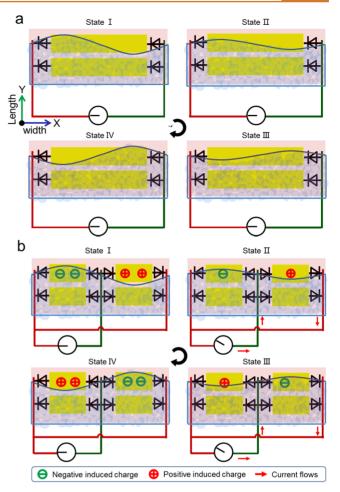


Figure 3. Current generation process of the NI-TENG. (a) No charge flow is produced from one column of electrode units. (b) Charge flow occurs for a NI-TENG with two columns of electrode units.

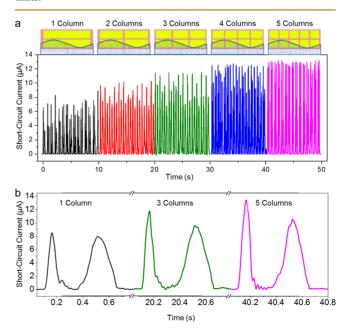


Figure 4. Electric current output of the NI-TENGs with different column numbers. (a) Short-circuit current from NI-TENGs with column numbers from 1 to 5. (b) One cycle of the current output from the NI-TENGs that have column numbers of 1, 3, and 5.

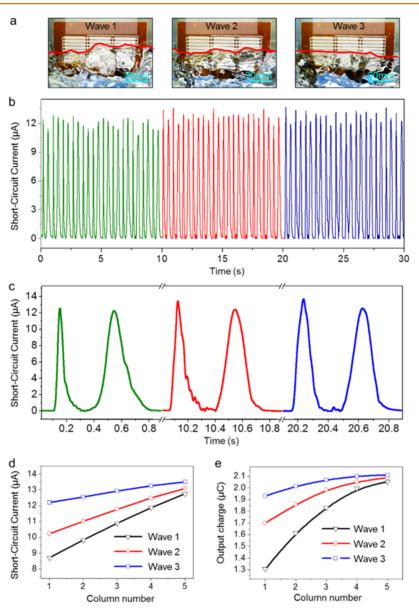


Figure 5. Output current characteristics of the NI-TENGs activated by different types of water waves. (a) Snapshots of different types of water waves that interact with a NI-TENG. Wave 1 represents the most random and dynamic water wave with a rough water level, while wave 3 represents the most smooth water wave with an almost linear water level. (b) Short-circuit current activated by the three types of water waves. (c) Enlarged view of one cycle of the output current. (d) Current amplitude and (e) induced charge carrying a current peak from the NI-TENGs with different column numbers as they are activated by the three types of water waves.

column number is small. If the column number exceeds 3, the amplitude of the current tends to saturate. The magnified view in Figure 4b shows one cycle of the electric current as a consequence of the dynamic interaction between the water wave and the NI-TENGs. One cycle of the interaction produces a pair of current peaks. The first peak corresponds to the submerging process, while the second one is in accordance with the emerging process. Both of the peaks have the same sign, indicating the same flow direction of the current as a result of the regulating p—n junctions.¹⁹ Although the two peaks carry the same quantity of charge, their amplitude differs. This is attributed to the fact that the submerging process is normally faster than then the emerging process.¹⁷ Consistent observations were also reported in previous works.¹³

The key advantage of the NI-TENG over previous TENGs lies in its adaptation to diverse types of water waves in practical

circumstances. To further elaborate this feature, a three-column NI-TENG was tested by using three different wave types. By changing the power of the multidirectional wave generator, we can tune the dynamics of the wave (Figure S1). A more dynamic water wave corresponds to a more rough and random water level that interacts with the NI-TENG. The water level is outlined and highlighted in Figure 5a. Figure 5b and magnified Figure 5c show the short-circuit current generated by the threecolumn device as the water wave changes from being violent (i.e., wave 1) to being smooth (i.e., wave 3). Regardless of how dynamic the water wave is, the NI-TENG maintains an almost constant output current. The correlation between the output current and the output charge on two major factors (i.e., column number and water wave type) is diagramed in Figure 4c and d, respectively. Increasing the column number results in enhanced electric output. If the water wave is smooth, changing

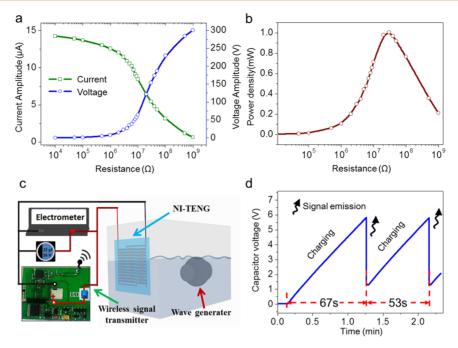


Figure 6. Electric output of a NI-TENG and its application as power source to drive wireless signal transmission. (a) Output voltage and output current as a function of load resistance. (b) Peak output power as a function of load resistance. (c) Setup for driving wireless signal transmission by a NI-TENG that harvests water wave energy. (d) Capacitor voltage as it is charged by the NI-TENG and then discharged to power the wireless signal transmission in a cyclic way.

the column number only slightly influences the electric output, while the influence becomes more significant as the water wave becomes more dynamic. Therefore, it is obtained that increasing the column number substantially benefits the tolerance of the NI-TENG to the condition of the ambient water wave, which then greatly expands the adaptation of the NI-TENG for its use in real circumstances.

To investigate the NI-TENG as a power supply, load matching curves were obtained by connecting an external load resistor that varies from 0.01 to 1000 M Ω (Figure 6a,b). The current amplitude decreases with the increase of the resistance, while the voltage amplitude builds up. Consequently, the instantaneous power reaches a maximum value of 1.03 mW at a load of 22 M Ω (Figure 6b). As a demonstration, the NI-TENG that efficiently harvests dynamic energy of random water waves was used to drive a wireless transmitter (Figure 6c and Video S1). The transmitter has a driving voltage of 5.8 V and a power consumption of 10 mW for wireless transmission. For the NI-TENG, it only takes 67 s to charge a 22 μ F capacitor to achieve the driving voltage of the transmitter. Upon releasing the stored electric power, the transmitter is triggered, and the voltage of the capacitor drops to 1.4 V. After the initial charging, it then takes 53 s to charge the capacitor for another transmission, which shows broad application prospects for long-term and real-time power supply for hydrological monitoring, environmental pollution detection, and even wireless sensor networks.

CONCLUSIONS

In conclusion, we propose a flexible solid—liquid contacting NI-TENG with two-dimensional electrode arrays, which can efficiently convert either regular or random water wave dynamic energy into electrical energy. Experimental results demonstrate that the two-dimensional arrayed electrode structure allows the NI-TENG to be unaffected by the water wave motion and achieve a high and stable electric output. The generated

electrical energy was successfully stored and released to power wireless signal transmission, which proves the practical use of the NI-TENG as a power supply for sensor nodes in a wireless sensing network. It can be potentially implemented for regular marine hydrology monitoring, pollution detection, locating/tracking, etc.

METHODS

Fabrication of the Thin-Film NI-TENG. A Kapton substrate with dimensions of 100 mm by 70 mm by 125 μ m was incised by laser cutting. The electrode units as well as the anode and the cathode buses were made of conductive textile defined by laser cutting. The width of the electrode units was 4.5 mm, and the interval between adjacent rows was 0.7 mm. A total of 10 rows were prepared. The electrode structure was pasted onto the substrate. Rectifying chips were connected to both ends of the electrode units by double-sided copper-based adhesive tape. A PTFE film (30 μ m in thickness) covered the entire structure by laminating a layer of adhesive glue in between.

Fabrication of the PTFE Nanowires. First, the PTFE film was cleaned successively by menthol, isopropyl alcohol, and deionized water. Then it was dried by compressed air. Second, a layer of Au of about 10 nm thick was deposited onto the PTFE film, which served as a nanoscale mask. Third, the PTFE film after the Au coating was etched by inductively coupled plasma to obtain the polymer nanowires. The etching gas was a mixture of O_2 , Ar, and CF_4 gases with a flow of 10.0, 15.0, and 30.0 sccm, respectively. A 200 W power source for generating plasma and a 100 W power for accelerating the plasma ions were used. The etching time was 600 s.

Data Acquisition. The thin-film NI-TENG was fixed on the side wall of a water tank. Deionized water was poured into the tank until the NI-TENG was half submerged by the water. A water wave that repeatedly submerged the NI-TENG was generated by a wave generator. It has different working modes that can generate corresponding types of wave levels that interact with the NI-TENG. In this work, we chose three working modes (Figure S1) to carry out the experiments. An electrometer (Keithley 6514) was used to acquire the electric output of the NI-TENG.

ASSOCIATED CONTENT

S Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsnano.7b08716.

Video demonstration of the NI-TENG harvesting dynamic energy of random water waves driving a wireless transmitter (AVI)

Image analysis for the random wave levels under different working modes of the wave generator (PDF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: zhuguang@binn.cas.cn.

ORCID ®

Guang Zhu: 0000-0003-2350-0369

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This research was supported by the National Key R&D Project from Ministry of Science and Technology (Grant Nos. 2016YFA0202701 and 2016YFA0202703), National Science Foundation of China (Grant No. 51572030), Beijing Natural Science Foundation (Grant No. 2162047), China Thousand Talents Program, and Chongqing Research Program of Basic Research and Frontier Technology (Grant No. cstc2016jcy-jA0236).

REFERENCES

- (1) Scruggs, J.; Jacob, P. Harvesting Ocean Wave Energy. *Science* **2009**, 323, 1176–1178.
- (2) Falcão, A. F. d. O. Wave Energy Utilization: A Review of the Technologies. *Renewable Sustainable Energy Rev.* **2010**, *14*, 899–918.
- (3) Lubick, N. Harnessing Waves for Energy. Environ. Sci. Technol. 2009, 43, 2204-2205.
- (4) Kornbluh, R. D.; Pelrine, R.; Prahlad, H.; Wong-Foy, A.; McCoy, B.; Kim, S.; Eckerle, J.; Low, T. Electroactivity in Polymeric Materials. In *From Boots to Buoys: Promises and Challenges of Dielectric Elastomer Energy Harvesting*; Rasmussen, L., Ed.; Springer US: New York, 2012; pp 67–93.
- (5) Muetze, A.; Vining, J. G. In *Ocean Wave Energy Conversion* Industry Applications Conference, 2006. 41st IAS Annual Meeting. Conference Record of the 2006 IEEE, Tampa, Florida, Oct. 8–12, 2006; Tampa, FL, 2006; pp 1410–1417.
- (6) Rhinefrank, K.; Agamloh, E. B.; von Jouanne, A.; Wallace, A. K.; Prudell, J.; Kimble, K.; Aills, J.; Schmidt, E.; Chan, P.; Sweeny, B.; Schacher, A. Novel Ocean Energy Permanent Magnet Linear Generator Buoy. *Renewable Energy* **2006**, *31*, 1279–1298.
- (7) Falnes, J. A review of wave-energy extraction. *Mar. Struct.* **2007**, 20, 185–201.
- (8) Gutfleisch, O.; Willard, M. A.; Brück, E.; Chen, C. H.; Sankar, S. G.; Liu, J. P. Magnetic Materials and Devices for the 21st Century: Stronger, Lighter, and More Energy Efficient. *Adv. Mater.* **2011**, 23, 821–842.
- (9) Wang, Z. L. Triboelectric Nanogenerators as New Energy Technology for Self-Powered Systems and as Active Mechanical and Chemical Sensors. *ACS Nano* **2013**, *7*, 9533–9557.
- (10) Zhang, Q.; Liang, Q.; Liao, Q.; Yi, F.; Zheng, X.; Ma, M.; Gao, F.; Zhang, Y. Service Behavior of Multifunctional Triboelectric Nanogenerators. *Adv. Mater.* **2017**, *29*, 1606703.
- (11) Ma, M.; Liao, Q.; Zhang, G.; Zhang, Z.; Liang, Q.; Zhang, Y. Self-Recovering Triboelectric Nanogenerator as Active Multifunctional Sensors. *Adv. Funct. Mater.* **2015**, 25, 6489–6494.

- (12) Zhu, G.; Su, Y.; Bai, P.; Chen, J.; Jing, Q.; Yang, W.; Wang, Z. L. Harvesting Water Wave Energy by Asymmetric Screening of Electrostatic Charges on a Nanostructured Hydrophobic Thin-Film Surface. ACS Nano 2014, 8, 6031–6037.
- (13) Zhao, X. J.; Zhu, G.; Fan, Y. J.; Li, H. Y.; Wang, Z. L. Triboelectric Charging at the Nanostructured Solid-liquid Interface for Area-Scalable Wave Energy Conversion and Its Use in Corrosion Protection. ACS Nano 2015, 9, 7671–7677.
- (14) Wang, Z. L.; Jiang, T.; Xu, L. Toward the Blue Energy Dream by Triboelectric Nanogenerator Networks. *Nano Energy* **2017**, *39*, 9–23. (15) Zhu, G.; Lin, Z. H.; Jing, Q.; Bai, P.; Pan, C.; Yang, Y.; Zhou, Y.; Wang, Z. L. Toward Large-scale Energy Harvesting by A Nanoparticle-Enhanced Triboelectric Nanogenerator. *Nano Lett.* **2013**, *13*, 847–852
- (16) Lin, Z. H.; Cheng, G.; Lin, L.; Lee, S.; Wang, Z. L. Water-Solid Surface Contact Electrification and Its Use for Harvesting Liquid-wave Energy. *Angew. Chem., Int. Ed.* **2013**, *52*, 12545–12549.
- (17) Madsen, P. A.; Sørensen, O. R.; Schäffer, H. A. Surf Zone Dynamics Simulated by a Boussinesq Type Model. Part I. Model Description and Cross-shore Motion of Regular Waves. *Coast. Eng.* 1997, 32, 255–287.
- (18) Falnes, J. Ocean Waves and Oscillating Systems: Linear Interactions Including Wave-Energy Extraction[M]; Cambridge University Press: Cambridge, UK, 2002; pp 75–84.
- (19) Meng, X. S.; Wang, Z. L.; Zhu, G. Triboelectric-Potential-Regulated Charge Transport Through p—n Junctions for Area-Scalable Conversion of Mechanical Energy. *Adv. Mater.* **2016**, *28*, 668–676.