Vertically aligned epitaxial KNbO₃ nanorod array for piezoelectric energy harvester and second harmonic generator

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Abstract
Vertical alignment of one-dimensional piezoelectric/ferroelectric materials is highly required to take full advantage of their unique electrical and optical properties for various applications. Here, we report the piezoelectric nanogenerator (NG) and second harmonic generator (SHG) applications of a vertically aligned single-crystalline KNbO₃ (KNO) nanorod (NR) array on a conducting Nb:SrTiO₃ substrate. A simple, cost-effective hydrothermal method at low temperature enables growth of ultra-long orthorhombic KNO NR array with a high piezoelectric coefficient. A corona-poled KNO NR array-based NG generates stable piezoelectric power under the compressive force. The open-circuit voltage and closed-circuit current almost linearly increase. In addition, the KNO NR array emits bright and sharp red, green, and blue visible light under the shining of infrared light. The SHG intensity is strongest along the KNO NR direction and weakest perpendicular to the NR direction. These results imply that the vertically aligned KNO NR array could be useful for an environment-friendly pressure sensor and a full-color display application.

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Introduction

One-dimensional ferroelectric nanomaterials have attracted a great deal of attention due to their intriguing size effect on piezoelectricity, ferroelectricity, and domain/crystalline structure as well as their emerging device applications like actuators, high-density memory, and water splitting [1-4]. Especially, a potassium niobate KNbO₃ (KNO) has shown interesting nanosize structural instabilities. Whereas bulk KNO has an orthorhombic structure at room temperature [5], hydrothermally grown KNO nanorods have tetragonal, orthorhombic, coexisting tetragonal and orthorhombic (morphotrophic phase boundary), and monoclinic crystal structures [6-8]. Both piezoelectricity and nonlinear optical property of KNO are sensitive to the deviation from centrosymmetry within the crystallographic unit cell. Therefore, various crystal structures in hydrothermally grown KNO suggest the facile modulation of its piezoelectricity and nonlinear optical property for nano-size devices.

To utilize the excellent structural instability of KNO nanostucture for application, vertical alignment rather than free standing is highly required [9-12]. For example, vertically aligned KNO nanostructures should be quite sensitive to tiny mechanical vibration [13]. Due to inherited large piezoelectric displacement of KNO NR array (width of 200 nm, height of 4 μm) was epitaxially grown on a conducting Nb:SrTiO₃ (Nb:STO) substrate using a simple hydrothermal reaction at low temperature (150 °C) for a short reaction time (12 h). Uni- and bi-polar electric-field-induced strain measurements confirm the ferroelectricity and piezoelectricity (piezoelectric coefficient of ca. 140 pm/V) of KNO NR arrays. The vertically aligned KNO NR array-based NG generates an open-circuit voltage of 0.5 V and a closed-circuit current of 10 nA under a compressive force of 1 kgf. Both the piezoelectric voltage and current increase almost linearly with the compressive force, suggesting the applicability of KNO NR array to pressure sensor devices. The vertically aligned KNO NR array emits bright red, green, and blue light under an infrared illumination. The SHG intensity is strongest along the NR direction and weakest perpendicular to the NR direction, suggesting the applicability of KNO NR array to polarization-sensitive full-color display. This work demonstrates the importance of vertical alignment, rather than free standing, for the multifunctional, environment-friendly NG and SHG applications of KNO NR arrays.

Experimental section

Synthesis and characterization of vertically aligned KNO NR array

A single-crystalline KNO NR array was hydrothermally grown on a conducting Nb:SrTiO₃ (Nb:STO) substrate. During this process, 225.0 mmol KOH (12.624 g, 90%) was dissolved in 15 mL of distilled (DI) water; 9.44 mmol Nb (0.8776 g, 99.99%) was then added to the KOH solution. After stirring for 2 h, the solution was transferred to a 25 mL Teflon-lined stainless steel autoclave. The substrates were positioned face down and placed ca. 3 cm above the bottom of the Teflon liner. The hydrothermal reaction was performed at 150 °C for 12 h. After the reaction was complete, the as-grown NR arrays were washed with DI water and dried at 80 °C for 24 h.

The crystallinity and microstructure of the KNO NRs were examined by high-resolution X-ray diffraction (HR-XRD) (Bruker, AXS D8 Discover), field-emission scanning electron microscopy (FE-SEM) (S-4200, Hitachi), and aberration-corrected high-resolution transmission electron microscopy (HR-TEM) (JEM-2100F, Jeol). Just before the HR-TEM measurement, a cross-section of the KNO NR array was prepared using a focused ion beam (FIB). Piezoelectricity and ferroelectricity were characterized by a laser Doppler vibrometer (AT500, Graphitec) equipped with a high-voltage amplifier (610E, Trek) and waveform generator (33250A, Agilent). For this measurement, the KNO NR array on a Nb:STO substrate was clamped to a thick alumina plate and coated with a Pt top electrode. Before coating, the KNO NR arrays were spin-coated with poly(methyl methacrylate) (PMMA) and etched by oxygen plasma to leave fresh, clean tips of the NRs. The Pt top electrode was illuminated by a He-Ne laser, and the displacement of the NR array was monitored during voltage application. To further investigate the piezoelectric and ferroelectric characteristic of a KNO NR, we performed piezoresponse force microscopy (PFM) measurement (JSPM-5410, JEOL). For this measurement, a single KNO NR was tightly attached to the Pt-coated Si substrate using a polymer (5 wt% poly(vinylpyrrolidone) dissolved in ethanol).

Piezoelectric power and second harmonic generation measurements

For the piezoelectric NG measurement of the KNO NR array, we used corona poling to align the piezoelectric/ferroelectric domains at 100 °C for 1 h [16]. In the corona poling process, a high direct-current (DC) voltage (10 kV) was applied to a needle, which was separated from the KNO NR array by 3 cm. After poling, we attached an Au/Cr-coated Kapton polyimide film (thickness of ca. 125 μm) to the top surface of KNO as a top electrode. The NGs were mounted on a custom-designed mechanical system, in which a linear motor was used to periodically apply and release compressive forces to the device. The pushing amplitude and frequency were varied over the course of the measurement, and the input force was instantaneously monitored with a force sensor. The output signal of the piezoelectric device was recorded by low-noise voltage (SR560, Stanford Research Systems) and current preamplifiers (SR570, Stanford Research Systems). All electrical measurements were conducted in a Faraday cage to minimize noise.

For the SHG measurement of the KNO NR array, we used an optical parametric amplifier (Topas Prime OPA, Spectra-Physics) as the excitation source. The reflected SHG light from the NR array was dispersed by a spectrophotometer and detected by a photo multiplier tube (PMT). For the SHG
measurement of a single KNO NR, we used a Ti: Sapphire laser as the excitation source. The polarization of the incident laser was modulated by a half-wave plate and focused onto a single NR via a micro-objective lens (NA: 0.75). The transmitted SHG light from a single NR was guided by an optical fiber to a Si-avalanche photodiode (PD). A short-pass filter was placed in front of the detector to eliminate the fundamental light.

Results and discussion

In Figure 1a and b, we show top and 45° tilt-view SEM images of the KNO NR array on a Nb:STO substrate, respectively. All of the KNO NRs were vertically aligned, having a width of ca. 200 nm and a height of ca. 4 μm. At the bottom of NR, several cubes (width of ca. 500 nm) were observable; which may provide a plausible growth mechanism of the NRs. As similarly discussed in a (K,Na)NbO₃ NR array [17], the KNO nanocubes are formed initially on the cubic Nb:STO substrate. As the reaction proceeds, the nanocubes adhere to the top rather than the side of the KNO nanocube, due to the higher growth rate of the top surface. Thus, the KNO NR array, rather than nanocube, was formed on the Nb:STO substrate.

Figure 1c shows a HR-TEM image of the cross-sectional KNO NR array. As shown in Figure S1 in supporting information, the HR-TEM images at the bottom, middle, and top of the KNO NRs were almost identical. Clear lattice-fringe and selected-area electron diffraction (inset of Figure 1c) indicate that the KNO NRs are single-crystal and grow along the [001]pc direction in pseudo-cubic (pc) notation [18]. Figure 1d shows the spatial variation of chemical elements at the interface between the KNO NRs and Nb:STO substrate. The sharp discontinuity of K and Nb elements at the interface implies chemical homogeneity of the KNO NRs and the absence of inter-diffusion between the NRs and the substrate.

Figure 2a and b show the HR-XRD patterns of the KNO NR array on a Nb:STO substrate for θ–2θ and ϕ scans, respectively. In the θ–2θ scan, only the (00l)pc peaks of KNO NR (red indices) and the (00l) peaks of Nb:STO (black indices) are observable. In the ϕ scan, four KNO peaks are evident at the same position of Nb:STO. These results imply that KNO NRs were epitaxially grown on the Nb:STO substrate. The epitaxial relationship between the KNO NRs and the Nb:STO substrate is [001]pc KNO || [001] Nb:STO and [100]pc KNO || [100] Nb:STO. In Figure 2c, we show the reciprocal space map of HR-XRD for the (− 103) Bragg peaks for KNO and Nb:STO. The in-plane (h) reciprocal vectors of KNO do not coincide with those of Nb:STO and have distributed values, which suggests the incoherent strain from the substrate. The epitaxial strain from the Nb:STO can be relaxed in ultra-long KNO NRs. From the center
position of the reciprocal map, the lattice constants of the KNO NRs are estimated as $a_{pc} = 4.009 \text{ Å}$ and $c_{pc} = 4.183 \text{ Å}$. Comparing the lattice constants of KNO bulk, i.e. $a_{pc} = 3.9739 \text{ Å}$ and $b_{pc} = c_{pc} = 4.036 \text{ Å}$ ($a_o = 5.6950 \text{ Å}$, $b_o = 5.7213 \text{ Å}$, and $c_o = 3.9739 \text{ Å}$ in orthorhombic (o) notation) [19], the out-of-plane lattice largely elongated probably due to the partial relaxation of the compressive strain from the Nb:STO substrate ($a = b = c = 3.905 \text{ Å}$) [20]. The relationship between orthorhombic and pseudo-cubic unit cell is schematically shown in Figure S2 in supporting information. The electric polarization of KNO is parallel to [010]o in orthorhombic unit cell, whereas parallel to [0 1 1]pc in pseudo-cubic unit cell.

In Figure 2d, we show a magnified view of HR-XRD $\theta$–$2\theta$ scans for $2\theta = 44–46^\circ$ at different temperatures. The (220)o and (002)o peaks showed successive change with increasing temperature. The evolution of the (220)o and (002)o peaks can be well-indexed as orthorhombic, tetragonal, and cubic crystal structures at 25, 250, and 400 °C, respectively [5]. After cooling down to 25 °C (a blue line), the (220)o and (002)o peaks have similar peak positions and relative intensities as compare to those of before heating, i.e. 25 °C (a black line). These results indicate a stable orthorhombic phase for the as-grown KNO NRs, rather than a metastable monoclinic phase. In free standing KNO NRs, which were grown at the same hydrothermal condition for KNO NR array on a Nb:STO substrate, we observed metastable monoclinic structure (Figure S3 in supporting information). Therefore, we believe that the epitaxial strain from the Nb:STO substrate may stabilize more symmetric orthorhombic structure, rather than monoclinic structure, in KNO NR array.

To investigate the piezoelectricity and ferroelectricity of KNO NR arrays, we used a laser Doppler vibrometer as schematically shown in Figure 3a. Comparing with a piezoresponse force microscopy, the laser Doppler vibrometer measured shifts of the amplitude and phase of He–Ne laser for piezoelectricity upon the application of an external voltage [21]. Due to the large electrode size as well as non-contact nature of the method, the laser Doppler vibrometer measurement provides a highly sensitive and reproducible piezoelectric coefficient of piezoelectric materials.

In Figure 3b and c, we show bi- and uni-polar electric-field-induced strain of KNO NR array, respectively. In bi-polar strain, the butterfly shape of strain is clearly appeared; which commonly observed in ferroelectric materials [22]. From the piezoresponse force microscope (PFM) measurement (Figure 3d), we have directly confirmed the ferroelectricity of KNO NR by observing an abrupt change of phase at the certain voltage, which is related with the switching of ferroelectric domains [23]. In uni-polar strain, the hysteresis of strain upon increasing and decreasing
voltage is rather small; which could be useful for an actuator application. Dividing the maximum strain by the maximum applied electric field, we obtained the piezoelectric coefficient of KNO NR array as $d_{33} = 140 \, \text{pm/V}$, which is comparable to single crystalline KNO [14].

Confirming the piezoelectricity and ferroelectricity of KNO NR, we fabricated a KNO NR array-based piezoelectric NG. To align the piezoelectric/ferroelectric domains of KNO NR, we used a corona poling [16]. In corona poling as schematically shown in Figure 4a, a suspended metal tip is subjected to high voltage, which ionizes the surrounding air. When corona discharge occurs, the ionized particles accelerate towards the ground and are deposited onto the top surface of the NRs. The charges that remain on the surface generate a poling electric field between the top surface and ground. Hence, corona poling can effectively align every domain of the KNO NRs with different heights.

Figure 4b shows the piezoelectric power generation of a KNO NR array-based NG. For an applied force of 1 kgf, the KNO NR array-based NG generates an open-circuit voltage of 0.5 V and a closed-circuit current of 10 nA (current density of ca. 20 nA/cm²). By polarity reversal test (Figure 4c), we confirmed that the signals come from piezoelectricity of KNO NR array rather than artifact. While the obtained piezoelectric power after corona poling is rather small, it is much larger than that of a NG without poling and a NG with usual metal poling (Figure 4c and Figure S4 in supporting information). By integrating the closed-circuit current with the elapse of time at a given applied force, we obtained the piezoelectric coefficient of KNO NRs as high as $d_{33} = 110 \, \text{pC/N}$; which suggesting the single crystalline quality of our KNO NRs [14]. Noticeably, both the piezoelectric voltage and current increase almost linearly with the compressive force, up to 1 kgf (Figure 5 in supporting information). Such a linear increase of the piezoelectric voltage/current upon the application of a compressive force could be useful for pressure sensor applications.

Confirming the piezoelectricity and ferroelectricity of KNO NR, we utilized the KNO NR array for SHG application. To measure the emission spectrum of SHG from KNO NRs, we employed an optical parametric amplifier and a spectrometer (see, Figure S6a in Supporting Information). Figure 5a-c show the emitted SHG spectrum of KNO NR array for an incident wavelength of 1200, 1100, and 972 nm, respectively. Bright and sharp red, green, and blue SHG spectra are clearly observable at nearly the half wavelength of incident light. Such an emission of the three primary colors could be useful for the full-color display applications.

To investigate the polarization dependence of SHG for a single KNO NR, we employed a Ti:Sapphire laser and a half-wave plate (see, Figure S6b in Supporting Information). Using a half-wave plate, we rotate the polarization by $10^\circ$ over a range of $2\pi$ radians. Figure 5d shows the polarization dependence of the SHG intensity for a KNO NR. Clearly, the SHG intensity is maximized along the NR direction and minimized perpendicular to the NR direction. The polarization direction is marked in the...
Due to the interaction of the transverse magnetic (TM) mode of incident light, which is parallel to the NR direction, with the ferroelectric polarization of KNO, which is $45^\circ$ off from the NR direction, the SHG intensity could be maximized along the NR direction, as consistent with recent reports\[24,25\]. For $0^\circ$ polarization, we examine the SHG intensity distribution along the NR and observe two bright spots near the one third and two thirds length of a NR (Figure 5e). Such resonance-like hot spots should be related with the interference of SHG standing waves inside the NR\[26\].

There are several merits of vertically aligned KNO NR array for NG and SHG applications. First, free standing piezoelectric/ferroelectric nanostructures have been mixed with polymers, such as polydimethylsiloxane (PDMS), for piezoelectric NG applications\[27-29\]. Since PDMS is rather weak for heat and organic solvent, however, composite based NG may not work at high temperatures and under certain chemical conditions\[30\]. Therefore, the vertically aligned KNO NR array-based NG may show better performance at harsh environments. Second, free standing piezoelectric/ferroelectric nanostructures can emit SHG. However, it should be very difficult to align, focus, and coherently control the SHG emitted from each NR\[24,25\]. Such difficulty results in a weak intensity of SHG light and a hindrance for emerging application, such as nano-laser. Therefore, vertically aligned KNO NR array-based SHG should be useful in nano-size optical components. Third, KNO does not contain any toxic elements, such as Pb, and has a high Curie temperature of $427^\circ$C\[5\]. Therefore, the vertically aligned KNO NR array-based NG and SHG should be environmentally friendly and quite stable against thermal fluctuations.

**Conclusion**

In summary, we have demonstrated piezoelectric NG and SHG applications of vertically aligned KNO NR array on a conducting Nb:STO substrate. Hydrothermal reaction at low temperature for short time results in a highly epitaxial KNO NR array with a stable orthorhombic structure. Novel laser Doppler vibrometer under uni- and bi-polar electric-field-induced strain measurements reveal the piezoelectricity and ferroelectricity of KNO NR arrays. Piezoelectric/ferroelectric KNO NR array generates an almost linear piezoelectric voltage/current upon the increase of compressive force, and emits red, green, and blue light upon the illumination of infrared light. Due to the vertical alignment, non-toxicity, and high Curie temperature, the KNO NR array should be useful for environment-friendly pressure sensor and optical component applications.
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Appendix A. Supplementary material

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2015.09.004.

References

Particular interests are photovoltaic and photocatalysis effects of nanoporous ferroelectric materials.

His recent research interest is focused on piezoelectric/pyroelectric/triboelectric nanogenerators families incorporated as sensing and actuating elements in micro-electromechanical systems (MEMS).

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