A nanowire based triboelectric nanogenerator for harvesting water wave energy and its applications

Xiaoyi Li, Juan Tao, Jing Zhu, and Caofeng Pan

Citation: APL Materials **5**, 074104 (2017); doi: 10.1063/1.4977216
View online: http://dx.doi.org/10.1063/1.4977216
View Table of Contents: http://aip.scitation.org/toc/apm/5/7
Published by the American Institute of Physics

A nanowire based triboelectric nanogenerator for harvesting water wave energy and its applications

Xiaoyi Li,[1,2] Juan Tao,[2] Jing Zhu,[1,a] and Caofeng Pan[2,a]
[1]*National Center for Electron Microscopy in Beijing, School of Materials Science and Engineering; The State Key Laboratory of New Ceramics and Fine Processing; Key Laboratory of Advanced Materials (MOE); Center for Nano and Micro Mechanics, Tsinghua University, Beijing 100084, People's Republic of China*
[2]*Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences; National Center for Nanoscience and Technology, Beijing 100083, People's Republic of China*

(Received 19 January 2017; accepted 9 February 2017; published online 6 March 2017)

The ocean wave energy is one of the most promising renewable and clean energy sources for human life, which is the so-called "Blue energy." In this work, a nanowire based triboelectric nanogenerator was designed for harvesting wave energy. The nanowires on the surface of FEP largely raise the contacting area with water and also make the polymer film hydrophobic. The output can reach 10 μA and 200 V. When combined with a capacitor, an infrared emitter, and a receiver, a self-powered wireless infrared system is fabricated, which can be used in the fields of communication and detecting. © *2017 Author(s). All article content, except where otherwise noted, is licensed under a Creative Commons Attribution (CC BY) license (http://creativecommons.org/licenses/by/4.0/).* [http://dx.doi.org/10.1063/1.4977216]

The growing crisis in energy becomes more and more serious in recent years, which call for renewable and clean energy to ensure the human civilization's sustainable development. The renewable energies, such as wind, water wave, and solar energy,[1–6] have attracted more and more scientists' attentions. The energy harvested from the ocean, also called blue energy, presents superior advantages when compared with other renewable energies due to its less dependence on weather, season, temperature, or the circadian rhythm.[3,7] In addition, the oceans are widely distributed in our planet and cover most surface of the earth; the blue energy is abundant and almost inexhaustible. However it is rather challenging to collect such widely distributed water energy because of the current technologies' limitations, and the energy in oceans still needs to be further harvested. Up to now, although the electromagnetic generators are expensive, easily corroded, heavy, and inefficient at the low frequency of ocean wave, they are still mostly used to collect the water wave energy by indirectly converting the wave energy to electric energy. Fortunately, the low-cost, chemical stable, lightweight, small-sized, and high efficient triboelectric nanogenerators (TENGs), which can directly convert the mechanical energy in the environment to electric energy, can minimize the problem.[8–12]

Herein we report a nanowire based TENG to collect the blue energy from ocean and its great potential for applications. First, the nanowire, which will largely add the roughness of surface and thus magnificently increase the contacting area of the FEP film and water, is fabricated by etching.[13,14] The friction process will be more sufficient between the FEP and water and the process will generate more charges. Therefore the output of the TENG is magnificently increased.[15] Then, an output current of 10 μA and a voltage of about 200 V are generated by the nanowire based TENG (a contact area of 30 cm^2). Due to the sufficient friction, the transferred charge of the submerging or emerging process can reach 200 nC, which is much higher than our previous reports.[16,17] The TENG is so powerful that it can charge a 3.3 μF capacitor to 1.1 V in 15 s. Finally, the energy stored in the capacitor can be used to drive the time measuring device, temperature or humidity sensors. A self-powered wireless infrared system is fabricated for the use of communication or detecting. The nanowire based TENG can also be used as a chemical sensor for the ethanol concentration in the liquid. This work extends

[a]Electronic addresses: cfpan@binn.cas.cn and jzhu@mail.tsinghua.edu.cn

 © Author(s) 2017

a novel method of harvesting the blue energy and provides the strategies for enhancing the TENG's output performance, which will largely broaden the TENG's applications.

The nanowire based TENG is fabricated according to the following steps in Fig. 1. A FEP film was cleaned by ethanol and deionized water in Fig. 1(a). Then a thin film consisting of Au nanopartical was coated on the polymer film by sputtering, which functioned as a nanoscale mask to fabricate the polymer nanowires. Then the polymer film was etched by the inductively coupled plasma (ICP) for 2 min. O_2 and Ar gases were induced into the action chamber by the ratios of 10 and 50 sccm, respectively. A 500 W source was utilized to create a large amount of plasma while a power (100 W) was applied to speed plasma ions up. More technical details of the etching could be seen in other relative works.[3,18] The surface structure will largely roughen the surface and thus magnificently increases the contacting area of the polymer and water.[19] So the friction process will be more sufficient between the polymer and water, which will generate more charges in the friction process.[20–22]

The working principle of the nanowire based TENG is demonstrated in Figs. 1(g)–1(k) to briefly demonstrate how the current is created by the TENG. The structure of the device is schemed in Fig. 1(g). The friction acts at the contact surface of FEP and water. Because the FEP material has a higher triboelectrical negative property, the negative charges from the water will be attracted to the FEP surface. The FEP material retain the negative charges for a period of time, as shown in Fig. 1(h). When the FEP is submerged into water, the electrode at the FEP side has a higher potential than the water and thus the current will be compelled to flow to the water through external circuit, shown in

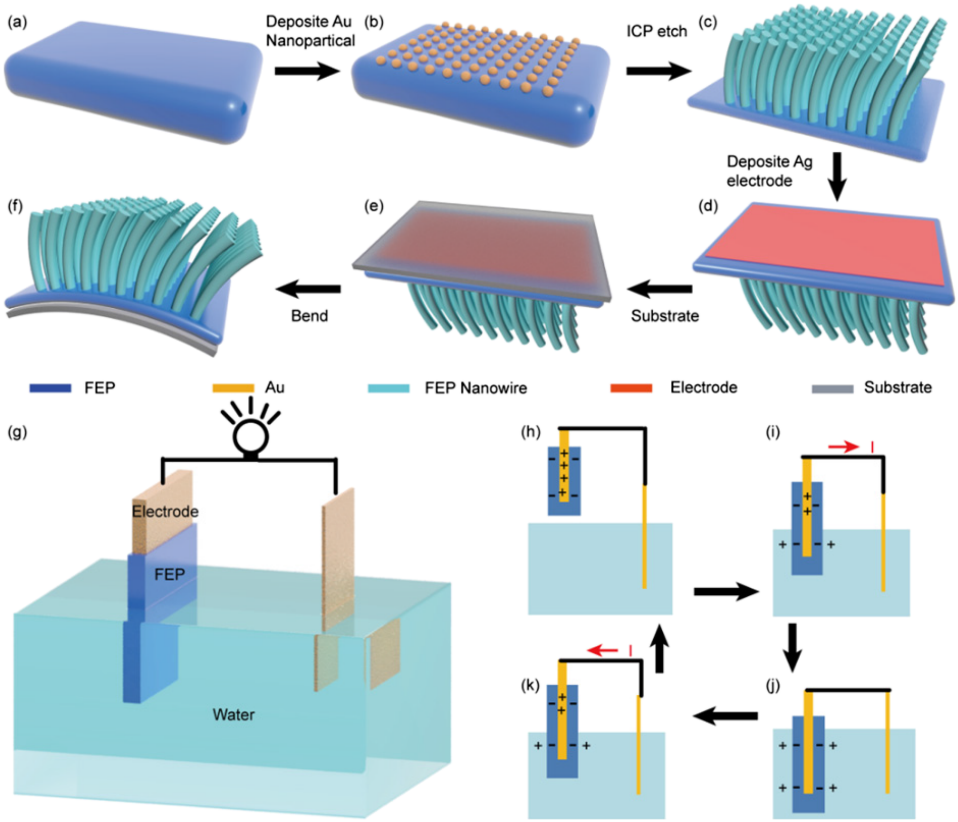

FIG. 1. (a) A schematic drawing of the FEP polymer film. (b) Au nanopartical was deposited on the FEP film as a nano-scale mask. (c) The nanowires structure was created on the FEP's surface by ICP etching. (d) Depositing the Ag electrode on the other side of the FEP film. (e) The fabricated device was attached to a flexible substrate. (f) Illustration of a bent nanowire based TENG. (g) The working principle of the nanowire based TENG. The up/down operation of the TENG will induce current between the two electrodes. Step-by-step illustration from the separate state (h) to the contact state (j) clearly shows the principle. When the TENG is submerged into water (i), the current runs from the electrode of FEP side to the electrode/water through the external circuit. When the TENG is emerged out of water (k), the current runs back to the FEP/electrode side.

Fig. 1(i). As the FEP is pulled out of water, the current will flow from the water to the electrode at the FEP side (Figs. 1(j) and 1(k)). During the repetitive operation, the electrons/currents will flow between the two electrodes causing the different directions of current (Fig. 2(c)).

The picture of the nanowire based TENG (the transparent FEP film and electrode on the back side of the film) is shown in Fig. 2(a), and the nanowire structure image taken by the scanning electron microscopy (SEM) is demonstrated in Fig. 2(b). The output signals of current, voltage, and the transferred charges are displayed in Figs. 2(c)–2(e), respectively.

It is obvious that the nanowire based TENG has a high output performance as the current of 10 μA (Fig. 2(c)), transferred charges of 200 nC (Fig. 2(e)), and voltage of 200 V (Fig. 2(d)).[23–25] During the submerging operation, the current and the voltage correspond to a narrow peak with high amplitudes, while during the emerging operation they correspond to a smaller and wider peak. Although the current of the submerging process is larger than the value of the emerging current, the integration areas of the two currents are almost the same. The result corresponds to the transferred charge in Fig. 2(e). When the nanowire based TENG is submerged into water, the charge reaches about 200 nC while it comes down to 0 nC after the emerging operation. To clearly discover the nanowire based TENG's properties, the voltage and current outputs of the nanowire based TENG are measured when under different resistances (Fig. 2(f)).[26] According to the results, the current has little decrease when the resistance is below 10 MΩ and the voltage is very small. Once the resistance is bigger than 10 MΩ, the current decreases rapidly and the output voltage increases sharply. Therefore, the maximum instantaneous power generated by the TENG reaches about 16 μW at a resistance of 20 MΩ, shown in the inset. And the signals of TENGs with and without nanowires are illustrated in Fig. S1 in the supplementary material to demonstrate the enhancement.

Interestingly, the TENG can be used not only as an energy generator but a chemical sensor as well. We demonstrated that the current of the nanowire based TENG decreased from 2.34 μA to 0.4 μA as the ethanol volume percentage in the liquid increased from 2.5% to 50% (Fig. 3(a)).

The decrease of current is caused by the decreasing total polarity and the conductive changes of the liquid when the water is mixed by ethanol. Previous study has verified that the dielectric constant and polarity of water will decrease when mixed by a less polar liquid, such as ethanol.[12] And the liquid's conductivity is also an important factor to the ability of generating triboelectric charges. Meanwhile, increasing the ethanol concentration in the liquid will enhance the interaction between

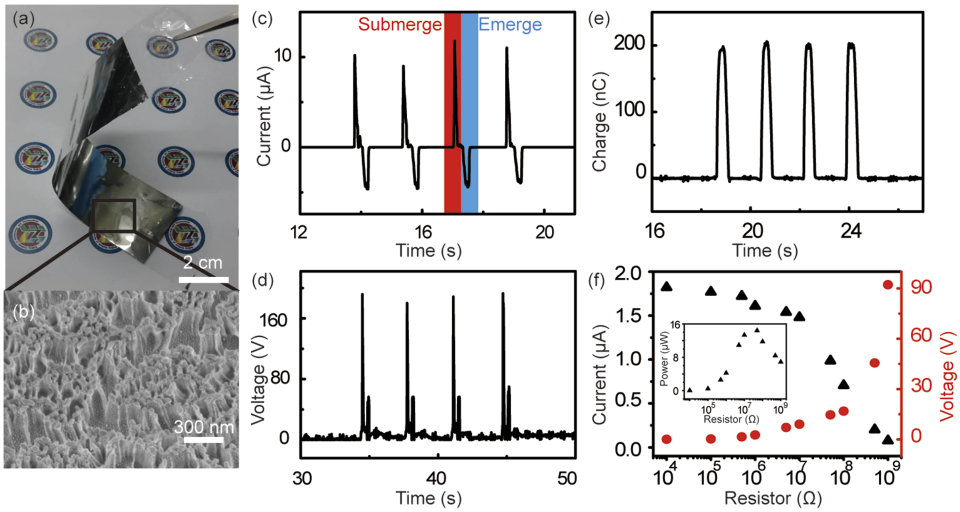

FIG. 2. (a) The photograph of the flexible nanowire based TENG (FEP and the back side electrode). (b) Photo of the nanowires at the FEP film surface by SEM. (c) The output signal of the current. The sharp positive signal is generated during the submerging process and the flat negative signal is created during the emerging process. (d) The voltage signal of the nanowire based TENG. The higher signal is generated during the submerging process and the lower signal is created during the emerging process. (e) The transferred charge during the submerge/emerge process. (f) Current amplitude and voltage amplitude under variable load resistance (inset: output power under different load resistances).

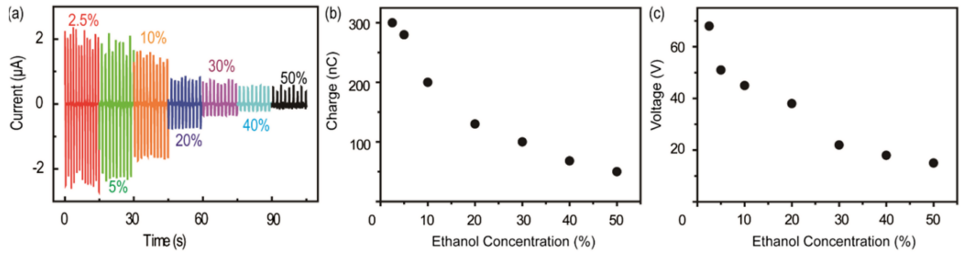

FIG. 3. (a) The current produced by the nanowire based TENG under different ethanol concentration by volume. The transferred charge (b) and the voltage (c) of the nanowire based TENG under different ethanol concentrations.

the FEP film and the liquid, making the hydrophobic film less hydrophobic. Therefore, the separation process of the liquid and the FEP film is impeded, which will largely decrease the transferred charge and the outputs of the nanowire based TENG. To clearly clarify this phenomenon, the transferred charge (Fig. 3(b)) and voltage (Fig. 3(c)) values of the nanowire based TENG were compared with different ethanol concentrations. These results can conclude that the signals generated by the nanowire based TENG (including current, voltage, and transferred charge) are all sensitive to the concentration of the ethanol in the liquid. Consequently, we can utilize the signal of the TENG to monitor the ethanol concentration in water. In the future, some functionalized nanomaterials or specific molecules can be used to modify the surface of the FEP film, so the TENG chemical sensor can selectively detect the target materials in the liquid. Once the functionalized nanomaterials or molecules catch the targets, the electrical output generated from the TENG will be different. This application will be promising and effective, as it can directly change the output signals upon detecting targets.

Of course, the main usage of the TENG is still the generators, which can be applied as an energy source to power other electric devices or sensors in our daily life.[27–30] Most of the sensor devices usually work with a long sleep and a short active mode. So the energy collected by the nanowire based TENG can be collected in a super capacitor during the long inactive mode and can completely power the sensor during the short active time.[31] As shown in Fig. 4(a), the nanowire based TENG is used to charge a 3.3 μF capacitor. When the nanowire based TENG is submerged in water, the voltage of the capacity increased by a small step, while the nanowire based TENG is emerged out of water the voltage increased for another small value. After 5 submerging-emerging operations, the voltage of the capacity can reach 1.1 V. The nanowire based TENG can also charge a much larger capacity, as 1 mF in Fig. 4(b), to 3.6 V for about 500 s. The energy stored in the 1 mF capacity can be used for many applications, like powering the time measuring device, humidity sensor and light-emitting diode array sensors.[32–34] The time measuring device powered by the nanowire based TENG and the 1 mF capacitor can time for more than 10 min. Fig. 4(d) presents the variation of the humidity and the temperature of Beijing city in winter for a day. The inset picture shows the data measured by the digital sensor.

To demonstrate a self-powered wireless infrared system, an electronic system consisting of the nanowire based TENG, a suitable capacitor, a resistance, a bridge rectifier, the infrared emitter, and receiver is presented in Fig. 5(a). The infrared LED powered by the TENG and capacitor will generate signals, shown in Fig. 5(c).

When the receiver detects the infrared light, it will generate current signals, corresponding to the peaks in red of Fig. 5(b). Once the power is off and there is no signal generated by the infrared LED, so the current of the receiver is almost 0 nA. The infrared imagery in Fig. 5(d) was taken by the infrared camera, showing that the LED can be clearly distinguished from other object. The inset is the optical image of the LED. The self-powered wireless infrared system can be used in various fields, such as communication, detecting, or medical care. As we all know, the wavelength of infrared light is larger than the wavelength of visible light, so the infrared signals can travel around some bigger objects than the visible light. In some emergent situation, such as in heavy fog or haze, the infrared signal would play a vital role in communication or detection.

In summary, a nanowire based TENG is fabricated to harvest a large amount of energy from water. It can transmit the mechanical energy of waves or rain drops to electric energy. Made of low

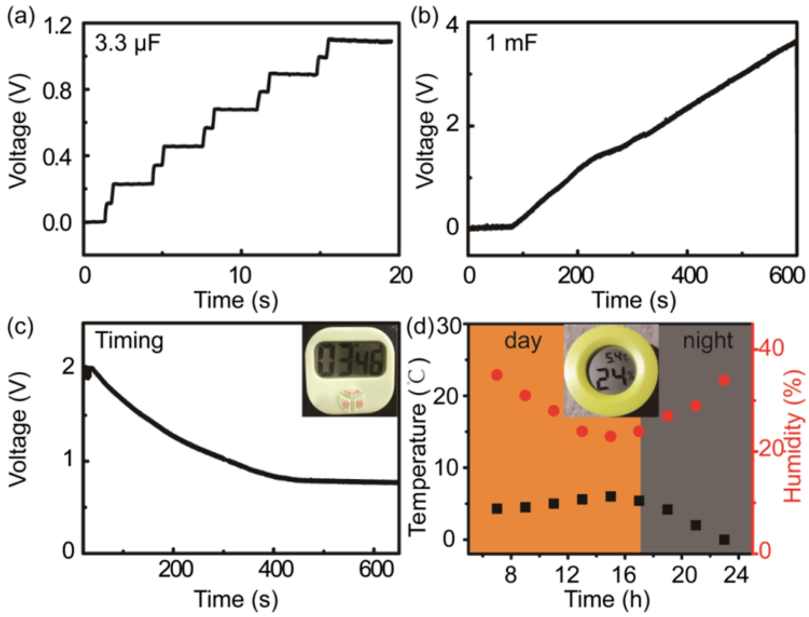

FIG. 4. (a) The 3.3 μF capacitor was charged to 1.1 V by 5 submerging-emerging processes of the nanowire based TENG in 15 s. (b) The voltage of the 1 mF capacitor when charged by the nanowire based TENG. The energy stored in capacitor (1 mF) could be used to drive a plenty of electric devices. (c) The time measuring device powered by the capacitor can work for more than 10 min. (d) The temperature and humidity sensor, powered by the nanowire based TENG and capacitor, measured the climate of Beijing during day and night.

cost polymer films, the nanowire based TENG is economic, chemically stable, lightweight, small-sized, and high efficient. The nanowire of the FEP surface plays an important role in enhancing the TENG's output power. The TENG generated an output current of 10 μA, a transferred charge of 200 nC, and an output voltage of 200 V. A chemical sensor for ethanol can be created based on the TENG, which can be used in sensing heavy metal ions or biomolecules in water when coupled with functionalizing materials. Meanwhile, powered by the nanowire based TENG/capacitor, different

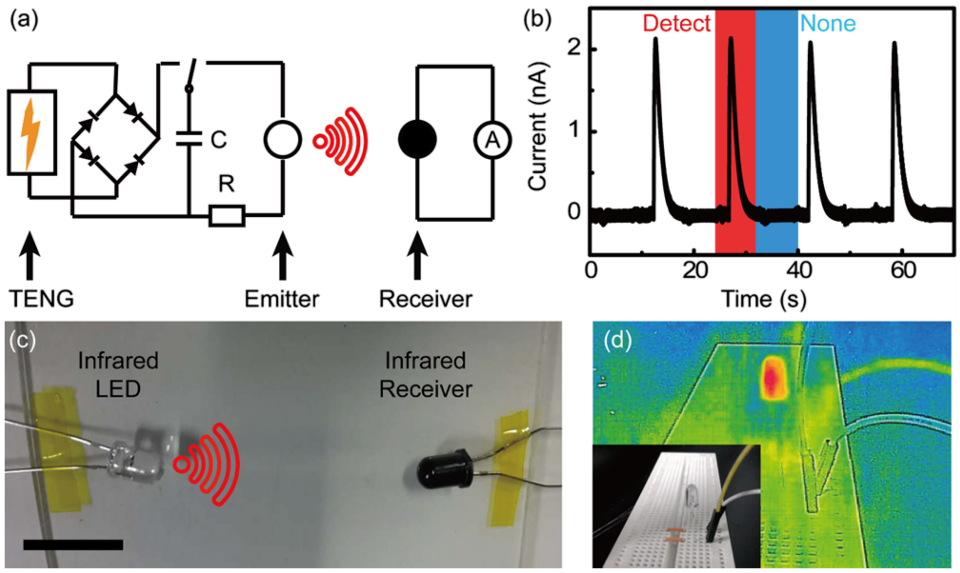

FIG. 5. (a) The equivalent circuit model of the self-powered wireless infrared system. (b) The current of the infrared receiver when detecting the infrared signals. (c) The photograph of the infrared LED and the receiver. (d) The image of the LED taken by the infrared camera (inset: the photograph of the LED).

kinds of self-powered wireless sensor system can be created to sense the temperature/humidity or emit the infrared signals. This study provides the possibility in utilizing water movements and expands its application scope.

See supplementary material for the signals of TENGs with and without nanowires.

The authors are thankful for support from National Natural Science Foundation of China (Nos. 51622205, 61405040, 61675027, 51432005, 61505010, 11374174, 51390471, 51527803, and 51502018), National 973 Project of China (No. 2015CB654902); National key research and development project from Minister of Science and Technology, China (Nos. 2016YFA0202703 and 2016YFB0700402); Beijing City Committee of science and technology (Z151100003315010); Beijing Natural Science Foundation (2164076); President Funding of the Chinese Academy of Sciences; and the "Thousand Talents" program of China for pioneering researchers and innovative teams. This work made use of the resources of the National Center for Electron Microscopy in Beijing, Tsinghua National Laboratory for Information Science and Technology, and Beijing Institute of Nanoenergy and Nanosystems, Chinese Academy of Sciences.

[1] C. F. Pan, S. M. Niu, Y. Ding, L. Dong, R. M. Yu, Y. Liu, G. Zhu, and Z. L. Wang, Nano Lett. **12**, 3302 (2012).
[2] M. L. Que, W. X. Guo, X. J. Zhang, X. Y. Li, Q. L. Hua, L. Dong, and C. F. Pan, J. Mater. Chem. A **2**, 13661 (2014).
[3] X. Y. Li, J. A. Tao, W. X. Guo, X. J. Zhang, J. J. Luo, M. X. Chen, J. Zhu, and C. F. Pan, J. Mater. Chem. A **3**, 22663 (2015).
[4] J. E. Trancik, Nature **507**, 300 (2014).
[5] W. X. Guo, X. J. Zhang, R. M. Yu, M. L. Que, Z. M. Zhang, Z. W. Wang, Q. L. Hua, C. F. Wang, Z. L. Wang, and C. F. Pan, Adv. Energy Mater. **5**, 1500141 (2015).
[6] J. H. Lee, J. Kim, T. Y. Kim, M. S. Al Hossain, S. W. Kim, and J. H. Kim, J. Mater. Chem. A **4**, 7983 (2016).
[7] G. Cheng, Z. H. Lin, Z. L. Du, and Z. L. Wang, ACS Nano **8**, 1932 (2014).
[8] W. X. Guo, X. Y. Li, M. X. Chen, L. Xu, L. Dong, X. Cao, W. Tang, J. Zhu, C. J. Lin, C. F. Pan, and Z. L. Wang, Adv. Funct. Mater. **24**, 6691 (2014).
[9] J. Chen, J. Yang, Z. L. Li, X. Fan, Y. L. Zi, Q. S. Jing, H. Y. Guo, Z. Wen, K. C. Pradel, S. M. Niu, and Z. L. Wang, ACS Nano **9**, 3324 (2015).
[10] W. M. Du, X. Han, L. Lin, M. X. Chen, X. Y. Li, C. F. Pan, and Z. L. Wang, Adv. Energy Mater. **4**, 1301592 (2014).
[11] Z. H. Lin, G. Cheng, S. Lee, K. C. Pradel, and Z. L. Wang, Adv. Mater. **26**, 4690 (2014).
[12] Z. H. Lin, G. Cheng, L. Lin, S. Lee, and Z. L. Wang, Angew. Chem., Int. Ed. **52**, 12545 (2013).
[13] X. F. Wang, S. M. Niu, Y. J. Yin, F. Yi, Z. You, and Z. L. Wang, Adv. Energy Mater. **5**, 1501467 (2015).
[14] G. Zhu, Y. J. Su, P. Bai, J. Chen, Q. S. Jing, W. Q. Yang, and Z. L. Wang, ACS Nano **8**, 6031 (2014).
[15] X. J. Zhao, G. Zhu, Y. J. Fan, H. Y. Li, and Z. L. Wang, ACS Nano **9**, 7671 (2015).
[16] M. X. Chen, X. Y. Li, L. Lin, W. M. Du, X. Han, J. Zhu, C. F. Pan, and Z. L. Wang, Adv. Funct. Mater. **24**, 5059 (2014).
[17] J. Liu, P. Fei, J. Zhou, R. Tummala, and Z. L. Wang, Appl. Phys. Lett. **92**, 173105 (2008).
[18] H. Fang, W. Z. Wu, J. H. Song, and Z. L. Wang, J. Phys. Chem. C **113**, 16571 (2009).
[19] Z. H. Lin, G. Cheng, W. Z. Wu, K. C. Pradel, and Z. L. Wang, ACS Nano **8**, 6440 (2014).
[20] Y. L. Zi, S. M. Niu, J. Wang, Z. Wen, W. Tang, and Z. L. Wang, Nat. Commun. **6**, 8376 (2015).
[21] Y. L. Zi, J. Wang, S. H. Wang, S. M. Li, Z. Wen, H. Y. Guo, and Z. L. Wang, Nat. Commun. **7**, 10987 (2016).
[22] Z. Q. Sun, T. Liao, K. S. Liu, L. Jiang, J. H. Kim, and S. X. Dou, Small **10**, 3001 (2014).
[23] D. Isakov, E. D. Gomes, B. Almeida, A. L. Kholkin, P. Zelenovskiy, M. Neradovskiy, and V. Y. Shur, Appl. Phys. Lett. **104**, 032907 (2014).
[24] Y. J. Su, J. Chen, Z. M. Wu, and Y. D. Jiang, Appl. Phys. Lett. **106**, 013114 (2015).
[25] A. Khan, M. A. Abbasi, M. Hussain, Z. H. Ibupoto, J. Wissting, O. Nur, and M. Willander, Appl. Phys. Lett. **101**, 193506 (2012).
[26] W. Tang, T. Jiang, F. R. Fan, A. F. Yu, C. Zhang, X. Cao, and Z. L. Wang, Adv. Funct. Mater. **25**, 3718 (2015).
[27] C. F. Pan, Z. T. Li, W. X. Guo, J. Zhu, and Z. L. Wang, Angew. Chem., Int. Ed. **50**, 11192 (2011).
[28] Y. L. Zi, L. Lin, J. Wang, S. H. Wang, J. Chen, X. Fan, P. K. Yang, F. Yi, and Z. L. Wang, Adv. Mater. **27**, 2340 (2015).
[29] Y. Jeon, X. G. Han, K. Fu, J. Q. Dai, J. H. Kim, L. B. Hu, T. Song, and U. Paik, J. Mater. Chem. A **4**, 18306 (2016).
[30] X. Wang, M. Que, M. Chen, X. Han, X. Li, C. Pan, and Z. Lin Wang, "Full Dynamic-Range Pressure Sensor Matrix Based on Optical and Electrical Dual-Mode Sensing," Adv. Mater. (published online).
[31] S. Jang, H. Kim, Y. Kim, B. J. Kang, and J. H. Oh, Appl. Phys. Lett. **108**, 143901 (2016).
[32] X. Y. Li, M. X. Chen, R. M. Yu, T. P. Zhang, D. S. Song, R. R. Liang, Q. L. Zhang, S. B. Cheng, L. Dong, A. L. Pan, Z. L. Wang, J. Zhu, and C. F. Pan, Adv. Mater. **27**, 4447 (2015).
[33] M. X. Chen, C. F. Pan, T. P. Zhang, X. Y. Li, R. R. Liang, and Z. L. Wang, ACS Nano **10**, 6074 (2016).
[34] C. F. Pan, L. Dong, G. Zhu, S. M. Niu, R. M. Yu, Q. Yang, Y. Liu, and Z. L. Wang, Nat. Photonics **7**, 752 (2013).