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Super-Flexible Nanogenerator for Energy Harvesting from Gentle Wind and as an Active Deformation Sensor

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Using an Al-foil of thickness ≈18 μm as a substrate and electrode, a piezoelectric nanogenerator (NG) that is super-flexible in responding to the wavy motion of a very light wind is fabricated using ZnO nanowire arrays. The NG is used to harvest the energy from a waving flag, demonstrating its high flexibility and excellent conformability to be integrated into fabric. The NG is applied to detect the wrinkling of a human face, showing its capability to serve as an active deformation sensor that needs no extra power supply. This strategy may provide a highly promising platform as energy harvesting devices and self-powered sensors for practical use wherever movement is available.

Energy harvesting from renewable and green energy resources, such as wind, solar and geothermal, has attracted considerable interest due to the energy crisis and global warming. Rationally designed materials and technologies have been subjects of active research and development.[1–3] Likewise, in the nanoworld, energy harvesting technologies based on the piezoelectric effect have been developed to convert very small-scale mechanical energy to electricity, which are highly expected to realize self-powered micro/nanosystems.[4–10] The fundamental mechanism of the piezoelectric nanogenerator (NG) is related to a piezoelectric potential generated in nanowires (NWs) when they are dynamically strained under an external force, and the corresponding transient current that flows through an external circuit to balance the potential. Over the years, many kinds of NGs have been demonstrated to effectively utilize the mechanical resources with variable frequencies and amplitudes in our living environment, such as light wind, body movement, vibrations and acoustic/ultrasonic waves.[11–15] For a wide variety of applications, most NGs have been fabricated based on flexible substrates or piezoelectric polymer, such as polyvinylidene fluoride. The NGs with high flexibility have shown potential applications as not only an energy harvesting device capable of scavenging energy from light wind such as respiration,[14] but also a sensitive sensor which can monitor the behavior of the human heart by detecting small physical motion such as pulse.[15] Furthermore, the high flexibility can provide an opportunity applicable to a target object without any limitation of its shape and movement due to its high conformability caused by the ultrathin thickness. However, although several research efforts have demonstrated the realization of ultrathin NGs with high flexibility and conformability, they are still difficult to be utilized as an economic approach for super-flexible NG owing to the high cost and the low-throughput process. Thus, it is necessary to develop innovative strategies toward achieving super-flexible, conformable and cost-effective NGs applicable to any target objects regardless of their surface shape and mode of moving.

In this work, we report a super-flexible and conformable NG based on cost-effective thin Al-foil electrodes which can not only enable energy harvest from a waving flag but also detect a skin movement when attached to a human face. ZnO nanowire (NW) arrays were uniformly grown on an ultrathin Al foil that was about 18 μm in thickness and used as both the electrode and the substrate. In order to prevent short-circuits or electrical leakage between the Al electrode and the ZnO NWs because of the semi-conducting properties of ZnO NW, a poly(methyl methacrylate) (PMMA) layer was coated on the Al foil to insulate them prior to the growth of ZnO NW. The super-flexible NG was able to easily flutter with high-amplitude of vibration under low-speed air flow (≈1.5 m/s), and the vibration frequency was over 20 Hz. The maximum output current and voltage showed a tendency to increase with the wind speed in the range of 0 to 5.5 m/s, and the measured maximum outputs were over

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200 nA and 50 mV, respectively. The super-flexible NG was able to serve as an energy harvesting device under the waving motion, which can be achieved by attaching it to the surface of a flag. Furthermore, we demonstrated the potential of the NG to work as an active sensor capable of detecting the skin movement due to its extremely low resistance to motion. This is a key step towards the development of energy harvesting devices or active sensors for practical use in environments where dynamic strain/stress is available without being limited to the shape and the motion of a target object.

For the super-flexible NG, it is important to make its ultrathin. Considering the thickness of the layers of device reported before, such as as-grown ZnO NWs (≈2 µm), spin-coated PMMA layer (≈2 µm) and deposited electrodes (less than 1µm),[12,13,16,17] it may be possible to easily achieve the super-flexible NG if thin Al foil is used as the substrate and the electrode. However, during chemical growth process of the ZnO NWs, unexpected ZnO particles are often attached to the ZnO NWs, and their size is roughly from hundreds of nanometers to tens of micrometers. It can cause short circuits between the ZnO NWs and the upper deposited electrode even when the 2-µm-thick PMMA is coated as the insulating layer between them, which consequently leads to a low-throughput process. Of course, the short circuit can be overcome by making the PMMA layer thick enough to prevent it, but it may decrease the flexibility and increase the piezoelectric potential-drop in the PMMA layer, which can cause a reduction in the NG performance. In addition, since the boehmite phase of the hydrated aluminum oxide formed on the Al surface in the chemical growth process makes the c-axis growth of ZnO NWs on the Al surface difficult, ZnO nanoplates are grown on the Al surface instead of the ZnO NWs.[18] Thus, we focused our research on designing a super-flexible NG without compromising the flexibility and the output performance. First, a 2-µm-thick PMMA layer was coated on the Al foil prior to the growth of ZnO NWs, as shown in **Figure 1**a. The PMMA layer coated on the Al foil can not only help ZnO NWs uniformly grow along c-axis by preventing the effect of the hydrated aluminum oxide in the chemical growth process but also lead to high-throughput processing by completely insulating between the ZnO NWs and the Al foil without significantly decreasing the flexibility and the NG performance. Following this, ZnO NWs were grown on the sputter-coated seed layer/spin-coated PMMA/Al foil by a hydrothermal process at 95 °C for 5 h. The nutrient solution for growing process was an aqueous solution of 0.05 M hexamethylenetetramine (HMTA) and 0.05 M zinc nitrate hexahydrate ($ZnNO_3 \cdot 6(H_2O)$). A 3-µm-thick PMMA layer was coated on the surface of as-grown ZnO NWs and a 40-nm-thick Al film was sputter coated on the PMMA surface

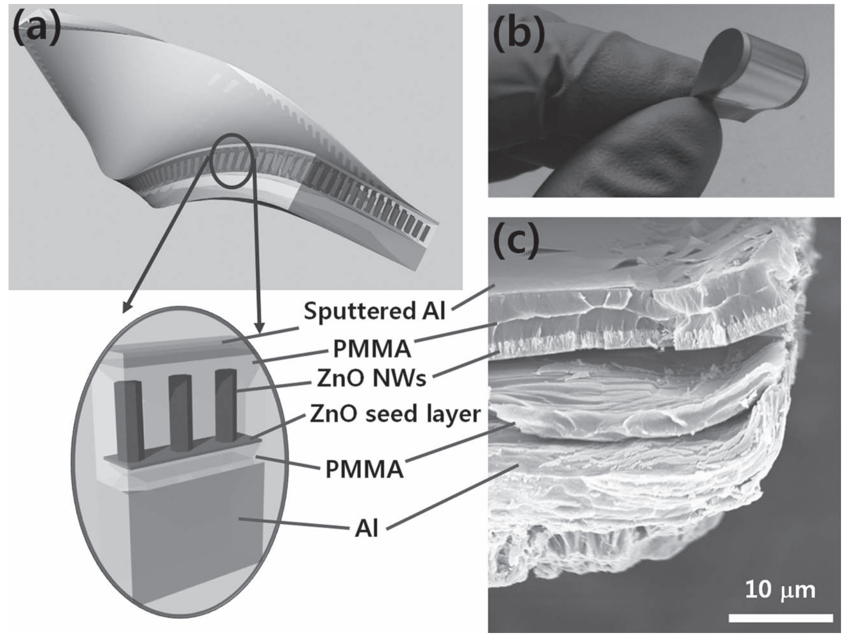

Figure 1. Super-flexible piezoelectric nanogenerator (NG). a) Scheme of the super-flexible NG base on ultrathin Al foil. The PMMA layer was coated on the Al foil prior to the growth of ZnO NWs in order to lead to high-throughput processing and the c-axis growth of ZnO NWs by preventing short-circuits and the boehmite phase effect, respectively. b) Photographic image of the super-flexible NG. c) SEM image of cross section of the NG.

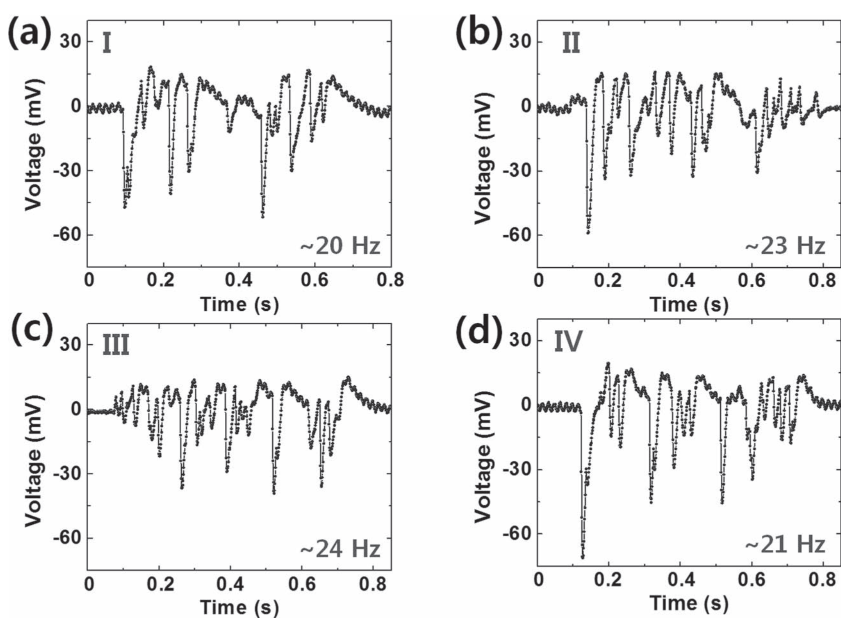

Figure 2. Investigation of the flexibility of the NG by measuring the frequency of vibration under low-speed air flow (≈1.5 m/s). a–d) Frequencies of vibration of the NG by a gentle exhalation.

serving as the other electrode of the NG (see Figure 1a). The densely grown ZnO NWs on the Al substrate were confirmed by a field-emission scanning electron microscopy image (see Supporting Information Figure S1a,b). Figure 1b shows an optical image of the bent super-flexible NG with a thickness of about 25 μm. The cross-section of the fabricated NG was confirmed from a FE-SEM image (Figure 1c).

In general, as the flexibility of the NG increases, the frequency and the amplitude of vibration will be increased even under low-speed air flow (≈1.5 m/s). Since it was difficult to immediately measure the flexibility of the NG, we first investigated the number of vibration when the NG was waving under the low-speed air flow. The size of the prepared NG was 1.6 cm × 3.5 cm, and its one side was fixed at the end of a rigid substrate. The wind speed was measured by a digital anemometer (JT-8908, Shenzhen Jingtengwei Industry Co., Ltd.). When blowing onto the NG by a gentle exhalation, the low-speed air made the NG flutter, resulting in the generation of an electricity output, as shown in **Figure 2**. The generated outputs were not regular due to the variable wind speed by the gentle exhalation. By counting the number of vibration in the output, the frequency was calculated, and the average value was over 20 Hz. We also found that the NG was able to flutter with high-amplitude of vibration under the low-speed air flow due to the super-flexibility (see Video 1 in the Supporting Information). Although the flexibility of the NG was indirectly measured from the fluttering motion for the above-mentioned reason, the high-frequency and the high-amplitude of vibration of the NG under the low-speed air flow clearly showed its super-flexibility. In other words, the super-flexible NG shows great promise as a sensitive sensor or an energy harvesting device capable of detecting or utilizing gentle movements, respectively. The output performance of the NG was also measured as wind speed increases in the same condition. Both the current and the voltage generated by the NG showed a tendency to increase with the wind speed in the range of 0 to 5.5 m/s, and the measured maximum outputs within the range were over 200 nA and 50 mV, respectively, as shown in **Figure 3**a,b. Interestingly, even if there were no significant differences in the amplitudes of vibration of the fluttering NG owing to its super-flexibility as wind speed increased, the output performance increased with the wind speed. This is probably due to the different strain rate that can influence the output performance of the NG, considering the previous results that the output voltage and current increase with the strain rate.[9,19] This supposition was supported by measuring the frequencies of the fluttering motion of the NG depending on the wind speed. As shown in Supporting Information Figure S2, the frequency of the fluttering motion increases with the wind speed, and it means that the strain rates of the NG increase with the wind speed. As a result, the increase of the wind speed leads to an increase of the output performance.

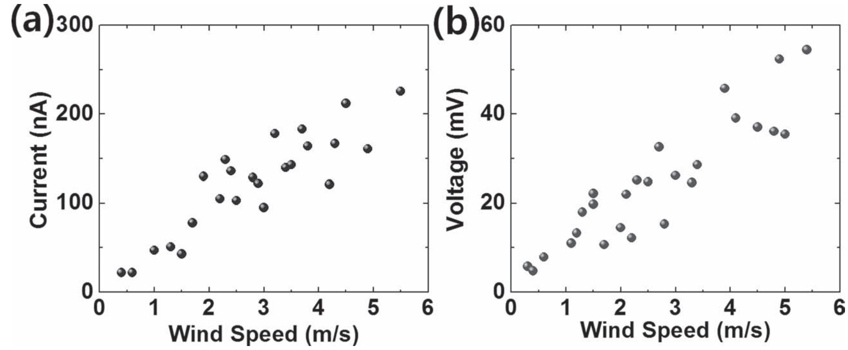

Figure 3. Performance of the NG depending on the wind speed. a) Output current and b) voltage of the NG according to the increase of wind speed from 0 to 5.5 m/s.

Since the device was aimed at super-flexible NG capable of harvesting energy from a waving flag, three NGs with similar output performance under the same experimental conditions were attached at different positions of the flag surface, as shown in **Figure 4**a. The devices with the size of 10 mm × 15 mm were firmly fixed on the flag surface in order to make them move following the waving motion of the flag. The electric fan was employed to provide the wind with speed high enough to make the flag wave at room temperature. Figures 4b,c show the measured output current and voltage at different positions (i.e., I, II, III in Figure 4a). The output of the position (I) was relatively low and that of the position (III) was relatively high, comparing

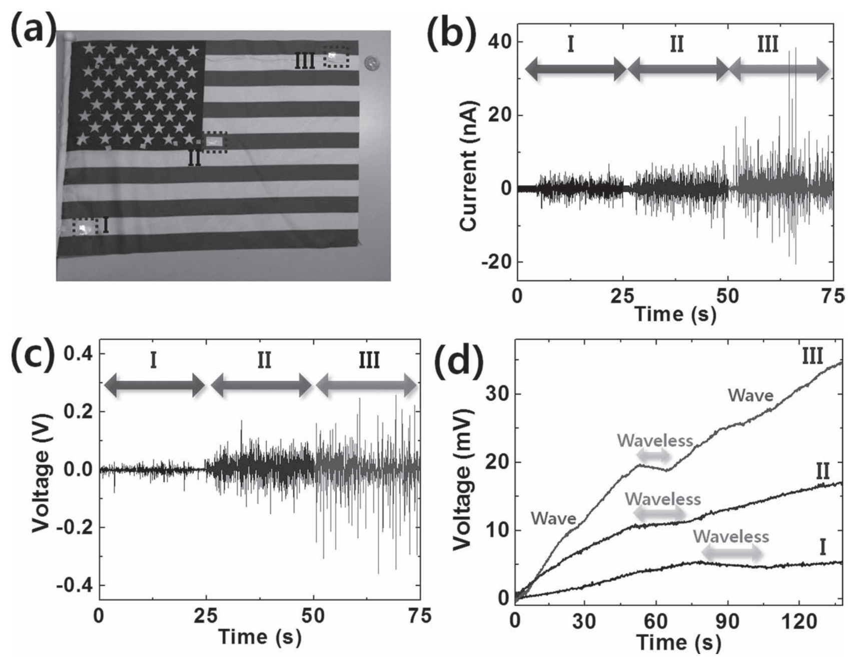

Figure 4. Performance of the super-flexible NG as an energy harvesting device under waving motion by attaching it to the surface of a flag. a) Three NGs attached at different positions (I, II, III) of the flag surface. b) Output current and c) voltage of the NG at the different positions. d) Voltage increase on a capacitor that was connected the NG through a bridge rectifier.

the results with that of the middle position (II). As shown in Video 3 in the Supporting Information, when the flag was fluttering in the wind, the waving motion, including the frequency and amplitude of the vibration, was different depending on the position of the flag, and consequently caused the different output performance. Then, in order to demonstrate the feasibility of converting energy from the wind to useful electricity, a 22 µF capacitor was connected to the NG through a bridge rectifier for a practical direct current (DC) power source, and the increasing voltage curves were shown in Figure 4d. The larger the output generated from each position was, the faster the charging speed of the capacitor was, and we confirmed that the charged voltage was generated from the NG by changing the waving motion of the NG-attached flag from turning the electric fan on and off (see Figure 4d and Video 2 in the Supporting Information). In other words, the result indicates that the super-flexible NG can harvest energy in an environment where dynamic motion is available regardless of its level of activity due to its excellent conformability.

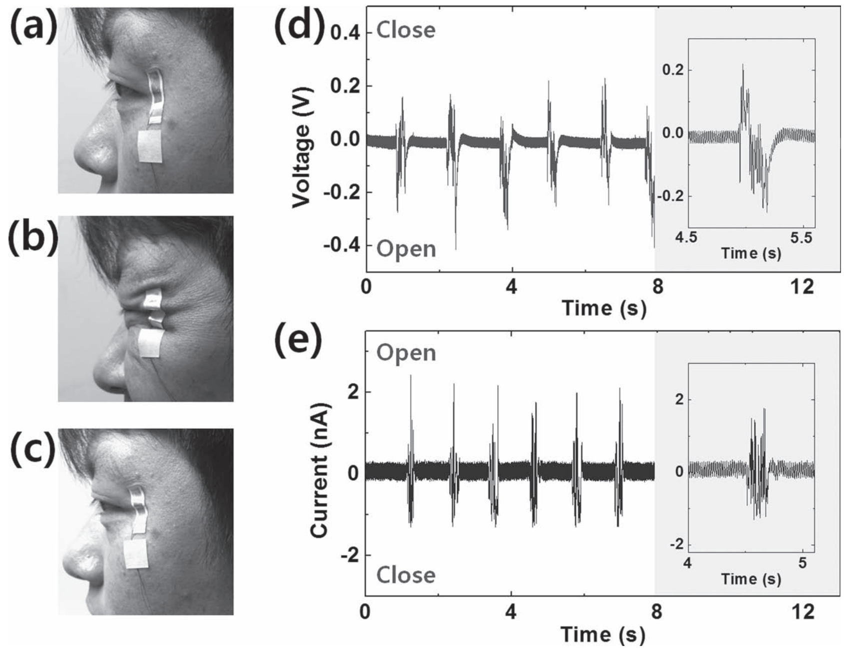

Figure 5. Performance of the super-flexible NG as an active sensor under skin movement. Photographic image of the NG attached to the skin; a) ready, b) wrinkled, and c) unwrinkled. d) Output voltage and e) current of the NG driven by blinking one eye.

The super-flexible NG can be used as an active sensor capable of detecting small amount of skin wrinkling due to its high sensitivity and high conformability. In order to demonstrate this possibility, an NG with a size of 5 mm × 13 mm was attached to the skin next to a human eye, as shown in **Figure 5**a. The device was firmly fixed on the skin with eyelash glue which has little influence on the skin movement. The NG was driven by blinking one eye and moved following the dynamic wrinkles due to its super-flexibility and high conformability, as shown in Figures 5b,c. The output voltage and current was about 0.2 V and 2 nA under the blinking motion, respectively, and we confirmed that the output signal was generated only when the NG was deformed by the dynamic wrinkles (see Figure 5d,e, and Video 3 and Video 4 in the Supporting Information). On the other hand, since the NG was deformed to the shape with two peaks by the wrinkles as shown in Figure 5b, the piezoelectric potentials with different polarities were generated in the same plane of the NG, and consequently the outputs could be reduced by canceling each other out; as-grown ZnO NWs on Al foil was subjected to a compressive stress at the peak, while they were subjected to a tensile stress at the valley, considering that the growth direction of the NWs was along the c-axis. If the NG is designed considering the shape and the size of a target surface, the sensor with an enhanced sensitivity can be achieved due to the increased output performance. In addition, since the super-flexible NG can be easily driven wherever movement is available due to its excellent conformability, it may be used as a sustainable and wireless self-powered sensor by itself without using a battery. These merits provide great potential for an ultrathin electronic platform such as self-powered smart skin.

In summary, we have successfully fabricated a super-flexible and conformable piezoelectric nanogenerator based on cost-effective Al foil. Coating the Al foil with thin PMMA layer before the growth of ZnO NWs, lead to not only the high-throughput process due to the complete insulation between as-grown ZnO NWs and the Al foil, but also the c-axis growth of ZnO NWs on the Al foil by preventing the boehmite phase effect of the hydrated aluminum oxide surface. The super-flexible NG can generate output power in a light wind and serve as an energy harvesting device under the waving motion of a NG-attached flag due to its excellent conformability. Furthermore, the super-flexible NG shows potential applications as an active sensor capable of detecting slight skin movement due to its extremely low resistance to motion. Our strategy provides a highly promising platform for energy harvesting devices and self-powered sensors for practical use wherever movement is available with no limitation of the surface shape.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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