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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$1 μm length) with piezoelectric coefficient ($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

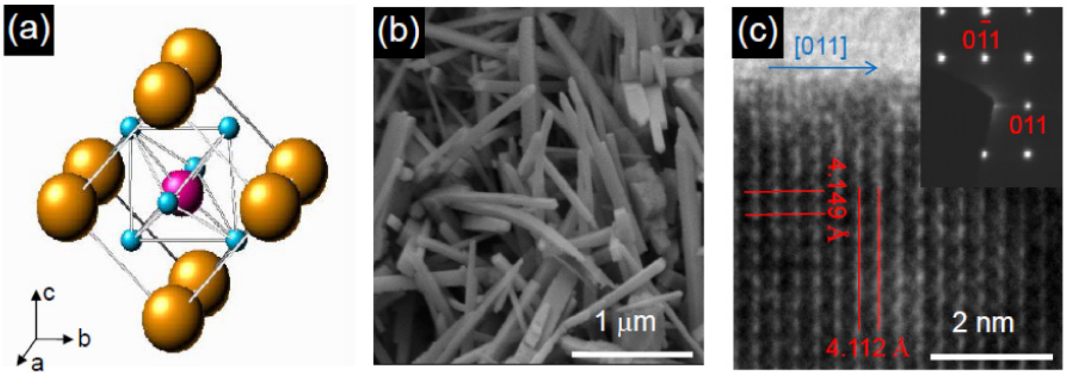

Figure 1. (a) Crystal structure of $KNbO_3$. Orange, purple, and blue spheres represent K, Nb, and O atoms, respectively. (b) Scanning electron microscopy (SEM) and (c) high-resolution transmission electron microscopy (TEM) images of $KNbO_3$ nanorods. In the inset of (c), we show the selected area electron diffraction (SAED) with the zone axis of [100].

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 $KNbO_3$ ferroelectric nanorods. Scanning/transmission electron microscopy and piezoresponse force microscopy measurements show that a single-crystalline $KNbO_3$ nanorod is rather short (typical length of $\sim$1 μm) but has a large piezoelectric constant ($d_{33} \sim 55$ pm V^{-1}). The $KNbO_3$ 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 $KNbO_3$–PDMS composite device shows an open-circuit voltage of 3.2 V and a closed-circuit current of 67.5 nA (current density 9.3 nA cm^{-2}), and powers a small liquid crystal display (LCD). Due to the small amount of $KNbO_3$ in PDMS (volume ratio $\sim$1:100), the electrical loss of the $KNbO_3$–PDMS composite is very small, i.e. less than 0.5 nA up to the 50 V of applied dc voltage and less than $\tan\delta = 0.006$ for the ac frequency range of 10^2-10^5 Hz. Meanwhile, the dielectric constant of $KNbO_3$–PDMS increases by 28% as compare with that of PDMS, i.e. 3.2 for $KNbO_3$–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 $KNbO_3$ nanorod, by further optimizing the device structure.

2. Experimental section

High quality $KNbO_3$ nanorods were synthesized by the hydrothermal method [14]. As-grown $KNbO_3$ 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 $KNbO_3$ 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 $KNbO_3$-based nanogenerator was fabricated by the spin-coating (4000 rpm for 15 s) of blended $KNbO_3$–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 $KNbO_3$ nanorods, we put $KNbO_3$ nanorods in DI water. By measuring the increased volume, we determined the volume of $KNbO_3$ nanorods.) We used a spin-coater and thermal evaporator to deposit PMMA (2–3 μm) and Au ($\sim$25 nm)/Cr ($\sim$10 nm) on Kapton film ($\sim$125 μm), respectively. Another PMMA and Au/Cr-coated Kapton film was sandwiched with the $KNbO_3$–PDMS composite. Finally, we attached the thick ($\sim$500 μm) polyester (PS) film to the Kapton film. We applied $\sim$150 kV cm^{-1} of electric field for 1 h at room temperature for electrical poling. A linear motor was used to periodically apply and release the compressive force with a frequency of 0.33 Hz. The output signal of the piezoelectric device was recorded by a low-noise voltage and current preamplifier. The current–voltage characteristics and complex dielectric constant ($=\varepsilon_1 + i\varepsilon_2$) 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 $KNbO_3$ 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 *Amm*2 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

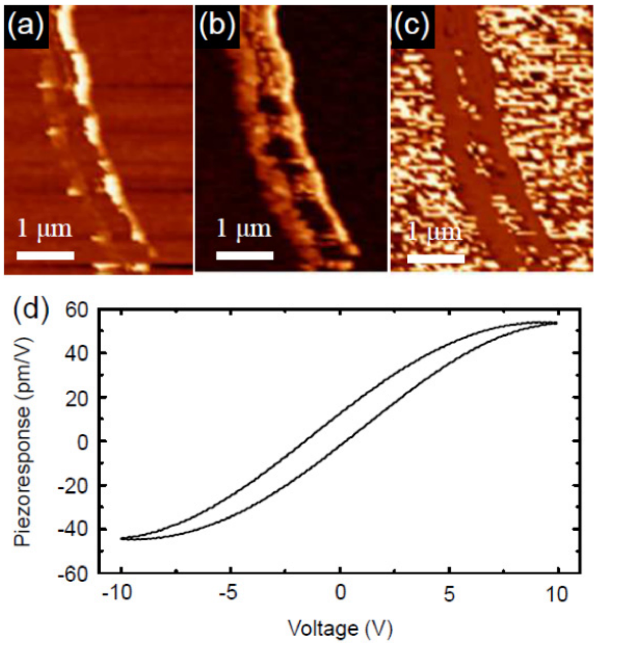

Figure 2. (a) Topography, (b) amplitude, (c) phase, and (d) hysteresis loop of the piezoelectric response for a single $KNbO_3$ nanorod.

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 $\Sigma Y_i t_i y_i = 0$ ($i = 1$–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

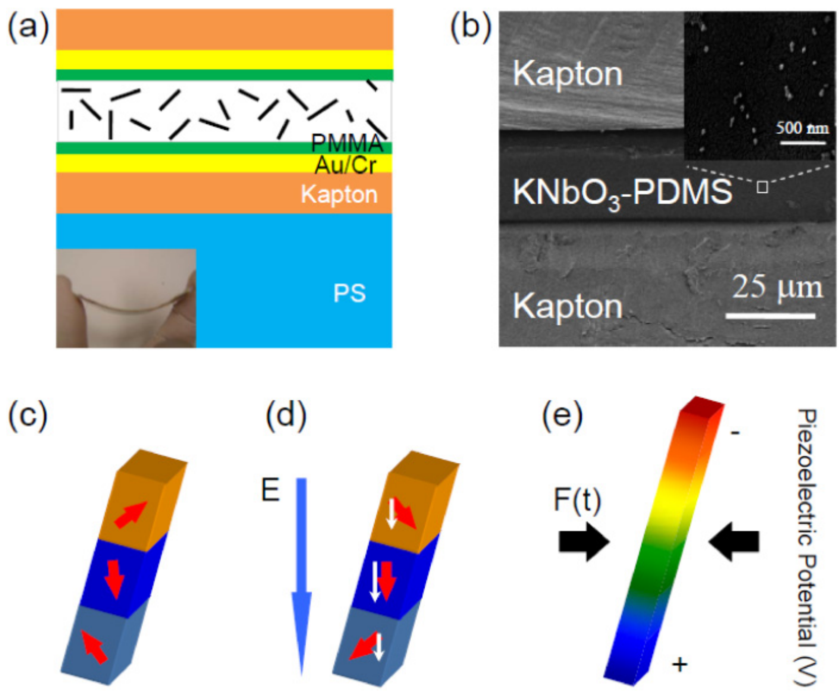

Figure 3. (a) Schematic diagram and (b) cross-section SEM image of the $KNbO_3$–PDMS composite nanogenerator. In the insets of (a) and (b), we show a photograph of the flexible device and the enlarged SEM image of $KNbO_3$ nanorods (white spots) inside PDMS (black background). Piezoelectric/ferroelectric domains (c) before and (d) after electric poling. The red and white arrows indicate the direction of electric polarization and the directional component along the applied electric field (E), respectively. (e) Piezoelectric potential after the compressive strain $F(t)$. The + and − indicate the sign of accumulated charges at each end of the nanorod.

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 (ε_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

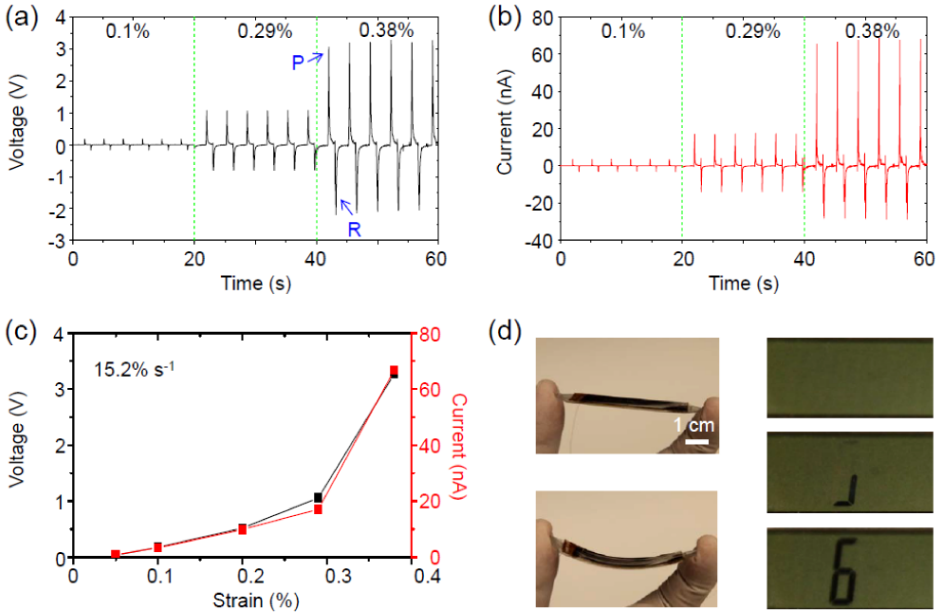

Figure 4. (a) Open-circuit voltage and (b) closed-circuit current of the $KNbO_3$–PDMS composite nanogenerator. In (a), the letters P and R represent press and release, respectively. (c) Strain-dependences of voltage (black squares) and current (red squares) on the change of strain at the fixed strain rate (15.2% s^{-1}). (d) Powering an LCD device using a bent $KNbO_3$–PDMS composite device.

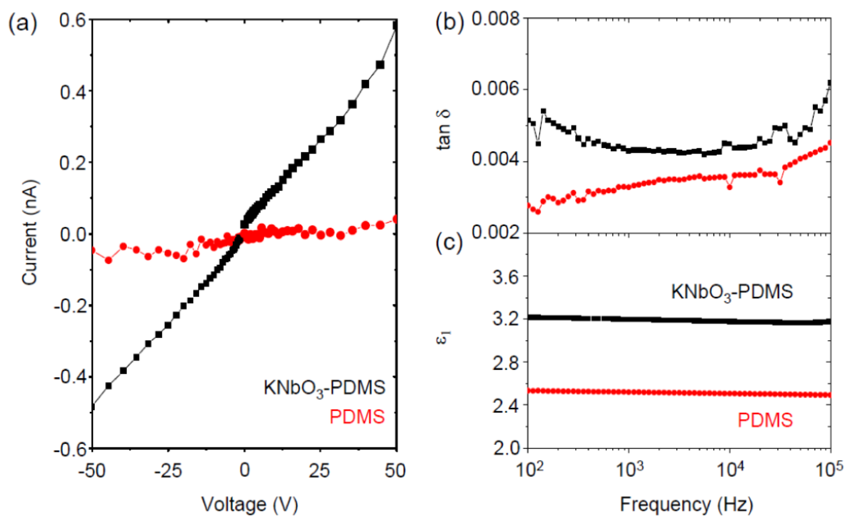

Figure 5. (a) Current–voltage characteristics, (b) dielectric loss tan δ, and (c) dielectric constant ε_1 of the $KNbO_3$–PDMS composite (black squares) and PDMS (red circles).

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 μm) 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.

Acknowledgments

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References

[1] Yun W, Urban J J, Gu Q and Park H 2002 *Nano Lett.* **2** 447–50
[2] Louis L, Gemeiner P, Ponomareva I, Bellaiche L, Geneste G, Ma W, Setter N and Dkhil B 2010 *Nano Lett.* **10** 1177–83
[3] Rørvik P M, Grande T and Einarsrud M-A 2011 *Adv. Mater.* **23** 4007–34
[4] Saito Y, Takao H, Tani T, Nonoyama T, Takatori K, Homma T, Nagaya T and Nakamura M 2004 *Nature* **432** 84–7
[5] Rödel J, Jo W, Seifert K T P, Anton E-M, Granzow T and Damjanovic D 2009 *J. Am. Ceram. Soc.* **92** 1153–77
[6] Wang Z L and Song J H 2006 *Science* **312** 242–6
[7] Wang X D, Song J H and Wang Z L 2007 *Science* **316** 102–5
[8] Qin Y, Wang X D and Wang Z L 2008 *Nature* **451** 809–13
[9] Chen X, Xu S, Yao N and Shi Y 2010 *Nano Lett.* **10** 2133–7
[10] Xu S, Hansen B J and Wang Z L 2010 *Nature Comms.* **1** 93
[11] Park K-I, Xu S, Liu Y, Hwang G T, Kang S J L, Wang Z L and Lee K J 2010 *Nano Lett.* **10** 4939–43
[12] Jung J H, Lee M, Hong J-I, Ding Y, Chen C-Y, Chou L-J and Wang Z L 2011 *ACS Nano* **5** 10041–6
[13] Wu J M, Xu C, Zhang Y and Wang Z L 2012 *ACS Nano* **6** 4335–40
[14] Magrez A, Vasco E, Seo J W, Dieker C, Setter N and Forro L 2006 *J. Phys. Chem.* B **110** 58–61
[15] Yun B K, Koo Y S, Jung J H, Song M and Yoon S 2011 *Mat. Chem. Phys.* **129** 1071–4
[16] Suyal G, Colla E, Gysel R, Cantoni M and Setter N 2004 *Nano Lett.* **4** 1339–42
[17] Park K-I *et al* 2012 *Adv. Mater.* **24** 2999–3004
[18] Ke T-Y, Chen H-A, Sheu H-S, Yeh J-W, Lin H-N, Lee C-Y and Chiu H-T 2008 *J. Phys. Chem.* C **112** 8827–31
[19] Zhang Y, Liu Y and Wang Z L 2011 *Adv. Mater.* **23** 3004–13
[20] Zhou J, Gu Y D, Fei P, Mai W J, Gao Y F, Yang R S, Bao G and Wang Z L 2008 *Nano Lett.* **8** 3035–40
[21] Ishikawa M, Takiguchi N, Hosaka H and Morita T 2008 *Japan. J. Appl. Phys.* **47** 3824–8
[22] Lee M, Chen C-Y, Wang S, Cha S N, Park Y J, Kim J M, Chou L-J and Wang Z L 2012 *Adv. Mater.* **24** 1759–64
[23] Zhu G, Wang A C, Liu Y, Zhou Y and Wang Z L 2012 *Nano Lett.* **12** 3086–90
[24] Ishikawa M, Yazawa K, Fujisawa T, Yasui S, Yamada T, Hasegawa T, Morita T, Kurosawa M and Funakubo H 2009 *Japan. J. Appl. Phys.* **48** 09KA14
[25] Molberg M, Leterrier Y, Plummer C J G, Walder C, Löwe C, Opris D M, Nüesch F A, Bauer S and Månson J E 2009 *J. Appl. Phys.* **106** 054112