## Supporting Information

## Orientation-Dependent Piezoresponse and High-Performance Energy Harvesting of Lead-Free (K,Na)NbO<sub>3</sub> Nanorod Arrays

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Figure S1. The estimated average length and aspect ratio of the KNN NRAs at different alkalinity.



Figure S2. The top-view SEM image of the KNN NRAs obtained at alkalinity of 8M.



Figure S3 High magnification SEM images of synthesized KNN nanorods at 8M. (a) KNN nanorod

arrays; (b-d) dispersed KNN nanorods through ultrasonic oscillation.



Figure S4. The XPS spectrum of the KNN nanorod array obtained at the alkalinity of 8 M.



Figure S5. The output voltage of VINGs with different load resistance



Figure S6. The output voltage and calculated power of VINGs with different load resistance



Figure S7. The output voltage of LINGs with different load resistance



Figure S8. The output voltage and calculated power of LINGs with different load resistance

## **Berry Phase method**

In a finite system, it is appropriate that polarization is defined as the total dipole moment divided by the volume of the system. However, in an infinite periodic solid, different electric polarization vector can be acquired if different unit cell is chosen. The modern theory of polarization points out that the change of the polarization can be interpreted as a displacement of the center of charge of the Wannier functions, and the problem of calculating polarization in periodic crystals can be solved by using the Berry phase of the electronic wavefunction. In this paper, we employ Berry phase method to calculate spontaneous polarization of KNN. In order to calculate the polarization and study the contributions of atoms to the polarization, a centric high-symmetry (or paraelectric) structure will be adopted as zero polarization reference.

**Table S1**. The structural information of the KNN orthorhombic lattice. The two distinguisheddisplacements of O,  $O_I$  is collinear with Nb along the [110] polarization direction.  $O_{II}$  is coplanar

with the two site.		
Atomic position	А	(0, 0, 0)
		(0.5, 0.5, 0)
	В	$(0.5, 0, 0.5 + \Delta_{O,Z}Nb)$
		$(0, 0.5, 0.5 + \Delta_{O,Z}Nb)$
	Ο <sub>Ι</sub>	$(0.5, 0, 0+\Delta_{O,Z}O_{I})$
		$(0, 0.5, 0+\Delta_{O,Z} O_{I})$
	Ο <sub>Π</sub>	$(0.25 + \Delta_{O,X} O_{II}, 0.25 + \Delta_{O,Y} O_{II}, 0.5)$
		$(0.75\pm \Lambda_{\odot}, 0.75\pm \Lambda_{\odot}, 0.75\pm \Lambda_{\odot}, 0.5)$
		(0.73 + 20, x + 0, 1, 0.73 + 20, y + 0, 1, 0.5)
	Оп	$(0.75 + \Delta_{O,X} O_{II}, 0.25 - \Delta_{O,Y} O_{II}, 0.5)$
		$(0.25 + \Delta_{0,X} O_{II}, 0.75 - \Delta_{0,Y} O_{II}, 0.5)$

with the Nb site.