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Flexible Nanogenerator Based on Single $BaTiO_3$ Nanowire

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ABSTRACT

Using ferroelectric materials which exhibit the combination of large piezoelectric coefficients and good flexibilities as nanogererator is desirable for improving the electric output. In this work, a flexible nanogenerator based on single $BaTiO_3$ nanowire is described. The flexible nanogenerator can generate an output voltage of up to 0.21 V and current of 1.3 nA by periodically bending and releasing the substrate. The electric outputs were found to be proportional to the strain and strain rate. Furthermore, the electric output was enhanced by connecting two generators in series and in parallel with the correct polarity and sequence. Therefore, the flexible nanogenerator demonstrates the energy harvesting using $BaTiO_3$ nanowires and the increase of the output electricity through integration of $BaTiO_3$ nanowires.

KEYWORDS: Electrospinning, $BaTiO_3$ Nanowire, Nanogenerator, Energy Harvesting.

1. INTRODUCTION

With the miniaturization of various functional devices down to microscale and nanoscale, searching high-quality power sources on the same scale is of utmost importance for powering these nanosystems. Various approaches have been developed to harvesting energy from the environment, such as solar cells,[1–4] thermoelectric cells,[5,6] and hydrogen fuel cells.[7,8] Nanogenerator converts mechanical energy into electric energy and is a unique energy-harvest system because of the ubiquity of the mechanical energy.[9,10]

Since the first nanogenerator was invented,[11] DC nanogenerator,[12] AC nanogenerator,[13] wearable fiber nanogenerator,[14] and integrated high output nanogenerators[15–18] have been demonstrated.

Improving the electric output of nanogenerators is essential for their practical applications on powering the electronic devices. By integration, an output voltage of 1.26 V can be achieved in nanogenerator based on ZnO nanowires, and the power generated is potentially sufficient to recharge an AA battery.[15] Another effectual way of increasing the electrical output is to utilize ferroelectric materials with larger piezoelectric coefficient and electromechanical conversion efficiency.[19–24] In regard to electromechanical coupling coefficient of a thin-long rod, the calculated longitudinal coupling factor k_{33} for single-crystal $BaTiO_3$ and lead zirconate titanate (PZT) can reach 0.56 and 0.68, respectively, which is higher than that of ZnO (0.42).[25] As a result, nanogenerators based on PZT have been studied.[21,26–28] Although the bulk piezoelectric coefficient of PZT is about dozens of times of the value of bulk ZnO, larger dielectric constant of piezoelectric materials could give rise to lower electric field strength and therefore lower electric potential assuming same piezoelectric charges created. And moreover, PZT contains lead which is a toxic element and thus is not an environment friendly material, which will hinder its practical applications. Compared with PZT, $BaTiO_3$ nanowire is another valuable candidate for piezoelectric nanogenerator due to the following merits. First, $BaTiO_3$ exhibits lower piezoelectric coefficient but smaller dielectric constant. Theoretical calculations of piezoelectric potential distributions by solving the constitutive equations of piezoelectric materials using the COMSOL software package show that, higher piezoelectric potential can be expected for the $BaTiO_3$ nanowire comparing with that of the PZT nanowire when their strain and size are same. Second, $BaTiO_3$ is a lead-free and biocompatible material, and shows great potential for implantable biological devices. However, $BaTiO_3$ is brittle and can hardly meet the generator's demands. Therefore, preventing $BaTiO_3$ nanowires from fracture and extending the life cycle are big challenges of the nanogenerator based on $BaTiO_3$ nanowires. Nanowires prepared by an electrospinning process exhibit an extremely high

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bending flexibility and high mechanical strength.[21, 26, 29] Accordingly, electrospinning is an appropriate way which can be adopted to prepare nanowires in energy harvesting technology. Furthermore, the package of the device on a flexible substrate with polydimethylsiloxane (PDMS) polymer can avoid stress concentration and improve the flexibility, which may enable the piezoelectric device to have a very higher stability and long lifetime.[13, 18, 26, 30]

In this paper, a flexible nanogenerator based on single $BaTiO_3$ nanowire is reported. $BaTiO_3$ nanowires were produced via electrospinning. A single $BaTiO_3$ nanowire was transferred onto a flexible polyethylene terephthalate (PET) substrate and the device was packaged with PDMS to make flexible nanogenerator based on single $BaTiO_3$ nanowire. The electric output of the device was studied. The results demonstrate the energy harvesting using $BaTiO_3$ nanowires.

2. EXPERIMENTAL PROCEDURES

2.1. Synthesis of the $BaTiO_3$ Nanowire

The $BaTiO_3$ nanowires were prepared as follows. First, 1.5 g of barium acetate was dissolved in 2 ml of deionized water to form solution *A*. Second, 2 g of tetrabutyl titanate was added into a mixed solution of ethanol (4 ml) and acetic acid (4 ml), the mixture was stirred for 40 min with magnetic stirring to form a homogeneous solution *B*. Then solution *A* was added into solution *B* drop by drop under continuous stirring to form solution *C*. After stirring for 1 h, the solution *C* was mixed with PVP ($Mw = 1300000$) ethanol solution (10%). As the stirring duration increased to 3 h, the $BaTiO_3$ precursor solution was formed.

Conventional electrospinning setup was used to fabricate $BaTiO_3$ nanowires, which includes a jet, a collector, and a high voltage source. The precursor was loaded in a plastic needle tube. The distance between the jet and the collector was fixed at 20 cm. Multipairs of parallel electrodes worked as collectors. When a high voltage of 13 kV was applied to the jet, the droplet of the $BaTiO_3$ precursor was elongated to nanowires. After electrospinning, the as-synthesized nanowire was dried in a vacuum oven at 80 °C for 4 h and then calcined at 800 °C for 2 h in a box furnace (CMF1100).

2.2. Fabrication and Measurement of the Generator

The flexible generator based on single $BaTiO_3$ nanowire is schematically shown in Figure 1(a). The $BaTiO_3$ nanowire was transferred onto a flexible PET substrate. Silver paste was used to fix the nanowire's two ends tightly on the flexible substrate and connect copper wires which act as electrodes to connect with the current/voltage measurement meter. Finally, this device was packaged with PDMS and polarized with a 100 kV/cm electric field at room temperature for 1 h to form a flexible nanogenerator.

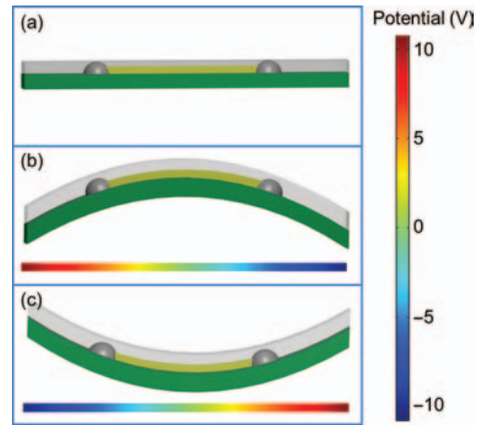

Fig. 1. (a) Schematic image of the flexible nanogenerator. (b) and (c) Mechanical bending of the substrate creates tensile strain and compressive strain in the nanowire, respectively. The corresponding piezoelectric potential in the nanogenerator is calculated and shown in the insets of (b) and (c).

A linear motor was used to periodically bend and release the PET substrate to periodically apply and release the tensile/compressive strain in the nanowire (Figs. 1(b) and (c)). The bending amplitude and the bending velocity or bending frequency can be tailored to control the strain and the strain rate, respectively. The voltage signal and current signal were measured through Stanford Research Systems (low-noise preamplifier SR560 and low-noise current preamplifier SR570). During the measurements, no external power source was introduced in the circuit.

3. RESULTS AND DISCUSSION

Figure 2(a) is the X-ray diffraction (XRD) spectrum of $BaTiO_3$ nanowires. All peaks can be indexed with perovskite phase. The results of XRD show that the nanowires are well-crystallized. A decrease in the diffraction peak's height and an increase in the diffraction peak width indicate a small crystal size of the nanowires. Figure 2(b) is a high-magnification SEM image of $BaTiO_3$ nanowires used for fabricating flexible nanogenerators. It can be seen from the SEM image that the nanowires are random oriented. According to the SEM image and the diameter distribution histogram (not shown here) of the nanowires, the diameters of the nanowires are between 150 nm and 350 nm. Figures 2(c) and (d) are the bright-field image and the image of selected area electron diffraction (SAED) of $BaTiO_3$ nanowires, respectively. The diffraction rings shown in the SAED pattern are assigned to $BaTiO_3$ with perovskite structure, which is consistent with XRD results. To investigate the performance of the flexible nanogenerator, the short-circuit current and open-circuit voltage were measured. As shown in Figure 3(a), at a bending amplitude of 15 mm and bending frequency of 0.33 Hz, peak voltage and current reach up to 18 mV and 0.17 nA,

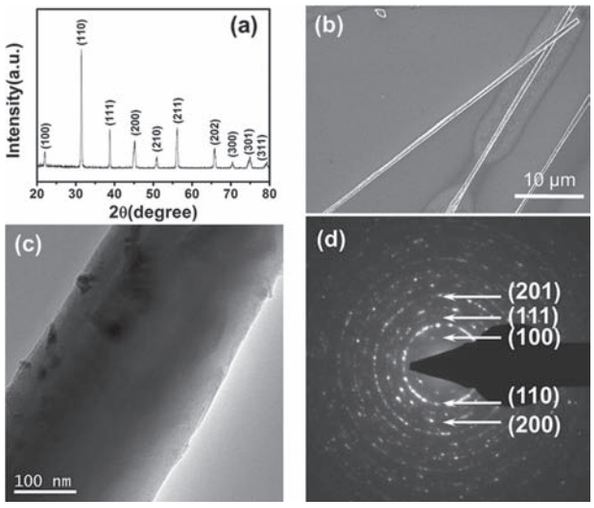

Fig. 2. (a) X-ray diffraction pattern of $BaTiO_3$ nanowires. (b) SEM image of $BaTiO_3$ nanowires used for fabricating flexible nanogenerators. (c) TEM image and (d) SAED pattern of $BaTiO_3$ nanowires.

respectively. To verify that the obtained signal came from the piezoelectricity of $BaTiO_3$ nanowire, well established switching-polarity test (Fig. 3(b)) and linear superposition tests (Fig. 4)[31] were also carried out. It can be seen obviously from Figure 3(b) that the signs of the output current and voltage are reversed when the measurement system was reversely connected with the nanogenerator and the superposition results shown in Figure 4 satisfy the true signal criteria, which mean that the output current and voltage were true signals. The electric output of another flexible nanogenerator is shown in Figure 5. The electrical output of the nanogenerator has a peak voltage of 0.21 V and current of 1.3 nA. The individual nanogenerators exhibit very similar behavior, highlighting the good reproducibility of our nanogenerators.

The power generation mechanism proposed previously for nanogenerators based on the ferroelectric nanowires[21,30] is applicable to the present single $BaTiO_3$ nanowire nanogenerator. When the PET substrate is bent, the $BaTiO_3$ nanowire is stretched and is under a tensile state (Fig. 1(b)). A piezoelectric potential difference induced by the strain appears along the axial direction of the nanowires[32] (the inset of Fig. 1(b)), which drives the carriers flowing through an external load and accumulating at the interface between the electrode and the nanowires. If the PET substrate is released, the tensile strain is released and the piezoelectric potential difference disappears, the accumulated charges will move back to the opposite direction and generates an opposite output signal. Consequently, periodically bending and releasing the substrate results in the generation of the alternating voltage and current. In this way, nanogenerator converts the energy of mechanical energy into electricity.

According to the mechanism, if the PET substrate is bent to another direction, the $BaTiO_3$ nanowire is compressed and is subject to compressive strain (Fig. 1(c)). The piezoelectric field created in the nanowire is reversed

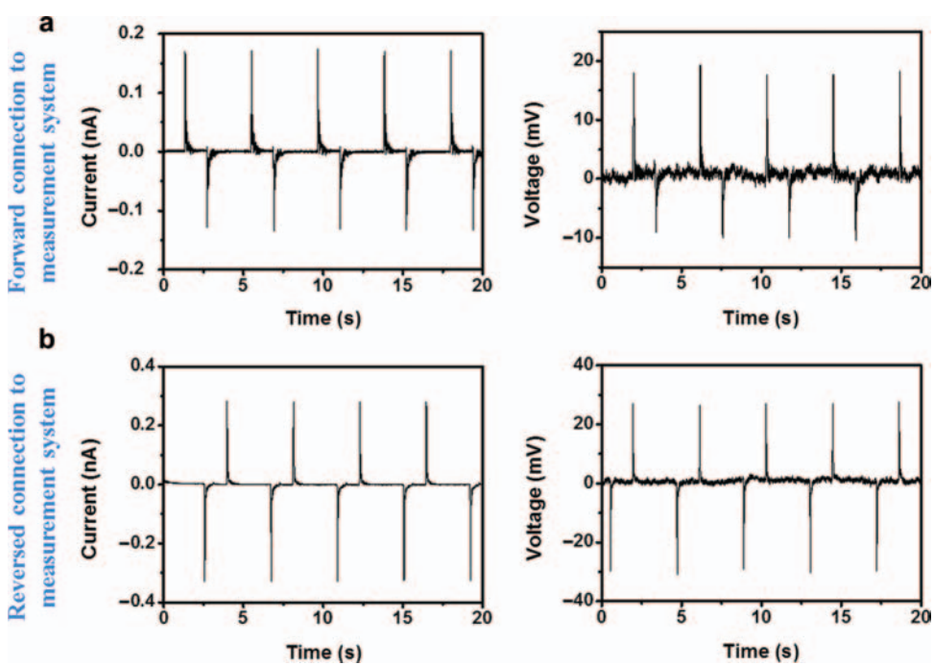

Fig. 3. Short-circuit current (left) and open-circuit voltage (right) of a flexible nanogenerator when subject to tensile strain. (a) Forward-connected to the measurement system and (b) reverse-connected to the measurement. Forward connection (FC) means the positive probe of the measurement system connecting with generator's positive end and the negative probe connecting with the negative end. Reversed connection (RC) means the connection with the two probes of the measurement switched.

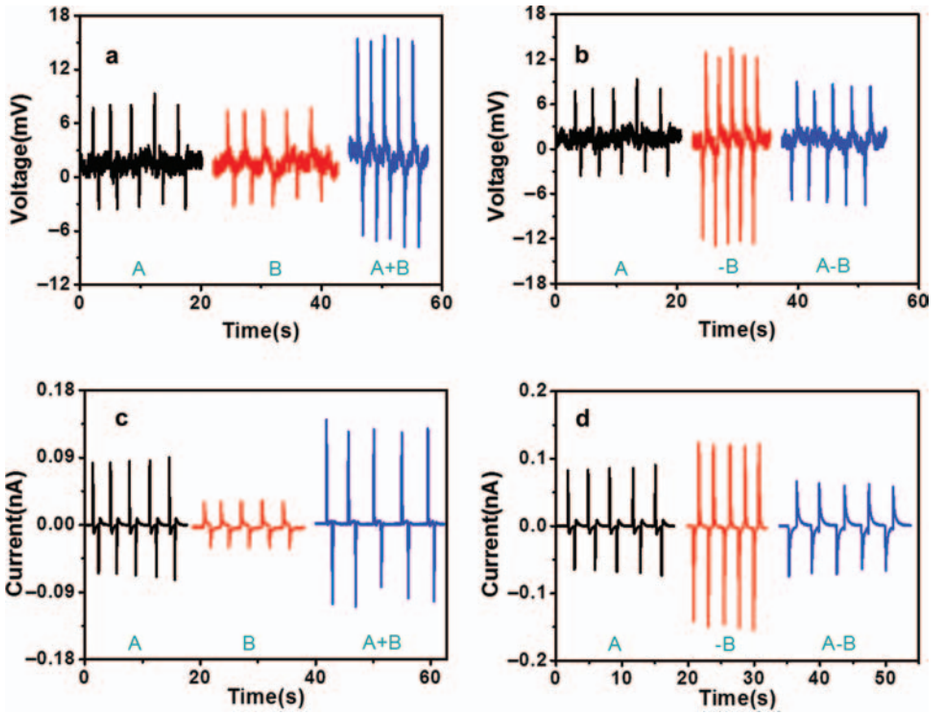

Fig. 4. Current and voltage output when two nanogenerators are connected in series (a), (b) and in parallel (c), (d) with various configurations.

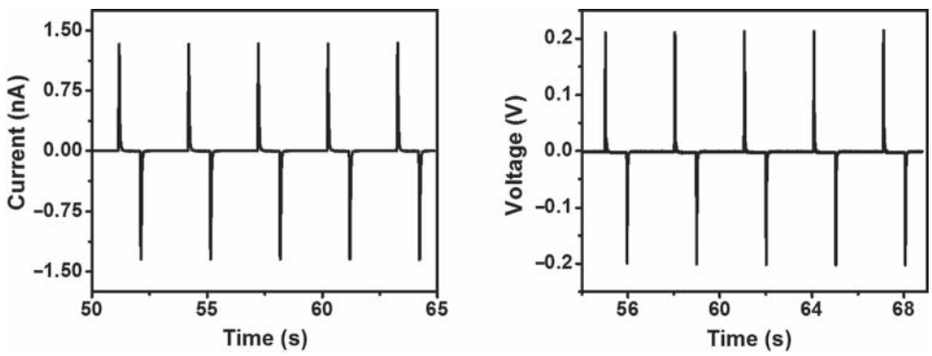

Fig. 5. Short-circuit current (left) and open-circuit voltage (right) of another flexible nanogenerator when forward-connected to the measurement.

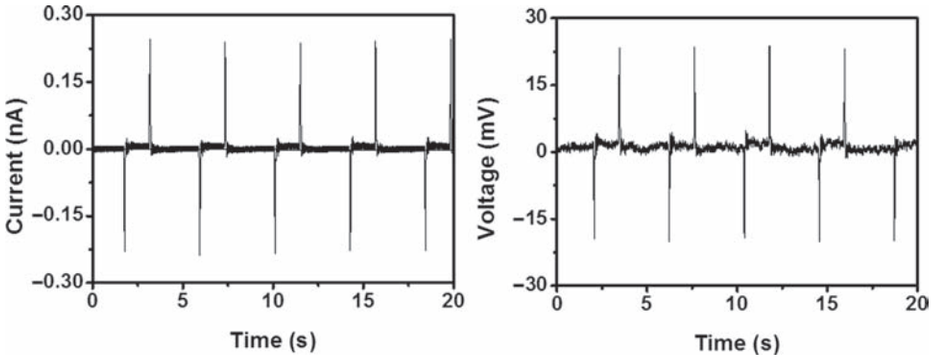

Fig. 6. Short-circuit current (left) and open-circuit voltage (right) of a flexible nanogenerator when subject to compressive strain and forward-connected to the measurement.

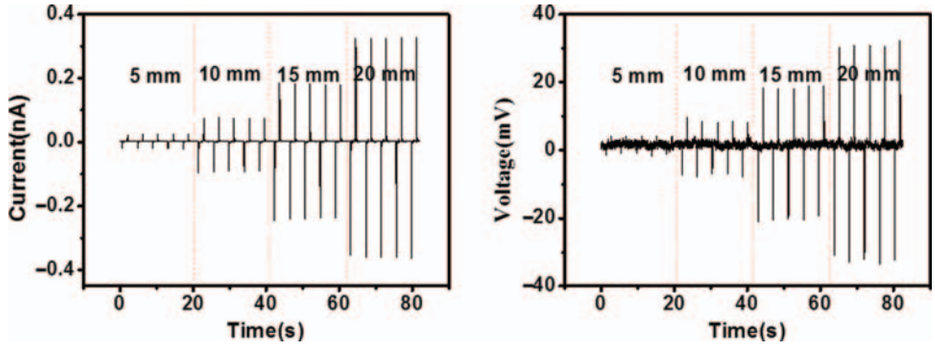

Fig. 7. Short-circuit current (left) and open-circuit voltage (right) of a flexible nanogenerator with different bending amplitudes (different tensile strains).

(the inset of Fig. 1(c)), which will give rise to the reversal in the sign of the output signal. Figure 6 is the short-circuit current and open-circuit voltage of a flexible nanogenerator when subject to compressive strain. The result proves the mechanism.

The performance of the nanogenerator depends sensitively on the strain. The strain of $BaTiO_3$ microwire is determined by the bending force applied on the nanogenerator, which is ultimately decided by the maximum displacement of the linear motor from its equilibrium position (bending amplitude). It can be expected that the strain increases with the increasing of bending amplitude. As a result, the piezoelectric potential between the two ends of $BaTiO_3$ nanowire will increase and the larger output voltage will be generated. Figure 7 is the short-circuit current and open-circuit voltage of a flexible nanogenerator with different bending amplitudes. As shown in Figure 7, with bending amplitude increasing from 5 to 20 mm, the output voltage increases from 2 to 21 mV.

The electrical output of the nanogenerator also relies on the strain rate. The strain rate of $BaTiO_3$ microwire can be controlled by the bending velocity (movement velocity of the linear motor) or bending frequency. At a constant strain, increasing the bending or releasing velocity leads to drastic increase in the corresponding output signals, which is shown in Figure 8. The enhanced output signals can be ascribed to the fact that the charges accumulation or release rates are significantly increased. In another words, the same amount of electrons in external circuit takes less time to flow between the two ends of the nanowire, which results in higher output voltage. Figure 9 exhibits the dependence of generated voltage and current

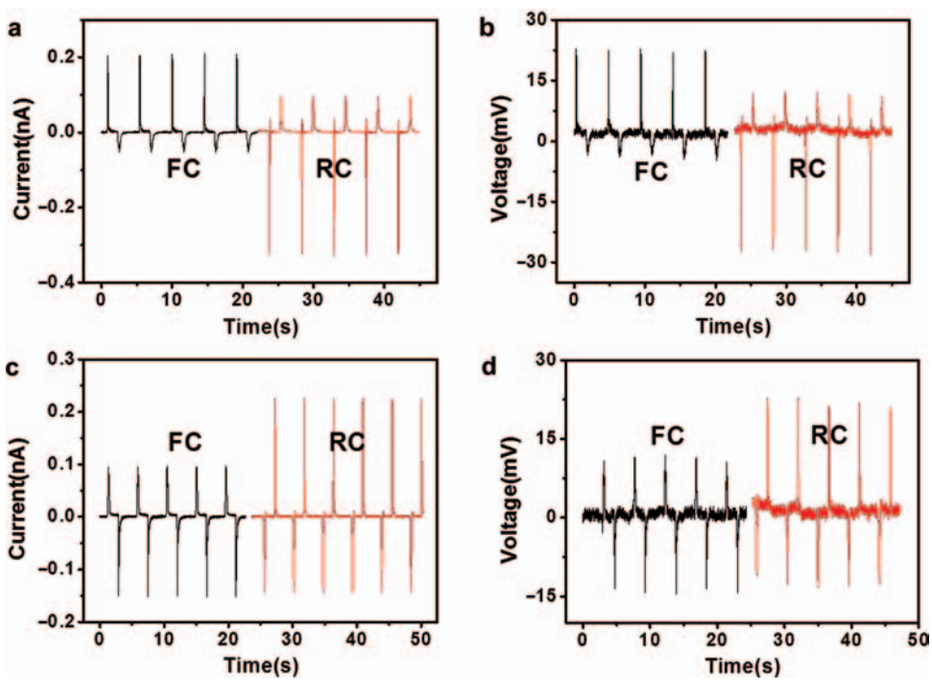

Fig. 8. Fast-strench-slow-release electrical signals (a), (b) and slow-strench-fast-release electrical signals (c), (d) of nanogenerator.

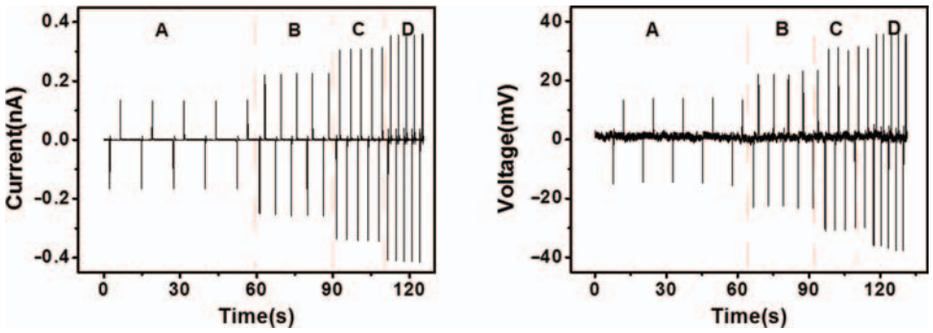

Fig. 9. Dependence of generated current and voltage on bending frequency of the substrate. (A, B, C, and D denote bending frequency of 0.08, 0.17, 0.25, 0.33 Hz, respectively).

on bending frequency. It is clearly evident that the outputs increase with the increasing bending frequency. The result has further confirmed the effect of strain rate on the performance of the nanogenerator. However, the outputs reach the saturation when the bending frequency beyond a certain value. This results mainly from the decrease of the piezoelectric coefficient with the increase of the driving stress frequency.[33]

To demonstrate the scaling of output signals, the flexible nanogenerators based on single $BaTiO_3$ nanowire were connected in series and in parallel at different configurations. The measurement results are shown in Figure 4. The output voltage and current of the generators are further improved by connecting the two $BaTiO_3$ nanowires with same polarity in series and in parallel, respectively. Otherwise, if the two nanowires have reversed polarities, the output voltage and current are depressed. The results clarify again that the output electricity produced by nanogenerators can be increased by integration of piezoelectric wires.[15, 34]

4. CONCLUSION

Theoretical simulations have shown that $BaTiO_3$ nanowires have superior piezoelectric potential between the two ends of the nanowire compared with that of PZT nanowire. A flexible nanogenerator based on single $BaTiO_3$ nanowire has been demonstrated. The electric outputs were found to be proportional to the strain and strain rate. Furthermore, the electric output can be scaled up by connecting two generators in series and in parallel with the correct polarity and sequence. This work, not only implies the potential of energy harvesting using $BaTiO_3$ nanowires, also exhibits the possibility of scale up of the electric outputs.

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