Flexible High-Performance Lead-Free Na$_{0.47}$K$_{0.47}$Li$_{0.06}$NbO$_3$ Microcube-Structure-Based Piezoelectric Energy Harvester

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*Supporting Information

ABSTRACT: Lead-free piezoelectric nano- and microstructure-based generators have recently attracted much attention due to the continuous demand of self-powered body implantable devices. We report the fabrication of a high-performance flexible piezoelectric microgenerator based on lead-free inorganic piezoelectric Na$_{0.47}$K$_{0.47}$Li$_{0.06}$NbO$_3$ (NKLN) microcubes for the first time. The composite generator is fabricated using NKLN microcubes and polydimethylsiloxane (PDMS) polymer on a flexible substrate. The flexible device exhibits excellent performance with a large recordable piezoelectric output voltage of 48 V and output current density of 0.43 μA/cm$^2$ under vertical compressive force of 2 kgf, for which an energy conversion efficiency of about 11% has been achieved. Piezoresponse and ferroelectric studies reveal that NKLN microcubes exhibited high piezoelectric charge coefficient ($d_{33}$) as high as 460 pC/N and a well-defined hysteresis loops with remnant polarization and coercive field of 13.66 μC/cm$^2$ and 19.45 kV/cm, respectively. The piezoelectric charge generation mechanism from NKLN microgenerator are discussed in the light of the high $d_{33}$ and alignment of electric dipoles in polymer matrix and dielectric constant of NKLN microcubes. It has been demonstrated that the developed power generator has the potential to generate high electric output power under mechanical vibration for powering biomedical devices in the near future.

KEYWORDS: lead-free piezoelectric, microstructures, ferroelectricity, piezoelectric generator, energy harvesting

1. INTRODUCTION

Piezoelectric micro/nanogenerators are emerging as promising energy harvesting tools for converting irregular and tiny mechanical energy with variable frequency and amplitude such as heartbeat, contraction of blood vessels, muscle stretching or eye blinking into electrical energy. Recently, lead-free piezoelectric materials have been extensively investigated for power generating device applications and their various potential applications in biomedical self-powered nanodevices and nanosystems, especially in implantable biomedical devices have been successfully demonstrated. Piezoelectric generator has been successfully utilized to power small electronic devices, such as the lighting liquid crystal display (LCD) screen and light emitting diodes (LED). Self-powered nanosensors such as gas, magnetic, mercury-ion detection, tactile have been also recently demonstrated using micro and nanogenerators. Up to now, various types of energy harvesters based on vertically and randomly aligned piezoelectric ZnO nanowires, GaN, and InN nanowires/nanorods, etc. have been reported for scavenging mechanical energy from the living environment. However, due to their coupling of piezoelectric and semiconducting dual properties, piezoelectric power output greatly reduced because of piezoelectric potential screening effect caused by the free electrons. Although an extensive efforts such as doping, thermal annealing, plasma treatment have been devoted to improve the power efficiency of nanogenerators, the output power was still not sufficiently high enough to operate a sustainable biomedical devices. In this regard, to enhance the power output, a new type of polymer assisted hybrid generators based on various piezoelectric nanostuctures such as Na$_3$NbO$_4$, BaTiO$_3$, LiNbO$_3$, and KNbO$_3$ have been recently designed and reported by many researchers because of their high piezoelectric charge coefficients compared to ZnO and GaN. In addition,
Under vertical mechanical strain. We achieved a very stable and high electric output voltage of 48 V and current density of 0.43 μA/cm² under application of 2 kgf vertical stress.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Na₀.₄₇K₀.₄₇Li₀.₀₆NbO₃ Microcubes and Fabrication of Energy Harvester. Single-crystalline Na₀.₄₇K₀.₄₇Li₀.₀₆NbO₃ (NKLN) microcubes was synthesized using the conventional solid state reaction method. In this process, high purity K₂CO₃ (>99%) and Na₂CO₃ (>99%), Nb₂O₅ (99.95%), and Li₂CO₃ (99.999%) of Sigma-Aldrich were used according to the stoichiometry. The powders were mixed homogeneously using ball mill for 10 h and then calcined at 850 °C for 10 h. After calcinations, powders were reground and mixed with binder (poly(vinyl alcohol)). Calcined powder was pressed into pellets after adding 2% weight of poly(vinyl alcohol). The pellets of the different samples were kept at 600 °C to burn the binder. Further, pellets were sintered at 1090 °C for 2 h. The sintered pellets were then ground using agate mortar for 3 h to get powders of NKLN microcubes. Proportion of each element in the Na₀.₄₇K₀.₄₇Li₀.₀₆NbO₃ is given in Table S1. Finally, obtained NKLN microcubes powders were thoroughly mixed with poly(dimethylsiloxane) (PDMS) with the volume ratio of 40:60, and then spin coated on the ITO coated PET substrate at 500 rpm for 15 s. 100 nm thick Al layer was deposited on PES substrates using a thermal evaporator as the top electrode, which was integrated with composite layers. The 10 nm thick chromium (Cr) was deposited on PES film by thermal evaporation prior to deposition of Al layer.

2.2. Characterization and Measurements. The synthesized NKLN microcubes underwent structural and crystallographic characterizations using XRD (Bruker D8 DISCOVER) with Cu Kα radiation (λ = 1.54 Å). The crystal shape of the sample was probed with ZEISS scanning electron microscope. The dielectric constant was measured by Agilent E4980A LCR meter. The piezoelectric charge coefficient was measured directly using a piezometer system (Piezotest PM300) by applying a tapping force of 0.25 N and frequency 110 Hz at RT. Ferroelectric hysteresis loop of the sample was recorded using a Sawyer–Tower circuit at 50 Hz of an automatic P–E loop tracer. A pushing tester (Labworks, Inc., model no. ET-126-4) was used to produce a vertical compressive strain on the device. A Tektronix DPO 3052 Digital Phosphor Oscilloscope with input impedance 1 MΩ and a low-noise current preamplifier (model no. SR570, Stanford Research Systems, Inc.) were used for electrical measurements. The device was electrically poled by applying a direct electric field of 50 kV/cm for 24 h at room temperature (RT) before the piezoelectric output signal measurements. The active size of the NKLN:PDMS based device was about 2.0 × 3.0 cm².

3. RESULTS AND DISCUSSION

Large-scale NKLN microcubes were synthesized through a simple solid state reaction method. The morphologies and
crystal structure of the as-synthesized perovskite NKLN samples were characterized using field-emission scanning electron microscopy (FE-SEM) and X-ray diffraction measurements, respectively. SEM image and X-ray diffraction (XRD) results of the NKLN microcubes is shown in Figure 1. Figure 1a shows the well-defined cubic morphology with an edge size of about in the range of 700 nm to 4 μm. Figure 1b presents the XRD pattern of NKLN showing the formation of a pure perovskite phase. No additional peak is detected in XRD pattern, confirming that the sample is of high quality with good crystallinity. The XRD pattern of the microcubes is identified according to the Joint Committee on Powder Diffraction Standards (JCPDS 11-0274) demonstrating that perovskite-structure NKLN is formed. The refined lattice constants of \( a = 3.8125 \) Å and \( c = 4.0659 \) Å for tetragonal crystal structure and \( a = 4.0005 \) Å, \( b = 4.0368 \) Å, and \( c = 3.9758 \) Å, for the orthorhombic phase were determined. Further, XRD pattern of NKLN microcubes indicates that the ratio of the peak intensities at (002) and (200) was nearly equal which suggests the formation of an equally mixed orthorhombic and tetragonal phase.42

The piezoelectric charge coefficient (\( d_{33} \)) and ferroelectric properties of the as grown microcubes were investigated with piezometer and ferroelectric P–E loop tracer at RT. To measure the piezoelectric charge coefficient of NKLN microcubes, electric poling with dc field of 40 kV/cm was applied at RT. A very high piezoelectric charge coefficient (\( d_{33} \)) about 450 pC/N was obtained, which is much higher than other reported lead-free perovskite samples.42–44 It has been reported that uniform grains formed with mixed orthorhombic and tetragonal phase (PPT) near RT leads to such a high value of piezoelectric coefficient of NKLN microcubes.51–53 To harvest mechanical energy, we subsequently had fabricated the power generating device, using the piezoelectric NKLN microcubes, it is noted that higher electric output is expected from micro or nanogenerators with high \( d_{33} \) piezoelectric materials.

Figure 2a–d presents the schematic diagram of the fabrication process of composite type microgenerator device based on the NKLN:PDMS composite structure. As shown in Figure 2, initially, the powder of NKLN microcubes and PDMS polymer in the volume ratio of 40:60 are homogeneously mixed, degassed, and uniformly spin-coated on the surface of ITO coated PET substrate. The composite was heated at 70 °C for 4 h. Then, Al/PES was mechanically integrated on the composite layer of NKLN:PDMS for top electrode preparation. The original image of flexible NKLN:PDMS composite was shown in the Figure 2e. Random distribution of NKLN microcubes in PDMS matrix was obtained in both sides of the composite film, as shown in Figure 2f (top view of composite) and Figure S1 (bottom view of composite). Further, a cross-sectional FE-SEM image of flexible film is shown in Figure S2, which shows that the thickness the composite film was about 525 μm. It is also clear that piezoelectric NKLN microcubes are randomly oriented inside.
the PDMS matrix, which results the electric dipoles are randomly aligned between the top and bottom electrodes in absence of any external field or pressure.

The piezoelectric output voltage and current from NKLN power generating device were measured under vertical pushing and releasing conditions using force simulator. The observed output voltage and current from the device are shown in Figure 3 and 4, respectively. A large output voltage of 48 V and current density of 0.43 μA/cm² were obtained under vertical compressive of 2 kgf at a frequency of 3 Hz, as shown in Figures 3 and 4, respectively. Switching-polarity tests were also carried out to confirm that the output voltage originated from the piezoelectric phenomenon. An opposite output signal is observed when the device is connected in reverse connection as shown in Figures 3b and 4b. Enlarged view of one cycle of output voltage (Figure 3c,d) and output current (Figure 4c,d) confirmed that the electric signals were reversible. Under forward and reverse connection, the difference of peak values between compress and release conditions are detected because of the difference in straining rate when applying and releasing the stress on the NKLN:PDMS device. The equivalent electric circuit of NKLN:PDMS piezoelectric power generator is given in Figure S3 of Supporting Information. To confirm that the large output voltage is produced from NKLN:PDMS based energy harvester, only PDMS based device (without NKLN microcubes) was also fabricated under identical condition and its output voltage is carefully measured. A negligible output voltage (~0.03 V) is obtained (Figure S4, Supporting Information) under the same mechanical stress. It is noted that, the device was electrically poled before the electric signal measurement. In the present work, the obtained electric output from the NKLN:PDMS based device are comparatively higher than previously reported composite-based piezoelectric energy harvesters (Table 1). It is demonstrated that the high output power of the generator can be used as a power source for self-powered biomedical devices.

The working mechanism and high performance of the power generator was also investigated on the basis of piezoelectric properties of NKLN microcubes, electric dipoles orientation, and the dielectric constant of the materials. It is expected that the charge-pumped electron flow is driven back and forth through an external load similar to phenomena of capacitor, where charging and discharging process results in alternating current (AC)-type charge generation. The details of power generation mechanism can be easily understood with the help of electric dipole alignment under application of mechanical stress and electric poling effect. It is noteworthy to point out that the electric dipoles can be oriented or switched in a particular direction after applying suitable electric field due to ferroelectric property of the NKLN microcubes.

Therefore, to confirm the capabilities of alignment and switching of electric dipoles, we have also investigated the ferroelectric property of the sample at RT by tracing its ferroelectric hysteresis loops. The ferroelectric study was performed and a well saturated P–E loop was obtained at RT, confirming the ferroelectric properties of NKLN micro-
cubes. The corresponding remnant polarization ($P_r$) and coercive field ($E_c$) were obtained as 13.66 $\mu$C/cm$^2$ and 19.45 kV/cm, respectively, at RT. The details of the ferroelectric and piezoelectric studies are given in our previous publication. The ferroelectric property of NKLN:PDMS composite film is further investigated using Sawyer–Tower ferroelectric loop tracer. The obtained $P–E$ loop is shown in the Figure 5. The result indicates that although the composite film does not show well saturated hysteresis like obtained $P–E$ loop of NKLN microcubes due to nonferroelectric characteristics of PDMS polymer, a ferroelectric property with comparatively smaller remnant polarization (0.2835 $\mu$C/cm$^2$) and slightly higher coercive field of 15.5 kV/cm than $P_r$ and $E_c$ of pure NKLN microcubes is still maintained. This result confirmed that electric dipoles alignment in the direction of applied field is possible under application of suitable electric poling.

Table 1. Comparison of Output Performance of Composite Energy Harvesters

<table>
<thead>
<tr>
<th>composite piezoelectric generator</th>
<th>output voltage (V)</th>
<th>output current/current density ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>LiNbO$_3$:PDMS</td>
<td>0.46</td>
<td>9.11 nA</td>
</tr>
<tr>
<td>BaTiO$_3$:PDMS</td>
<td>5.50</td>
<td>350 nA</td>
</tr>
<tr>
<td>NaNbO$_3$:PDMS</td>
<td>3.20</td>
<td>16 nA/cm$^2$</td>
</tr>
<tr>
<td>ZnSnO$_2$:PDMS</td>
<td>9.70</td>
<td>0.9 $\mu$A/cm$^2$</td>
</tr>
<tr>
<td>PMN–PT:PDMS</td>
<td>7.80</td>
<td>2.29 $\mu$A</td>
</tr>
<tr>
<td>Na$<em>{0.47}$K$</em>{0.47}$Li$_{0.06}$NbO$_3$:PDMS</td>
<td>48.00</td>
<td>0.45 $\mu$A/cm$^2$ present work</td>
</tr>
</tbody>
</table>

Figure 5. Ferroelectric $P–E$ hysteresis curve of NKLN:PDMS composite.
matrix are aligned along the electric-field direction from top to bottom. However, under the absence of any external pressure, the device remains in equilibrium state and no electric signal is detected.

When a vertical compressive force is applied (step 2), a piezoelectric potential is developed, which results in a change of polarization across the electrodes in such a way negative charges generated on the top side and positive charge is generated on the bottom side of device, due to strong alignment of electric dipoles in a single direction which results in a significant potential across the electrodes is created (Figure 6b). Further, in order to screen the piezoelectric electric potential, positive and negative charges are accumulated at the top and bottom electrodes, respectively, resulting in a generation of voltage and current output signals from the device. Further, when the vertical compressive force is removed, the compressive strain is released and the piezoelectric effect diminishes, and the accumulated charges transported back to the reverse direction and an electric signal is detected in opposite direction (step 3).

Therefore, AC-type voltage and current output signals from the NKLN device was obtained during continuous application and releasing of the compressive strain. It is also noted that, in addition to high $d_{33}$ output voltage/current of the device are also greatly influenced by the dielectric constant. In the present study, the output voltage and current from single cell of the NKLN based device are much higher than previously reported composite type piezoelectric power generators (Table 1), to confirm the influence of dielectric constant on piezoelectric power output, we have carefully measured the dielectric constant of NKLN at RT. It was observed that dielectric constant showed a decreasing trend with frequency in which is due to the space charge contribution at lower frequencies (data not shown here for NKLN, details).42 Dielectric constant reached up to the value of 551 at RT, which is relatively smaller than other reported values of lead-based piezoelectric materials such as PbZnNbO$_3$–PbTiO$_3$ [PZNT], PbMnNbO$_3$–PbO$_3$ [PMNT] etc.55,56 Piezoelectric output voltage from the device can be expressed as $V = \varepsilon_{33}E$, where $\varepsilon_{33}$ is the piezoelectric voltage constant, $\varepsilon$ is the strain, and $E$ is the Young’s modulus of the materials.8,49 Further, piezoelectric voltage constant, $\varepsilon_{33}$, is directly proportional to the $d_{33}$ and their mathematical relation can be expressed as $\varepsilon_{33} = d_{33}/(\varepsilon_0 K)$, where $\varepsilon_0$ is the permittivity of free space and $K$ is the relative dielectric constant of the NKLN microcubes, which also suggest that, piezoelectric output signal increased with decreasing dielectric constant. Moreover, dielectric constant of NKLN:PDMS composite film was also measured at various applied frequencies (Figure 7) at RT. It is observed that the dielectric constant of composite was significantly reduced (72.9 at 200 Hz), because of lower dielectric constant of PDMS (2.5) than NKLN microcubes.47

The average energy conversion efficiency of the flexible piezoelectric NKLN:PDMS-based device was estimated and found to be $\approx 11.12\%$. The energy conversion efficiency is
obtained by dividing the output electrical energy (1.63 × 10⁻⁸ J) per cycle with strain energy (1.46 × 10⁻⁷ J) developed in the device under mechanical pressure per cycle. Details about the calculation are given in the Supporting Information.

4. CONCLUSIONS

In conclusion, we fabricated a high-performance lead-free NKNL-microcube-based generator for scavenging mechanical energy. The flexible power generating device was fabricated using composite structure of NKNL:PDMS (40:60) on ITO coated PET substrate. The output voltage and current from the generator reached a record value of 48 V and 0.43 μA/cm², respectively, under vertical compressive force, which is much larger than other reported lead-free energy harvesters. The high-output voltage and current from the device was explained in the light of high d₃₃ (430 pC/N), low dielectric constant, and strong alignment of electric dipoles due to its well-defined ferroelectric properties. Our results indicate that the device has a great potential for self-powered implantable device due to its high power output.

■ ASSOCIATED CONTENT

# Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsami.5b09485.

Low-resolution FE-SEM image of NKNL:PDMS composite, cross-sectional FE-SEM image of NKNL:PDMS composite, high-resolution cross-sectional FE-SEM image, equivalent circuit of NKNL:PDMS power generator, output voltage from only PDMS-based device under mechanical stress, and detail of calculations of energy conversion efficiency of flexible NKNL:PDMS power generator. Proportion of element in the Na₀.₇K₀.₇Li₀.₀₆NbO₃ microcubes. (PDF)

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Notes

The authors declare no competing financial interest.

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