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Lead-free KNbO$_3$ ferroelectric nanorod based flexible nanogenerators and capacitors

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Abstract

In spite of high piezoelectricity, only a few one-dimensional ferroelectric nano-materials with perovskite structure have been used for piezoelectric nanogenerator applications. In this paper, we report high output electrical signals, i.e. an open-circuit voltage of 3.2 V and a closed-circuit current of 67.5 nA (current density 9.3 nA cm$^{-2}$) at 0.38% strain and 15.2% s$^{-1}$ strain rate, using randomly aligned lead-free KNbO$_3$ ferroelectric nanorods ($\sim 1 \mu$m length) with piezoelectric coefficient ($d_{33}$ $\sim$ 55 pm V$^{-1}$). A flexible piezoelectric nanogenerator is mainly composed of KNbO$_3$–poly(dimethylsiloxane) (PDMS) composite sandwiched by Au/Cr-coated polymer substrates. We deposit a thin poly(methyl methacrylate) (PMMA) layer between the KNbO$_3$–PDMS composite and the Au/Cr electrode to completely prevent dielectric breakdown during electrical poling and to significantly reduce leakage current during excessive straining. The flexible KNbO$_3$–PDMS composite device shows a nearly frequency-independent dielectric constant ($\sim$3.2) and low dielectric loss ($<0.006$) for the frequency range of $10^2$–$10^5$ Hz. These results imply that short and randomly aligned ferroelectric nanorods can be used for a flexible high output nanogenerator as well as high-$k$ capacitor applications by performing electrical poling and further optimizing the device structure.

(Some figures may appear in colour only in the online journal)

1. Introduction

Over the last several decades, ferroelectric nano-materials with perovskite structure have attracted a great deal of attention because of their novel physical properties, distinct from those of their bulk counterpart [1, 2], and their extensive applications, such as in nano-sensors and nano-actuator/transducers [3]. Among ferroelectric nano-materials, alkaline niobates such as (K, Na)NbO$_3$ have been considered as a strong candidate for lead-free piezoelectric devices due to their high piezoelectricity, high Curie temperature, large dielectric constant, and electromechanical coupling [4].

One of the most challenging applications of ferroelectric nano-materials is in nanogenerators which can effectively convert tiny mechanical vibrations into electricity. By virtue of the non-toxicity, cost-effectiveness, and high piezoelectricity [5], one-dimensional alkaline niobates (nanowires, nanorods, and nanotubes) should be quite
useful for environment-friendly nanogenerator applications. Distinct from ZnO nanowires that have mostly been used for nanogenerators [6–8], hydrothermally grown alkaline niobates are usually short (<10 μm) and randomly aligned. Because of these demerits, probably, there are only a few reports of piezoelectric nanogenerators by using ferroelectric nanostructures [9–13]. To fully utilize the merit of high piezoelectricity, it is necessary to develop a suitable device structure for short and randomly aligned one-dimensional alkaline niobates.

In this paper, we report a high output piezoelectric nanogenerator based on lead-free KNbO₃ ferroelectric nanorods. Scanning/transmission electron microscopy and piezoresponse force microscopy measurements show that a single-crystalline KNbO₃ nanorod is rather short (typical length of ~1 μm) but has a large piezoelectric constant (d_{33} ≈ 55 pm V⁻¹). The KNbO₃ nanorods were blended with poly(dimethylsiloxane) (PDMS) polymer (total thickness of 25 μm) and electrically poled to align piezoelectric domains. With a small strain of 0.38%, the KNbO₃–PDMS composite device shows an open-circuit voltage of 3.2 V and a closed-circuit current of 67.5 nA (current density of 1.1 μA cm⁻²), the electrical loss of the KNbO₃–PDMS composite is very small, i.e. less than 0.5 nA up to the 50 V of applied dc voltage and less than tan δ = 0.006 for the ac frequency range of 10²–10⁵ Hz. Meanwhile, the dielectric constant of KNbO₃–PDMS increases by 28% as compare with that of PDMS, i.e., 3.2 for KNbO₃–PDMS and 2.5 for PDMS. This work provides an insight into high performance flexible nanogenerators and high-k capacitors by using short and randomly aligned ferroelectric one-dimensional nanostructures, including the KNbO₃ nanorod, by further optimizing the device structure.

2. Experimental section

High quality KNbO₃ nanorods were synthesized by the hydrothermal method [14]. As-grown KNbO₃ nanorods were thermal annealed at 600°C for 12 h to completely remove hydroxyl defects [15]. Crystalline structures of the nanorod were characterized by high-resolution x-ray diffraction (HR-XRD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) measurements. We used piezoresponse force microscopy (PFM) to investigate the piezoelectricity and piezoelectric/ferroelectric domains of the KNbO₃ nanorods. The PFM measurement was performed using an atomic force microscope (Nanofocus N-Tracer) at 1 V and 70 kHz. To scan the surface, we used Pt/Ir-coated tips with a force constant of 3 N m⁻¹. Before scanning, we thoroughly dispersed and tightly attached the nanorods to the Pt-coated Si substrate by using a polymer (5 wt% poly(vinylpyrrolidone) dissolved in ethanol) [16]. A piezoelectric KNbO₃-based nanogenerator was fabricated by the spin-coating (4000 rpm for 15 s) of blended KNbO₃–PDMS composite (volume ratio of 1:100) on the poly(methyl methacrylate) (PMMA) and Au/Cr-coated Kapton film [17]. (To determine the volume of KNbO₃ nanorods, we put KNbO₃ nanorods in DI water. By measuring the increased volume, we determined the volume of KNbO₃ nanorods.) We used a spin-coater and thermal evaporator to deposit PMMA (2–3 μm) and Au (~25 nm)/Cr (~10 nm) on Kapton film (~125 μm), respectively. Another PMMA and Au/Cr-coated Kapton film was sandwiched with the KNbO₃–PDMS composite. Finally, we attached the thick (~500 μm) polyester (PS) film to the Kapton film. We applied ~150 kV cm⁻¹ of electric field for 1 h at room temperature for electrical poling. A linear motor was used to periodically apply and release the compressive force with a frequency of 0.33 Hz. The output signal of the piezoelectric device was recorded by a low-noise voltage and current preamplifier. The current–voltage characteristics and complex dielectric constant (ε = ε₁ + iε₂) of the device were obtained through an I–V source-meter unit and an LCR meter, respectively.

3. Results and discussion

Figure 1(a) shows the crystal structure of KNbO₃ obtained from the Rietveld analysis of high-resolution x-ray diffraction (HR-XRD) measurements. Following the typical perovskite structure, the K atoms (orange spheres) are located at the
corner positions, the Nb atom at the body centered position, and the O atoms at the face centered position. An important point is that the Nb$^{5+}$ ion does not locate at the center of the O$^{2-}$ ions cage, but shifts along the edges of NbO$_6$ octahedra. Due to the off-centering of Nb$^{5+}$ and O$^{2-}$ ions, electric polarization is spontaneously formed without applying the electric field.

Figures 1(b) and (c) show the scanning electron microscopy (SEM) and the high-resolution transmission electron microscopy (TEM) images, respectively, of hydrothermally grown KNbO$_3$. The KNbO$_3$ has a one-dimensional nanorod shape with a width of 60–180 nm and length of 200 nm–1.5 µm. The clear lattice images and electron diffraction patterns suggest the single-crystalline quality of KNbO$_3$ nanorods. Combining the results of HR-XRD with TEM, we notice that the KNbO$_3$ nanorod grows along the [011] direction and has lattice constants of $a = 3.994$ Å, $b = 5.699$ Å, and $c = 5.699$ Å with Amm2 symmetry.

We investigate the piezoelectricity of hydrothermally grown KNbO$_3$ nanorods using piezoresponse force microscopy (PFM) measurement. By scanning the surface of nanorods with a metal-coated conducting tip, two-dimensional mapping of piezoresponse amplitude and phase signals can be obtained at the nanoscale as well as the topography. Figures 2(a)–(c) show the topography, the amplitude, and the phase of piezoelectric response of a KNbO$_3$ nanorod, respectively. The response amplitude could be considered as an unexpected geometrical overlap with the cantilever. However, we confirmed a contact-mode and non-contact-mode scan of the surface in order to eliminate the possible artifacts from the irregular surface protrusions. The brightness of the amplitude map represents the strength of piezoelectric response while the contrast of the phase map stands for the direction of electric polarization in the nanorod. From figures 2(b) and (c), we notice that the piezoelectric domains of the KNbO$_3$ nanorod seem to form along the growth direction of the nanorod, i.e. along [011].

Figure 2(d) shows the switching of piezoelectric/ferroelectric domains with the application of dc voltage. The amplitude of the piezoresponse shows a clear hysteresis loop and becomes saturated above 7 V. These features imply the ferroelectricity of KNbO$_3$ nanorods. We estimated the piezoelectric coefficient $d_{33}$ value by fitting the root-mean-square (RMS) amplitude of the tip deflection divided by the RMS amplitude of the applied voltage [18]. The saturated $d_{33}$ value of the KNbO$_3$ nanorod is estimated to be $\sim 55$ pm V$^{-1}$.

Confirming the ferroelectricity and large piezoelectric coefficient of KNbO$_3$ nanorods, we used them for a high output piezoelectric nanogenerator. Figure 3(a) shows the schematic diagram of the KNbO$_3$–PDMS composite based flexible nanogenerator. The nanogenerator is basically composed of four layers. The KNbO$_3$–PDMS composite layer (solid lines in white background) plays the role of a piezoelectric potential source for the device. Two Au/Cr-coated Kapton films act as top and bottom electrodes. Thin PMMA layers between the KNbO$_3$–PDMS composite and the Au/Cr completely prevent the electrical shorting between electrodes during electric poling and excessive straining. A thick PS film takes the role of the main straining source. Due to all polymer layers, as shown in the inset of figure 3(a), the device is easily bent by the small mechanical stress. The cross-section SEM image (figure 3(b)) indicates that the KNbO$_3$–PDMS layer is $\sim 25$ µm thick. In the magnified SEM image (inset of figure 3(b)), the KNbO$_3$ nanorods (white spots) are clearly visible in PDMS (black background).

In figures 3(c)–(e), we schematically show the power generation mechanism of KNbO$_3$–PDMS composite device. The KNbO$_3$ nanorod has piezoelectric/ferroelectric domains along the nanorod direction. When we apply strong electric field, i.e. electrical poling, the domains tend to rotate along the electric field direction. Some domains will be parallel to the poling direction while some are not. However, every domain has an electric dipole component parallel to the electric field, as marked by white arrows. If we apply the stress $F(t)$, the nanorods are subjected to compressive strain and piezoelectric potential is induced due to the piezoelectricity of the KNbO$_3$ nanorod. To screen the piezoelectric potential, positive and negative charges will be accumulated at the top and bottom electrodes, respectively. If the compressive strain is released, the piezoelectric potential should be diminished and the accumulated charges will move back in the opposite direction. Therefore, the continuous applying and releasing of the compressive strain will result in an alternating voltage and current [19]. Note that the output voltage and current should come from the averaged contribution from randomly distributed KNbO$_3$ nanorods.

To quantify the strain, we first calculated the strain neutral line from the equation of $\Sigma Y_{it}y_i = 0$ ($i = 1$–$4$), where $Y$, $t$, and $y$ represent the Young’s modulus, thickness, and the distance from the strain neutral line to the center of each
layer. We used the $Y$ of KNbO$_3$–PDMS, Kapton, and PS film as 0.66 GPa, 2.5 GPa, and 3.25 GPa, respectively [20]. For the calculation of the $Y$ for KNbO$_3$–PDMS composite, we used the rule of mixtures with the known values of $Y$ (volume fraction) of 91 GPa (0.01) for KNbO$_3$ and 0.615 GPa (0.99) for PDMS [21]. Then, we calculated the strain by the equation of $\varepsilon = 2t' \times h/(a^2 + h^2)$, where $a$, $h$, and $t'$ represent the half-width of the arc, height of the arc, and the distance from the strain neutral line to the center of the KNbO$_3$–PDMS composite layer, respectively [22]. Note that there should be a distribution of strain for KNbO$_3$–PDMS composite due to the finite thickness of the layer (∼25 µm). Therefore, the strain listed below should be considered as an averaged value for the KNbO$_3$–PDMS layer. The actual strain of KNbO$_3$ should be quite small as compared with the averaged strain value for KNbO$_3$–PDMS composite, since the $Y$ of PDMS (0.615 GPa) is smaller than that of KNbO$_3$ (91 GPa).

In figures 4(a) and (b), we show the strain-dependence of open-circuit voltage and closed-circuit current, respectively. Through the polarity reversal test [12], we have confirmed that the signals really originate from the piezoelectricity of KNbO$_3$. With the increase of strain, both voltage and current increase continuously (figure 4(c)). In particular, we obtained an open-circuit voltage of 3.2 V and a closed-circuit current of 67.5 nA (with a current density of 9.3 nA cm$^{-2}$) at 0.38% strain and 15.2% s$^{-1}$ strain rate. While the obtained values are smaller than for recent ZnO based nanogenerators [23], the obtained voltage and current are enough to power a small liquid crystal (LCD). As shown in figure 4(d), there is no number on the LCD screen without bending. With bending, part of the number ‘6’ is lit up and then all the segments are continuously lit up on the LCD screen.

Electrical loss is one of the important factors for the reliable performance of the KNbO$_3$–PDMS composite nanogenerator. To retain the generated electrical signals from the piezoelectricity of KNbO$_3$, the electrical loss at dc as well as ac frequency should be very small. In figures 5(a) and (b), we show, respectively, the dc current–voltage characteristics and ac dielectric loss ($\tan \delta \equiv \varepsilon_2/\varepsilon_1$) of the KNbO$_3$–PDMS composite. The dc current is less than 0.5 nA up to 50 V and the $\tan \delta$ is less than 0.006 up to $10^5$ Hz. Due to such small values of electrical loss, the KNbO$_3$–PDMS composite nanogenerator outputs electrical signals without fatigue, as shown in figures 4(a) and (b).

Inorganic KNbO$_3$ has a large dielectric constant (∼500) but is fragile to external stress, while organic PDMS has good flexibility but very small dielectric constant (∼2.5) [24, 25]. Since the device geometry of the nanogenerator is nearly the same as for the capacitor, we tested the possible flexible high-$k$ capacitor application. As shown in figure 5(c), the dielectric constant ($\varepsilon_1$) of the KNbO$_3$–PDMS composite is around 3.2 and is nearly frequency-independent. The increased dielectric constant of the KNbO$_3$–PDMS composite, as compared with that of PDMS itself, implies that the flexible nanogenerator may also be used for the storage of generated electricity.

Note that we mixed KNbO$_3$ and PDMS with a volume ratio of 1:100. If we increase the volume ratio of KNbO$_3$, the output voltage, current, and dielectric constant of the device should increase. Accordingly, however, the dielectric...
Figure 4. (a) Open-circuit voltage and (b) closed-circuit current of the KNbO$_3$–PDMS composite nanogenerator. In (a), the letters P and R represent press and release, respectively. (c) Strain-dependences of voltage (black squares) and current (red squares) on the change of strain at the fixed strain rate (15.2% s$^{-1}$). (d) Powering an LCD device using a bent KNbO$_3$–PDMS composite device.

Figure 5. (a) Current–voltage characteristics, (b) dielectric loss tan $\delta$, and (c) dielectric constant $\varepsilon_1$ of the KNbO$_3$–PDMS composite (black squares) and PDMS (red circles).

loss should also increase. By optimizing the blending ratio between KNbO$_3$ and PDMS, we expect a more significant performance of the flexible nanogenerator and a greater increase in the dielectric constant of the capacitor.

4. Conclusion

In summary, we report a high output piezoelectric nanogenerator by using relatively short (<1 $\mu$m) and randomly aligned lead-free KNbO$_3$ ferroelectric nanorods. By blending the KNbO$_3$ and PDMS polymer in the volume ratio 1:100, we obtained an open-circuit voltage of 3.2 V and a closed-circuit current of 67.5 nA, and successfully lit up a small liquid crystal display. We discuss the blending ratio, electric poling, and thin PMMA layer to demonstrate the device performance.

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