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Lead-Free NaNbO_3 Nanowires for High Output Piezoelectric Nanogenerator

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ABSTRACT

Perovskite ferroelectric nanowires have rarely been used for the conversion of tiny mechanical vibrations into electricity, in spite of their large piezoelectricity. Here we present the lead-free NaNbO_3

1 nanowires based piezoelectric device for the high output and cost-effective flexible nanogenerator. The
2 device consists of a NaNbO₃ nanowires-poly(dimethylsiloxane) (PDMS) polymer composite and Au/Cr
3 coated polymer films. High quality NaNbO₃ nanowires can be grown by hydrothermal method at low
4 temperature and can be poled by an electric field at room temperature. The NaNbO₃ nanowire-PDMS
5 polymer composite device shows an output voltage of 3.2 V and output current of 72 nA (current
6 density of 16 nA/cm²) under a compressive strain of 0.23%. These results imply that NaNbO₃ nanowires
7 should be quite useful for the large-scale lead-free piezoelectric nanogenerator applications.
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18 KEYWORDS: lead-free, NaNbO₃ nanowire, high output, piezoelectric nanogenerator
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1 Effective conversion of ubiquitous mechanical energy into electricity is one of the most important
2 issues in scientific community.^{1,2} In particular, the need for self-powering nanodevices from tiny
3 vibrations such as air pressure and heart beat have inspired the interest for developing high performance
4 piezoelectric nanomaterials. Till now, piezoelectric ZnO nanowires are the most outstanding candidate
5 for nanogenerator (NG).³⁻⁶ Among piezoelectric materials, displacive ferroelectrics such as lead
6 zirconate titanate exhibit very large piezoelectric coefficients.⁷⁻⁹ But the use of ferroelectric material for
7 harvesting mechanical energy is rare possibly due to the difficulty in forming one-dimensional
8 nanostructures and the elevated temperature required for the growth.

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11 As for piezoelectric NG using ferroelectric nanowires, $\text{Pb}(\text{Zr,Ti})\text{O}_3$ and BaTiO_3 have been
12 investigated. Chen *et al.* synthesized $\text{Pb}(\text{Zr,Ti})\text{O}_3$ nanofibers by electrospinning using which an output
13 voltage of 1.63 V and output power of 0.03 μW were achieved.¹⁰ Using the aligned $\text{Pb}(\text{Zr,Ti})\text{O}_3$
14 nanowires grown by chemical method at relatively low temperature, Xu *et al.* reported an output voltage
15 of 0.7 V and current density of 4 $\mu\text{A}/\text{cm}^2$, and the lit up of a commercial LED.¹¹ Park *et al.* synthesized
16 BaTiO_3 thin film by rf sputtering and fabricated NGs by micro-fabrication and soft lithographic printing
17 techniques.¹² By bending the flexible substrate, they obtained output voltage of 1.0 V and current
18 density of 0.19 $\mu\text{A}/\text{cm}^2$. While above results are outstanding, we still need a cost-effective device of
19 high output power by using easily accessible and non-toxic ferroelectric nanowires.^{13,14}

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22 In this paper, we report the piezoelectric NGs fabricated using lead-free NaNbO_3 nanowires. Large
23 amount of high-quality NaNbO_3 nanowires can be produced after one time reaction at low temperature.
24 By forming a composite of NaNbO_3 nanowires with poly(dimethylsiloxane) (PDMS) polymer, flexible
25 NG was fabricated easily after applying a direct poling process. Under a compressive strain of 0.23%,
26 we obtained very stable and high output piezoelectric signals, *i.e.* an open circuit voltage of 3.2 V, a
27 closed circuit current of 72 nA, and a power density of 0.6 mW/cm^3 by considering the volume fraction
28 of NaNbO_3 nanowire inside PDMS polymer.

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RESULTS AND DISCUSSION

There are two different morphologies of NaNbO₃ with nearly the same lattice constant and symmetry (Figure 1). As described in experimental section, nanowire is formed at short reaction time and nanocube is at long reaction time by simple hydrothermal method. As grown Na₂Nb₂O₆-H₂O nanowires are successively transformed into NaNbO₃ nanowires with the increase of annealing temperature as confirmed by *in-situ* x-ray diffraction measurement (supporting information, Figure S1a).^{15,16} Figure 1a,c show scanning electron microscopy (SEM) images of nanowires and nanocubes, respectively. The NaNbO₃ nanowires have several tens of μm in length and ~200 nm in diameter. On the other hand, the NaNbO₃ nanocubes have 0.5-1.0 μm in lengths. Figure 1b,d show transmission electron microscopy (TEM) images of a nanowire and a nanocube, respectively. Both nanowire and nanocube show clear lattice fringes and electron diffraction patterns (insets of Figure 1b,d); suggesting their crystalline quality. Dark field images show that there are twins along the growth direction for nanowire and in facet for nanocube (supporting information, Figure S2). X-ray diffraction and electron diffraction give lattice parameters of a=5.567 Å, b=7.764 Å, c=5.515 Å, and symmetry of P2₁ma for both annealed nanowires and as-grown nanocubes (Figure 1e).

Having a P2₁ma ferroelectric symmetry rather than Pbcm antiferroelectric symmetry in NaNbO₃ nanostructures is crucial for NG application, since the former exhibits large piezoelectricity while the latter does not. Bulk crystalline NaNbO₃ has long been indexed as Pbcm symmetry with a=5.506 Å, b=5.566 Å, c=15.520 Å lattice constants.¹⁷ The antiferroelectric Pbcm symmetry is also known to be changed into ferroelectric P2₁ma symmetry by applying electric field.¹⁸ However, the exceptionally long *c*-axis has been questioned by several sophisticate experiments.¹⁹⁻²¹ Especially, Shiratori *et al.* reported that the antiferroelectric Pbcm symmetry in bulk changes into the ferroelectric P2₁ma symmetry in submicron sized NaNbO₃.²² By accepting the interesting size effect in NaNbO₃ nanowires and nanocubes, we further performed the Rietveld analysis for high-resolution x-ray diffraction pattern (supporting information, Figure S1b). The obtained x-ray diffraction results can be better fitted by

P2₁ma than Pbcm symmetry, as evidenced by smaller fitting error.

Having the ferroelectricity (and inherited piezoelectricity) of NaNbO₃ nanowires, we use them for fabricating a NG. Lead-free NaNbO₃ nanowires can be obtained at a relatively large quantity. As shown the photograph of obtained nanowires (Figure 2a), one time reaction in 25-mL-sized vessel can produce more than 1.2 g of NaNbO₃ nanowires without any different morphologies and impurities.

Due to the merit of ferroelectricity (piezoelectricity) and the demerit of random alignment, we formed a composite of the NaNbO₃ nanowire and PDMS polymer in a volume ratio of 1:100 to imbue our NGs with flexibility. The piezoelectric device mainly consists of four layers as schematically shown in Figure 2b. The Au/Cr coated Kapton films act as top and bottom electrodes, the NaNbO₃ nanowire mixed with PDMS composite serves as a source of piezoelectric potential, and the thick polyester (PS) film works as a main driving source of strain. Due to the use of all polymer layers in our NG, the device could be bent and released for the generation of electricity (inset of Figure 2b). Top view of NaNbO₃ nanowire-PDMS polymer composite shows that the nanowires were randomly oriented and well-dispersed without aggregations (left panel of Figure 2c). For 100×100 μm² area, we observed 150-200 numbers of nanowires. Cross-section view of the device shows ~100 μm thick NaNbO₃-PDMS composite (right panel of Figure 2c) in which upper and lower layers are Au/Cr coated Kapton films.

Now let us briefly discuss the power generation mechanism. The spontaneous electric dipoles in NaNbO₃, originated from Nb⁵⁺ ion movement in NbO₆ octahedra, can have six possible orientations along <001> directions. As shown in Figure 1b, the growth direction of NaNbO₃ nanowire is not parallel to any crystallographic axes. Therefore, the electric dipoles are neither parallel nor perpendicular to the growth direction of nanowire. Furthermore, the nanowires are randomly oriented inside the PDMS polymer. When the high electric field is applied, the electric dipoles (black arrows) would tend to align along the electric field direction (upper panel of Figure 2d). Some ferroelectric domains (hence piezoelectric domains) will align along the electric field direction, while some domains may tilt from the electric field direction. However, all of domains have electric dipole components along

1 the electric field direction (green arrows). For each NaNbO_3 nanowire, we simply considered the same
2 electric dipole component along the electric field direction. If we apply a compressive force $F(t)$ parallel
3 to the plane, the NaNbO_3 nanowires are under compressive strain (lower panel of Figure 2d). The strain-
4 induced electric polarization will align to the dipole direction; hence the piezoelectric potential inside
5 the nanowire is higher at the bottom electrode region than at the top electrode region. In order to screen
6 the piezoelectric potential, positive and negative charges will be accumulated at the top and bottom
7 electrodes, respectively. If the compressive strain is released, the piezoelectric potential should be
8 diminished and the accumulated charges will move back to the opposite direction. Therefore, the
9 continuously applying and releasing the compressive strain results in the alternating voltage and current,
10 as similarly discussed in ZnO nanowire based NGs.^{23,24}

11 The NaNbO_3 nanowire-PDMS polymer composite is sandwiched by two Kapton films and a PS
12 supporting film is placed at the bottom. When we bend the piezoelectric device, a strain neutral line is
13 located near the PS film. Therefore, the NaNbO_3 nanowire-PDMS polymer composite is subject to
14 compressive strain. From the given Young's modulus and thickness of each layer, we can calculate the
15 position of strain neutral line and strain value as shown in supporting information, Figure S3. Since the
16 thickness of NaNbO_3 nanowire-PDMS polymer composite is not thin enough, there should be a
17 distribution of strain value. To quantitate the value of strain, we determined the strain of composite as
18 the constant value at the middle of the NaNbO_3 nanowire-PDMS polymer composite layer. Since the
19 Young's modulus of PDMS (360-870 kPa) is smaller than that of NaNbO_3 (80-104 GPa),^{25,26} the actual
20 strain of NaNbO_3 should be quite small as compared with the strain value of NaNbO_3 -PDMS composite
21 listed in the following.

22 Figure 3a,b show the strain dependences of generated open circuit voltage and closed circuit current,
23 respectively. To confirm that the obtained signal comes from the piezoelectricity of NaNbO_3 , we
24 performed the polarity change test (supporting information, Figure S4).²⁷ In addition, we observed
25 negligible signals for the device without any electric poling. The generated voltage and current are
26

1 proportional to the applied strain. The different values of voltage and current between press (P) and
2 release (R) are due to the difference in straining rate when applying and releasing the strain. As clearly
3 seen, for example, the time interval of generated current for press is almost four times shorter than that
4 for release. We confirmed that the area in the current-time curve, which related to the total transported
5 charges, is nearly the same for pressing and releasing. At the strain value of 0.23% and strain rate of
6 12.8% s⁻¹, the output voltage and current (current density) are estimated to be ~3.2 V and ~72 nA (~16
7 nA/cm²), respectively, which is enough to power a small liquid crystal display (LCD) (supporting
8 information, Figure S5). Since NaNbO₃ nanowire is mixed with PDMS with a volume ratio of 1:100, we
9 can assume that the generated power solely from NaNbO₃ nanowire is ~0.6 mW/cm³. These values are
10 higher or comparable to the previous Pb(Zr,Ti)O₃ and BaTiO₃ based piezoelectric device.¹⁰⁻¹²

11 To understand the large output power of NaNbO₃ nanowire based NGs, we performed two control
12 experiments. First, we tested the power generation only from PDMS polymer without NaNbO₃
13 nanowire. The output voltage and current are negligible under the same experimental conditions (strain,
14 strain rate, and poling voltage). Second, we tested the power generation from NaNbO₃ nanocubes based
15 NG fabricated using the same procedure. Under the same experimental conditions listed above and the
16 same mixing ratio with PDMS, the output voltage and current from nanocube based NG is almost half
17 of that from nanowire based NG for all strain values (Figure 4). Since one-dimensional nanowires are
18 superior to zero-dimensional nanocubes in percolation, a nanowire-based NG could effectively delivers
19 generated piezoelectric potentials to the outside electrodes compared to a nanocube-based one.

20 We tested the stability of the NaNbO₃ nanowire based piezoelectric NG by continuously applying and
21 releasing the compressive strain. During almost 30 h, we continuously applied ~36,000 cycles of
22 straining. While there is some fluctuations, the output voltage and current are very stable (Figure 5a,b).
23 The mean and standard deviation of output voltage (current) are 3.06 V (70.0 nA) and 0.18 V (3.84 nA),
24 respectively.

25 There are several merits for the NaNbO₃ nanowire-PDMS composite based NG. First, a massive

1 production of NaNbO₃ nanowires through wet chemistry and subsequent annealing enables us the
2 fabrication of piezoelectric device at a large scale. Especially, the fact that the NaNbO₃ nanowire does
3 not contain any toxic elements implies further applications like a lead-free nanoactuator. Second, the
4 electric field can effectively pole random piezoelectric domains to one direction due to the
5 ferroelectricity of NaNbO₃ nanowire. Till now, there have been few reports to align the perovskite
6 ferroelectric nanowire in one direction. Although the NaNbO₃ nanowires are randomly aligned, easy
7 electric poling enables the constructively adding each piezoelectric signal from individual nanowire.
8 Large piezoelectric coefficient inherited to the perovskite ferroelectric material is demonstrated to be
9 quite useful for energy harvesting applications. Third, the PDMS polymer may play a role of preventing
10 the cracking and breaking the NaNbO₃ nanowires upon excessive mechanical straining. It may enable
11 the piezoelectric device to have a very long stability. Fourth, the piezoelectric signal is related to the
12 percolation according to our controlled experiments. Below the break-down of flexibility, the
13 piezoelectric signal should increase with the volume fraction of NaNbO₃ nanowire inside the composite
14 polymer.

35 CONCLUSIONS

37 In summary, we report the piezoelectric nanogenerator fabricated using a lead-free NaNbO₃
38 nanowire-PDMS polymer composite. For the 0.23% of compressive strain and the 12.8% s⁻¹ of strain
39 rate, we obtained the 3.2 V of open circuit voltage, the 72 nA of closed circuit current (the 16 nA/cm² of
40 current density), and the 0.6 mW/cm³ of power density by considering the volume fraction of NaNbO₃
41 nanowire inside PDMS polymer. Considering the massive production at relatively low temperature and
42 the easy control of piezoelectric domains by electric field, we conclude that NaNbO₃ nanowire is a
43 valuable candidate for nanogenerator.

57 EXPERIMENTAL METHODS

1 NaNbO₃ nanowire and nanocube were synthesized by the hydrothermal method. The 0.24 mol of
2 NaOH (9.6 g, 98%) was dissolved in the 20 mL of distilled water and then the 3.76 mmol of Nb₂O₅ (1 g,
3 99.99%) was added into the NaOH solution. After stirring for 30 min., the stirred solution was
4 transferred into a 25 mL Teflon lining in a stainless steel autoclave to undergo hydrothermal reaction at
5 150 °C. To obtain nanowire and nanocube, the reaction was performed for 4 h and 10 h, respectively.
6
7 Obtained white powders were filtered, washed with distilled water, and dried at 80 °C for 12 h. As-
8 grown nanowires were further annealed at 600 °C for 12 h. Annealed NaNbO₃ nanowires were
9 thoroughly mixed with poly(dimethylsiloxane) (PDMS) with the volume ratio of 1:100. (For controlled
10 experiment, we also mixed as-grown NaNbO₃ nanocubes with PDMS at the same volume ratio.) The
11 small amount of mixtures was spin-coated on an Au/Cr coated Kapton polyimide film at 1000 rpm for
12 15 sec. The 25-nm-thick Au and 10-nm-thick Cr were deposited on Kapton film by thermal evaporation.
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14 Another Au/Cr coated Kapton film was attached to the surface of spin-coated NaNbO₃-PDMS
15 composite. The Kapton films sandwiched NaNbO₃-PDMS composite was finally attached to polyester
16 (PS) film. The thickness of Kapton and PS films were 125 and 500 μm, respectively. We applied ~80
17 kV/cm of electric field for electric poling at room temperature. Note that electric polarization of
18 epitaxial NaNbO₃ film is almost saturated above 60 kV/cm.²⁸ A linear motor was used to periodically
19 apply and release the compressive force. We used 0.33 Hz of frequency and changed the bending
20 amplitude. The output signal of piezoelectric device was recorded by a low-noise voltage and current
21 preamplifiers.
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57 **Supporting Information Available:** The contents of Supporting Information includes the following:
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(1) *In-situ* x-ray diffraction pattern and Rietveld analysis, (2) dark field TEM images, (3) determination of strain value, (4) polarity change test of piezoelectric signal, (5) powering a small liquid crystal display. This material is available free of charge *via* the Internet at <http://pubs.acs.org>.

Figure 1. Structural characterization of NaNbO₃. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) images of NaNbO₃ nanowire (a,b) and nanocube (c,d). We show the selected area electron diffraction patterns for a nanowire along [101] zone axis (inset of b) and for a nanocube along [100] zone axis (inset of d). (e) Comparison of x-ray diffraction patterns for NaNbO₃ nanowire and nanocube.

Figure 2. (a) Photograph of obtained NaNbO₃ nanowires after one time reaction. (b) Piezoelectric device scheme. Yellow, blue, and light blue layers correspond to the Au/Cr coated Kapton film, NaNbO₃-PDMS composite, and PS film, respectively. We show the photograph of flexible NG device (inset). (c) Top-view optical microscope (left) and cross-section SEM (right) image of device. For top-view image, upper Kapton film is removed. (d) Schematics of piezoelectric power generation mechanism. Top: Alignment of dipoles after poling. Individual nanowire has ferroelectric (piezoelectric) domains with different electric dipoles. Each dipole (black arrows) has component parallel to electric field (green arrows). For each nanowire, we simply draw the same electric dipole component along the electric field direction. Bottom: Accumulation of free carriers in electrodes after compressive strain (see text for details).

Figure 3. Power generation of NaNbO₃ nanowire (black lines) and nanocube (red lines) based NGs at given compressive strain. (a) Open circuit voltage and (b) closed circuit current. PDMS itself (blue lines) does not show any signals. Here, ϵ , P, and R stand for the strain value, press, and release, respectively.

Figure 4. Comparison of generated power for NaNbO₃ nanowire (solid circles) and nanocube (open cubes) based NGs. For all compressive strain values, the output voltage (black symbols) and current

(red symbols) of nanowire based NG are almost two times larger than those of nanocube based NG.

Figure 5. Stability of NaNbO₃ nanowire-PDMS polymer composite piezoelectric NG. Compressive strain ($\epsilon=0.23\%$) is continuously applied for 30 h with the frequency of 0.33 Hz, *i.e.* almost 36,000 times. (a) Open circuit voltage and closed circuit current after the given elapsed time. (b) Cycling number dependences of peak values for voltage and current. Dashed lines represent the averaged values.

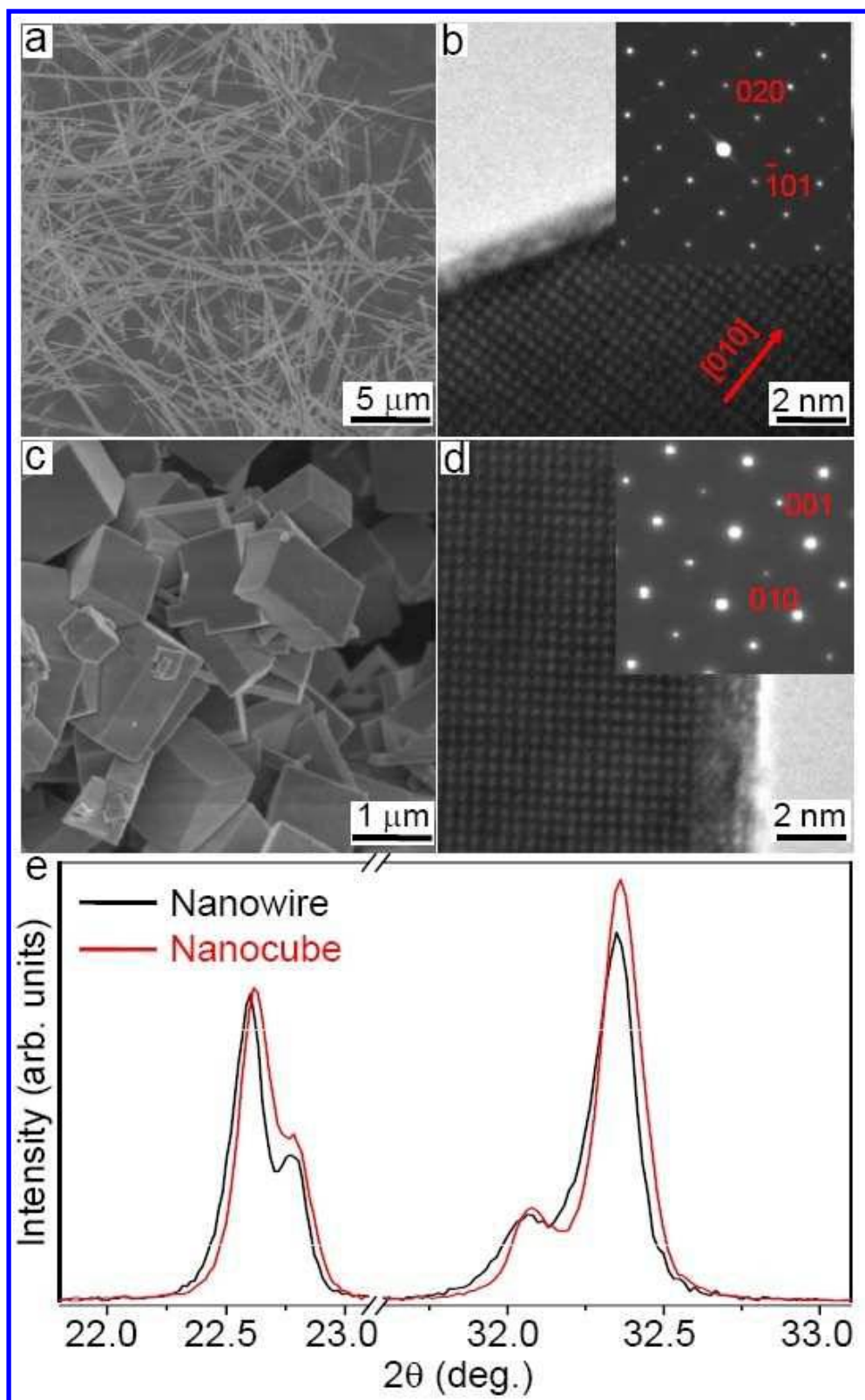


Fig. 1

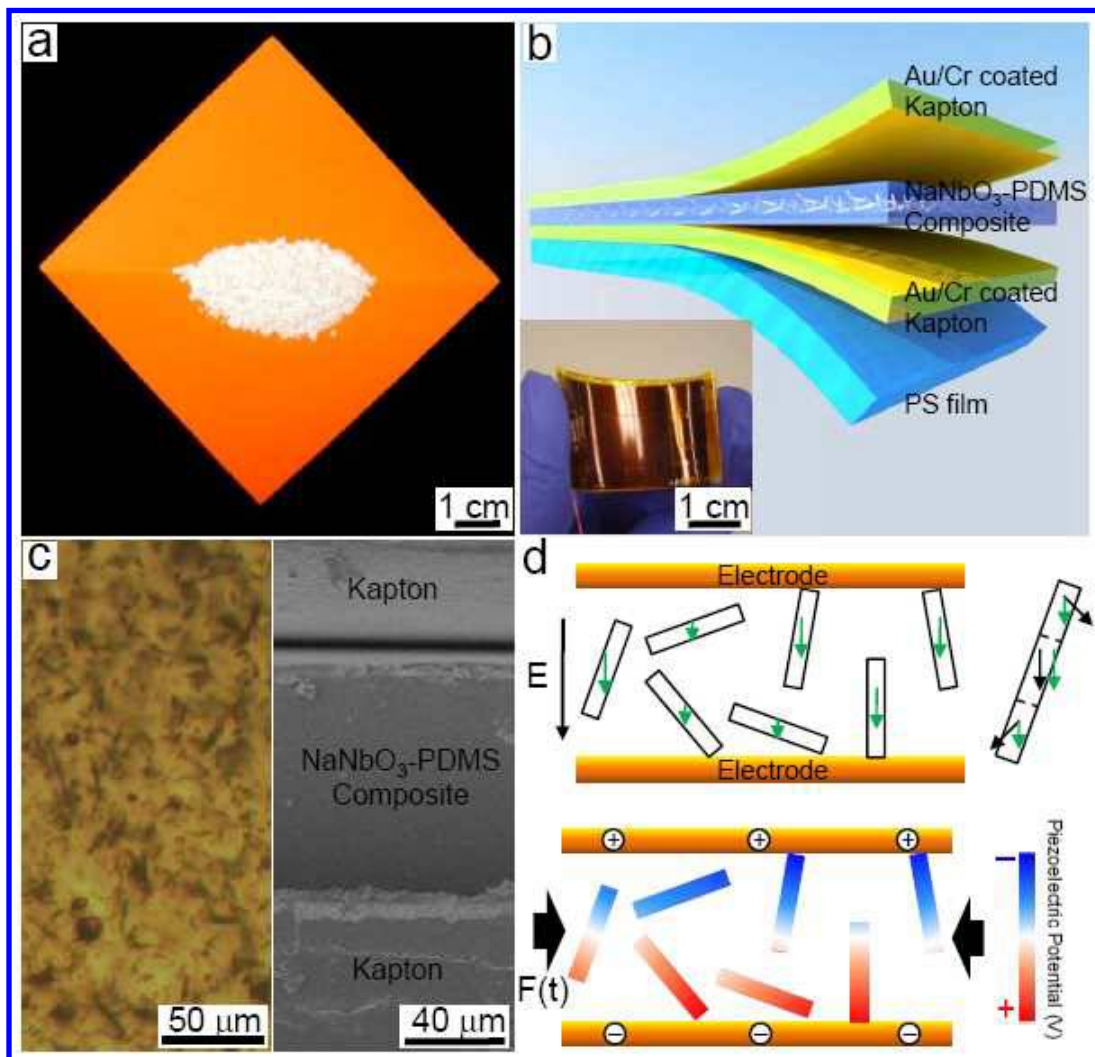


Fig. 2

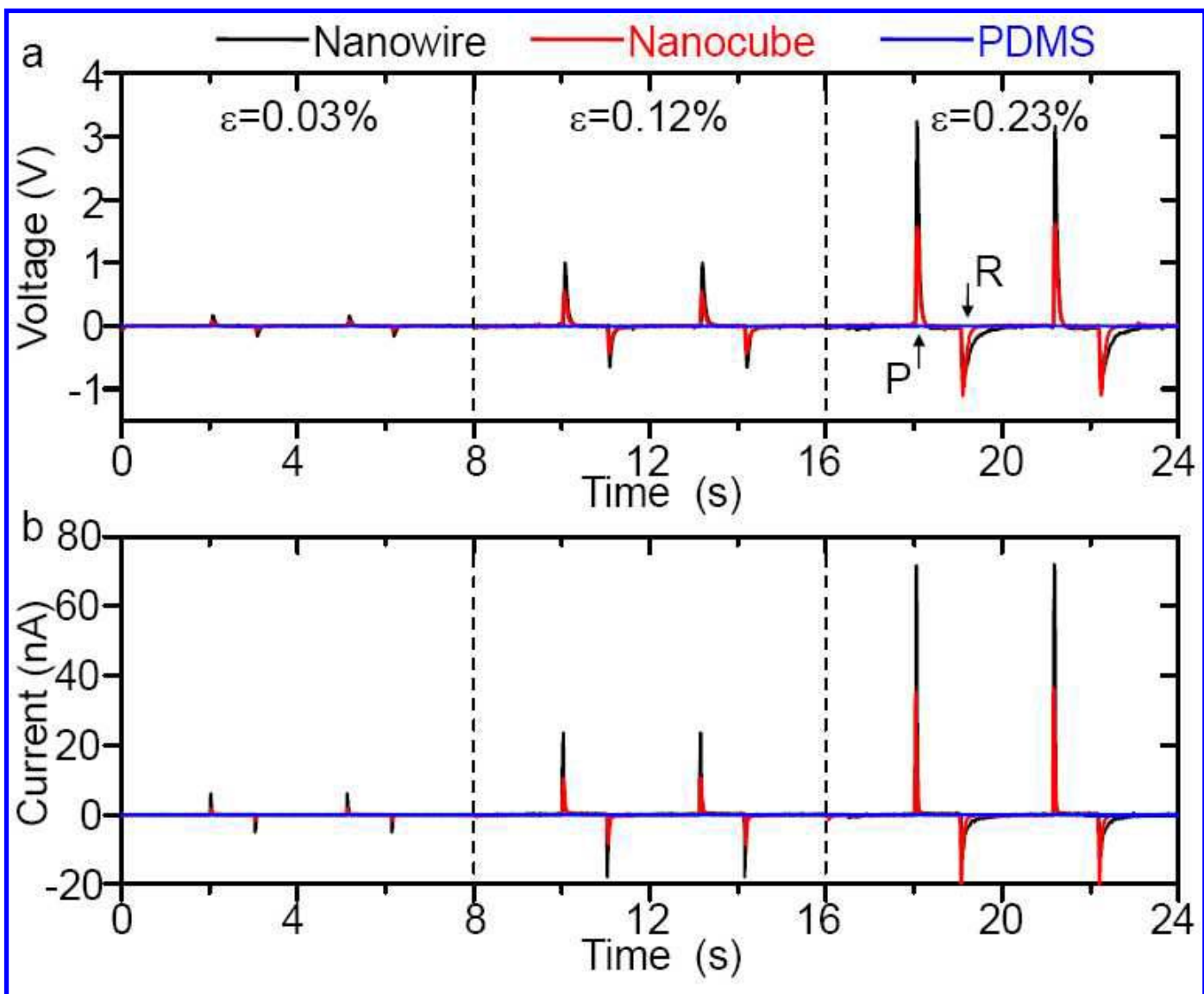


Fig. 3

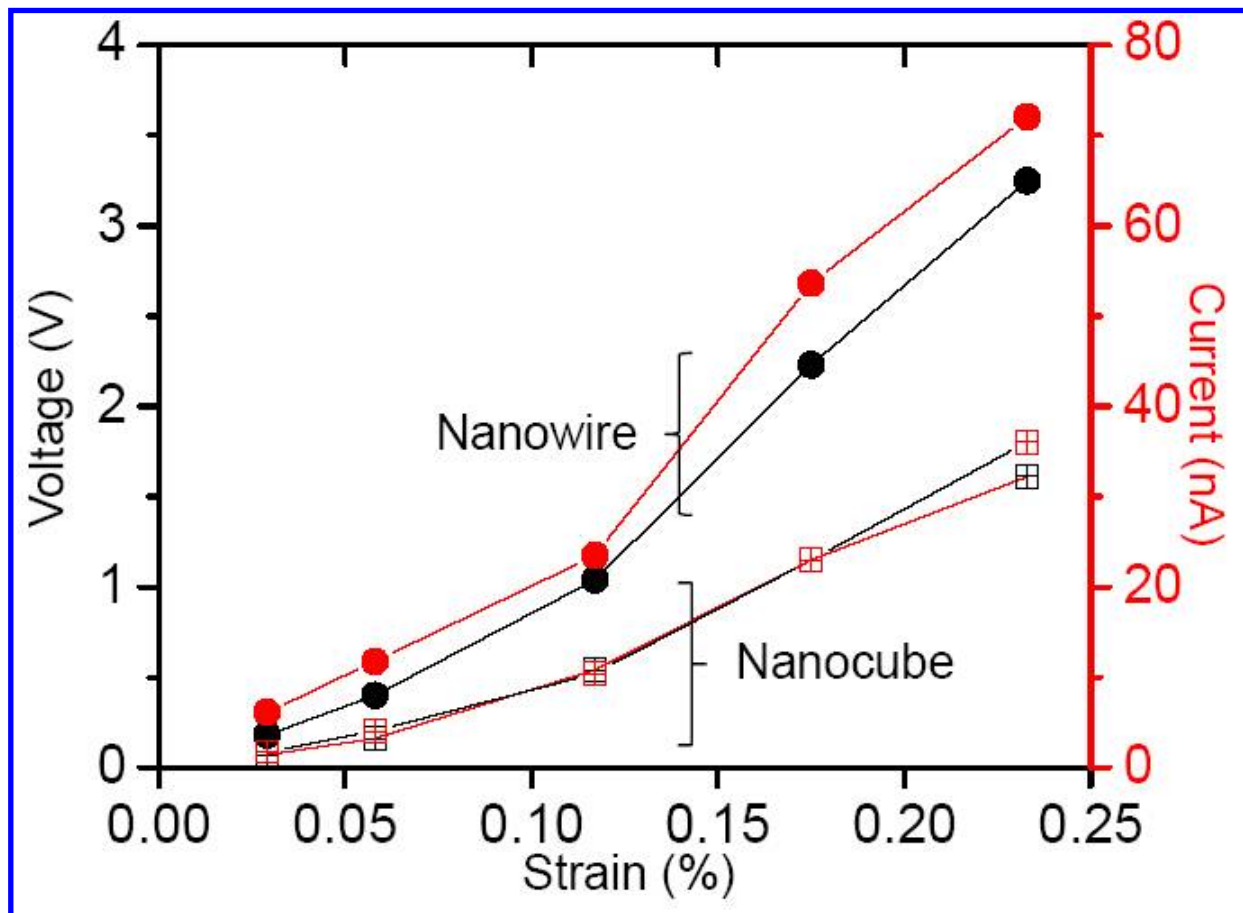


Fig. 4

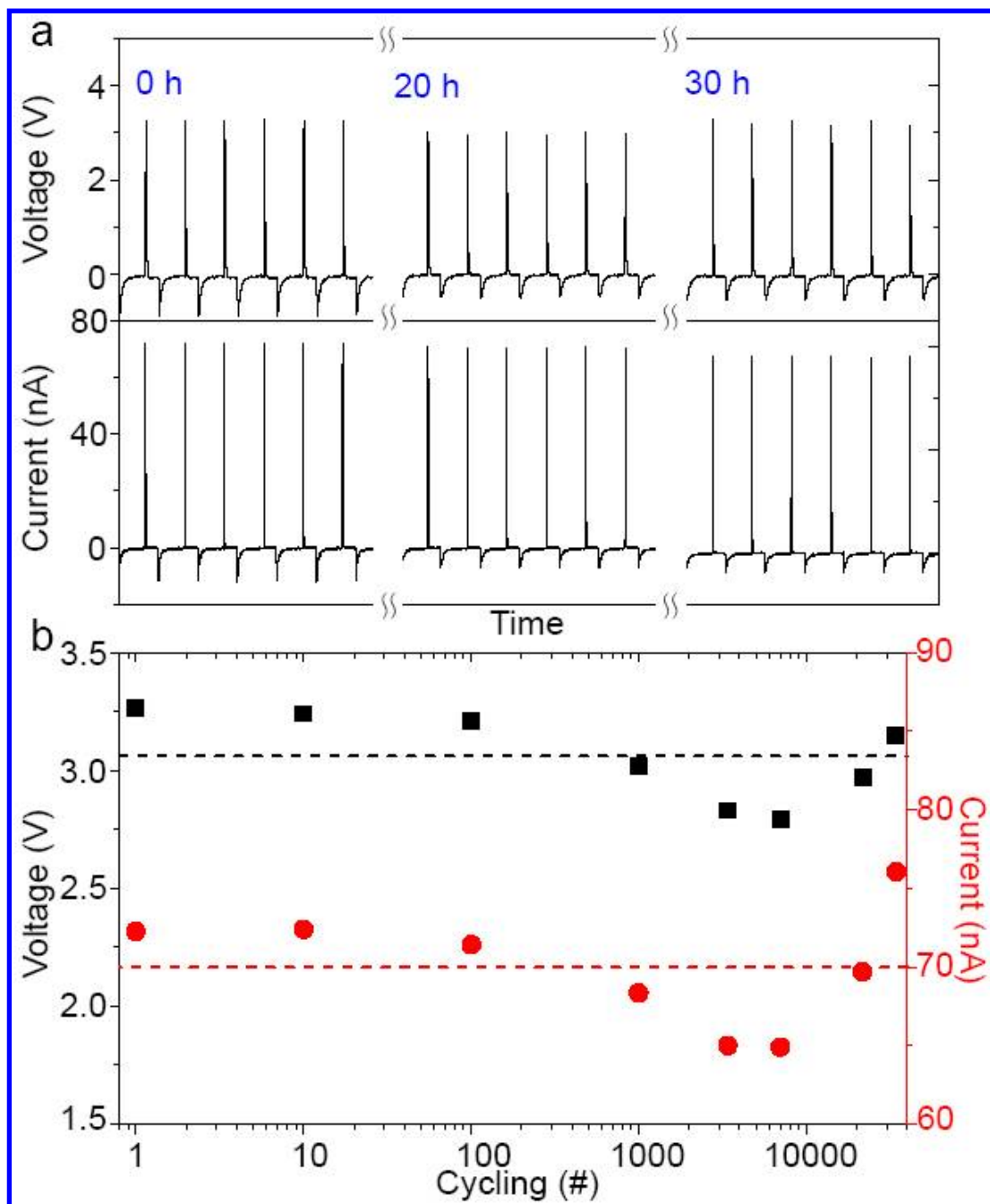


Fig. 5

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TOC

We present a piezoelectric nanogenerator device fabricated using a lead-free NaNbO_3 nanowire and poly(dimethylsiloxane) (PDMS) polymer composite. Under the compressive strain of 0.23%, the device shows high output voltage of 3.2 V and current of 72 nA. Due to the merits of the massive production at relatively low temperature and the easy control of piezoelectric domains by electric field, NaNbO_3 nanowire should be quite useful for the large-scale high output piezoelectric nanogenerator applications.

