Supporting information

Flexible Lead-Free Piezoelectric Arrays for High-Efficiency Wireless Ultrasonic Energy Transfer and Communication

Laiming Jiang,[a]* Bo Wu,[b]* Xiaowei Wei,[a] Xiang Lv,[a] Haoyue Xue,[a] Gengxi Lu,[c] Yushun Zeng,[c] Jie Xing,[a] Wenjuan Wu[d] and Jiagang Wu[a]*

[a] *College of Materials Science and Engineering, Sichuan University, Chengdu 610064, China*

[b] *Sichuan Province Key Laboratory of Information Materials, Southwest Minzu University, Chengdu, 610041, PR China*

[c] *Department of Biomedical Engineering Viterbi School of Engineering, University of Southern California, Los Angeles, CA 90089, USA*

[d] *Sichuan Province Key Laboratory of Information Materials and Devices Application, Chengdu University of Information Technology, Chengdu 610225, P. R. China*

† Electronic supplementary information (ESI) available.

**Corresponding authors: laimingjiang@scu.edu.cn (Laiming Jiang), wubo7788@126.com (Bo Wu), and msewujg@scu.edu.cn (Jiagang Wu)*

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1. Experimental Section

1.1 Synthesis of the KNN Ceramics

Using conventional solid-state technique, $0.963K_{0.5}Na_{0.5}Nb_{0.96}Sb_{0.04}O_3$-$0.007BiFeO_3$-$0.03(Bi0.5Na_{0.5})_{0.9}(Li_{0.5}Nd_{0.5})_{0.1}ZrO_3$ (abbreviated as KNN) lead-free piezoceramics were synthesized with the raw materials of Bi_2O_3 (99%), Li_2CO_3 (99.0%), Na_2CO_3 (99.8%), K_2CO_3 (99.0%), Nb_2O_5 (99.5%), ZrO_2 (99.0%), Sb_2O_3 (99.9%), Fe_2O_3 (99%), and Nd_2O_3 (99.5%). These powders were weighed in stoichiometric proportions and ball-mixed in an ethanol medium for 24 hours, and then calcined at 860 °C for 6 hours. The calcined powders were molded into disks with polyvinyl alcohol binder under a pressure of 10 MPa. All specimens were sintered at 1050 °C for 3 hours after burning off polyvinyl alcohol. Poling was carried out under a direct current field of 3 kV mm^{-1} for 30 min in a silicone oil bath.

1.2 Fabrication of the f-LFPA

A dicing-filling technology (Tcar 864-1, Thermocarbon) was first employed to fabricate the KNN/epoxy 1-3 piezoelectric composites composed of an array of regularly shaped KNN pillars and an epoxy resin filling (EPO-TEK 301).[1] After that, the fabricated composites were mechanically thinned and polished to the desired thickness, and both sides were sputtered with chromium/gold (Cr/Au ≈50/100 nm) electrodes using a sputtering system (NSC-3000 Sputter Coater, Nano-Master). The composites were then diced into small cubes with volumn of 1 mm × 1 mm × 1 mm. Next, integration and encapsulation of f-LFPA was conducted. The process is initiated with the design of flexible electrodes based on flexibility expected to be achieved by the device. Copper wires with a diameter of 100 μm were wound equidistantly around a metal rod with 0.5-mm-diameter. The “spiral structure” was then removed from the rod and pressed into a flat surface with two pieces of flat glass to obtain a soft wavy electrodes. After that, arrays with 5 × 4 piezoelectric units were properly arranged on a glass sheet bonded with water-soluble tape. Solder paste (E-Solder 3022) was used to assemble the top and bottom flexible electrodes with the piezo-units. A sandwich device was encapsulated and finished by using a silicone elastomer (Ecoflex 00-30) to fill the gaps. The glass sheets were finally removed after the elastomer was fully cured, yielding a freestanding flexible piezo-array.

1.3 Fabrication of the 2.08-MHz ultrasonic Transmitter

The structural dimension of the flat ultrasound transmitter were first optimized based on the commercial PZT ceramic (DL-48, DeL Piezo) using a modeling software PiezoCAD. The optimized PZT ceramic plate with a thickness of ~ 0.92 mm and a diameter of 25 mm was custom fabricated by Del Piezo Specialties, LLC. The ceramic plate with silver electrodes on both surfaces was mounted in a customized brass housing. A wire was used to connect the back electrode of the ceramic plate and a subminiature version A connector. A common ground connection was then formed via sputtering an Au (100 nm) electrode across the front electrode of the ceramic plate and the brass housing. Lastly, a protective layer was formed on the whole external surface of the transmitter via depositing 30 μm-thick parylene layer.

1.4 Materials characterization

The crystal structure of the prepared KNN ceramics was characterized by X-ray diffraction (XRD, DX2700). The surface and cross-section morphologies along with energy dispersive spectroscopy (EDS) studies were carried out via Field-emission scanning electron microscopy (FE-SEM, JSM-7500). The impedance spectra and the capacitance were characterized using an impedance analyzer (4294A, Agilent). The domain structures were checked via piezoresponse force microscope (PFM, MFP-3D, USA). The piezoelectric factor d_{33} was analyzed using a d_{33} meter (YE2730A, A Mrayl Products). The electrical and acoustic parameters of the KNN ceramics and the manufactured composites were calculated by the following formulas,[2, 3] respectively:

$$\frac{\varepsilon^T}{\varepsilon_0} = \frac{C^T h}{\varepsilon_0 A}, \tag{1}$$

$$FOM = d_{33} \cdot g_{33} = \frac{d_{33}^2}{\varepsilon_{33}^T}, \tag{2}$$

$$k_t \; or \; k_{33} = \sqrt{\frac{\pi f_r}{2 f_a} tan(\frac{\pi}{2} \frac{f_a - f_r}{f_a})}, \tag{3}$$

$$c_p = f \cdot \lambda = 2 f_r \cdot h, \tag{4}$$

$$Z_a = \rho \cdot c_p, \tag{5}$$

1.5 Finite element analysis (FEA)

FEA simulations were carried out using COMSOL (COMSOL Multiphysics 5.3a) to simulate the sound field distributions of ultrasound waves and the piezo-potential distributions in piezo-units under the ultrasonic excitation. Physics fields, including pressure acoustics (frequency-domain), solid mechanics, and electrostatics, as well as the coupled interfaces of the piezoelectric effect and acoustic-structure boundary, were considered in the FEA simulations. The material parameters were set based on experimentally measured results.

1.6 Electrical output measurement

The ultrasound-induced output of the f-LFPA device was evaluated using a multifunctional ultrasonic test platform, which includes a computer for signal control, a function generator (AFG3252C, Tektronix) for generating trigger signal to ultrasound transmitter, a power amplifier (75A250A, AR RF/Microwave Instrumentation) for amplifying the trigger signal, a 5-axis motorized stage (Opto-Sigma) for mounting the transmitter, a water tank for providing water environment (as sound transmission medium), and a digital oscilloscope (TDS 5052, Tektronix) for measuring the output signal. During the experimental tests, a flat ultrasound transmitter with center frequency of 2.08 MHz was mounted on the 5-axis motorized stage. The relative position of the transmitter can be regulated by the motor. The f-LFPA was placed flat on the glass sheet or wrapped on a curved surface under the end face of the ultrasound transmitter. The ultrasound transmitter was driven by sinusoidal pulses, which were given by the function generator and then amplified with the amplifier (50 dB). The produced output voltages of the f-LFPA were directly measured using the digital oscilloscope.

1.7 Biocompatibility evaluation

For the biocompatibility evaluation, prostate cancer (PC-3) cell line was cultured and maintained in the complete growth medium. The ethanol-sterilize 1-3 composites were prepared and placed on the bottom of the Petri-dish to perform the cell culture experiment for 3 days with glass plates as control.

2. Supporting Tables

Table S1 Technical parameters of Eco-flex 00-30 silicone (Smooth-On, Inc, Easton PA).

Specifications	Values
100% Modulus	68 kPa
Tensile Strength	1.38 MPa
Elongation @ break	900%
Mixed Viscosity	3000 cps
Cure Time	4 hours
Useful Temperature (max)	232 ℃
Color	Translucent

The technical parameters in the table refer to the Eco-flex 00-30 data sheet. https://www.smooth-on.com/products/ecoflex-00-30/

Table S2 The electrical and acoustic properties of the KNN bulk ceramic and the as-fabricated 1-3 composite

Specifications	**KNN bulk ceramic**	**1-3 composite**
Piezoelectric constant d_{33} (pC N^{-1})	535	503
Electromechanical coupling coefficient k_t or k_{33}	0.50	0.58
Relative free permittivity $\varepsilon_{33}^T/\varepsilon_0$ (at 1 kHZ)	2200	1260
Curie temperature T_C (°C)	232 °C	N/A
Dielectric loss tan δ	0.025	0.02
Piezoelectric voltage coefficient g_{33} (×10^{-3} V m N^{-1})	27.5	39.8
Thickness h (mm)	1	1
Density ρ (kg m^{-3})	4450	3010
Resonant frequency f_r (MHz)	2.91	2.08
Acoustic velocity c_p (m s^{-1})	5820	4016
Acoustic impedance Z_a (MRayl)	25.9	12.5

3. Supporting Figures

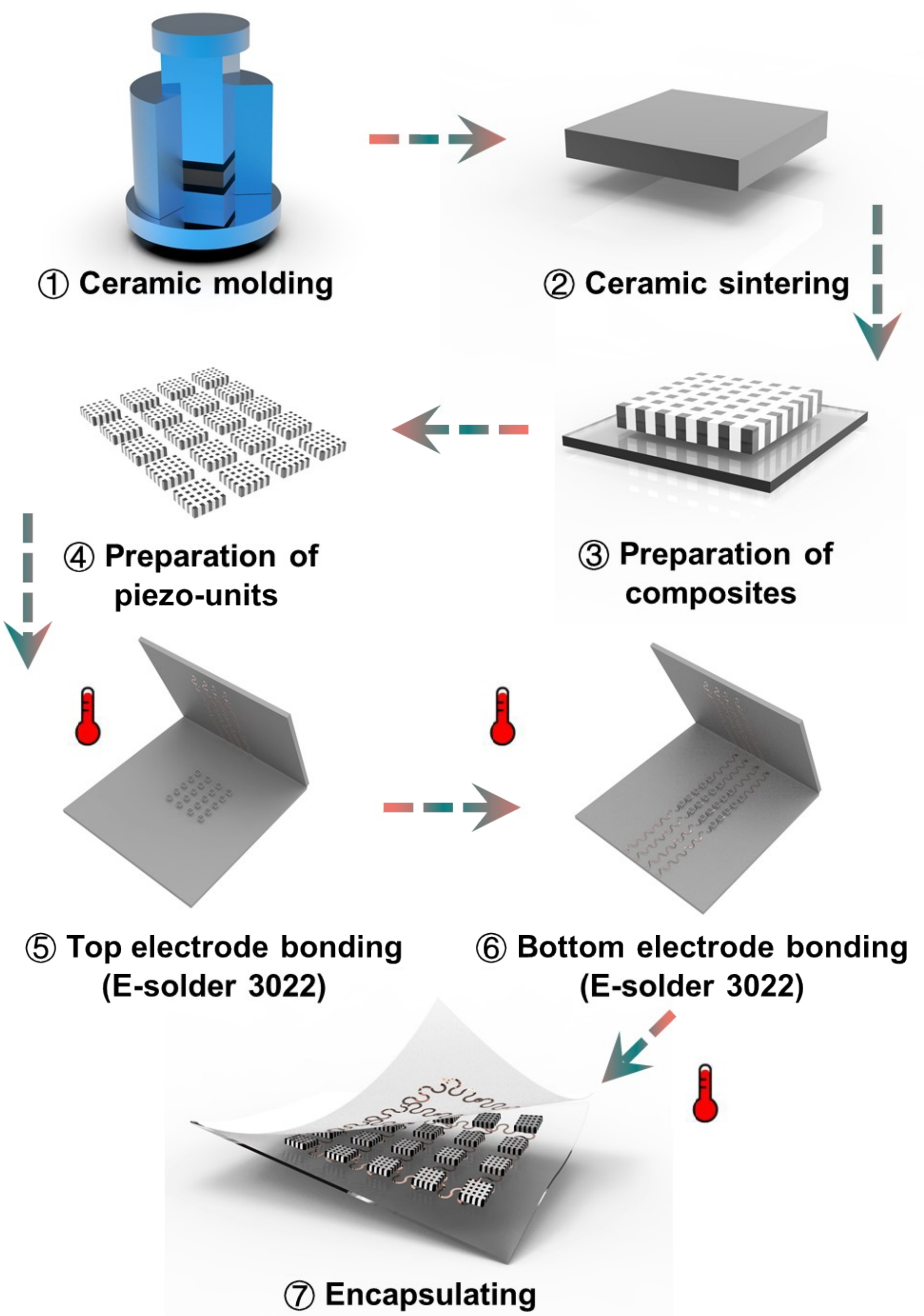

Fig. S1 Manufacturing process of the f-LFPA. The entire manufacturing process includes ceramic molding, ceramic sintering, composite structure preparation, piezo-unit preparation, top and bottom electrode bonding, encapsulation, etc.

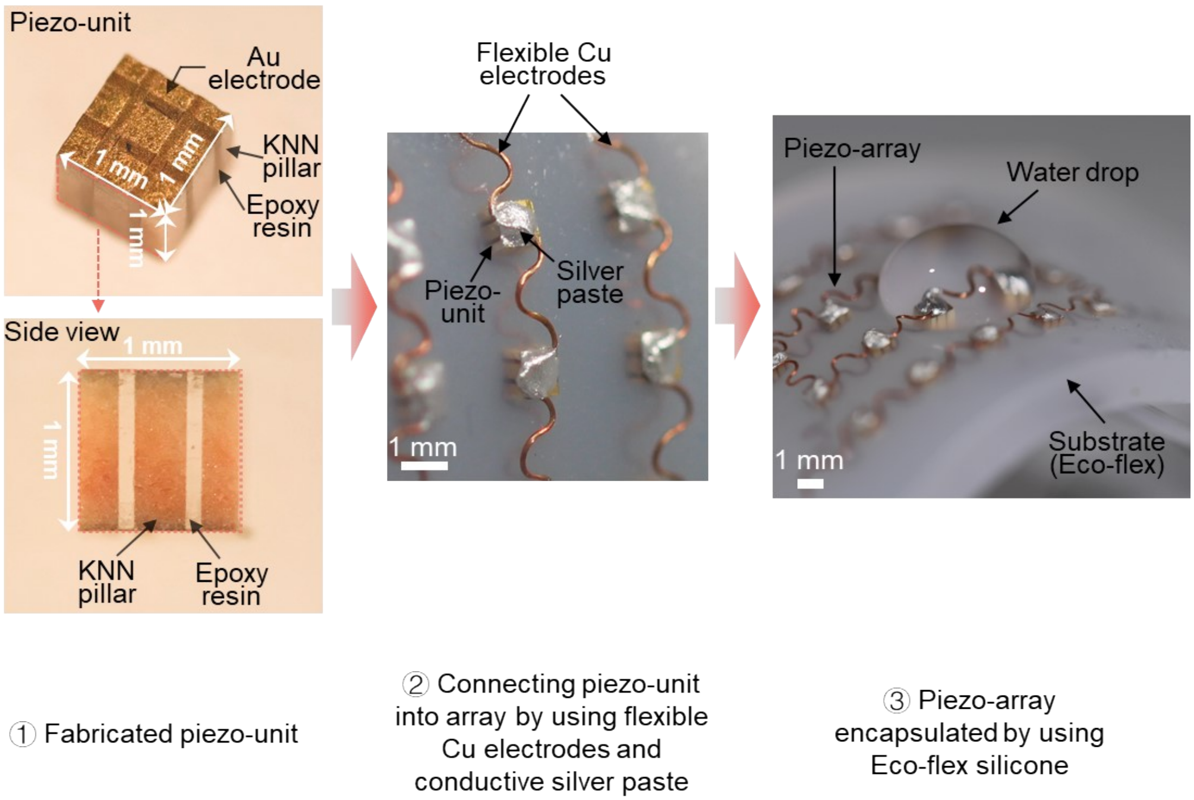

Fig. S2 Optical image showing the preparation and roles of 1-3 piezo-units into flexible piezoelectric array by using each component. First, the KNN-based 1-3 piezo-units with ceramic pillars and epoxy resin filler were fabricated via a dicing-filling method. Then, the piezo-units were connected into arrays by using wave-like flexible Cu electrodes and conductive silver paste. Finally, the piezoelectric array was encapsulated in Eco-flex silicone. The detailed preparation process is described in the **Experimental Section**.

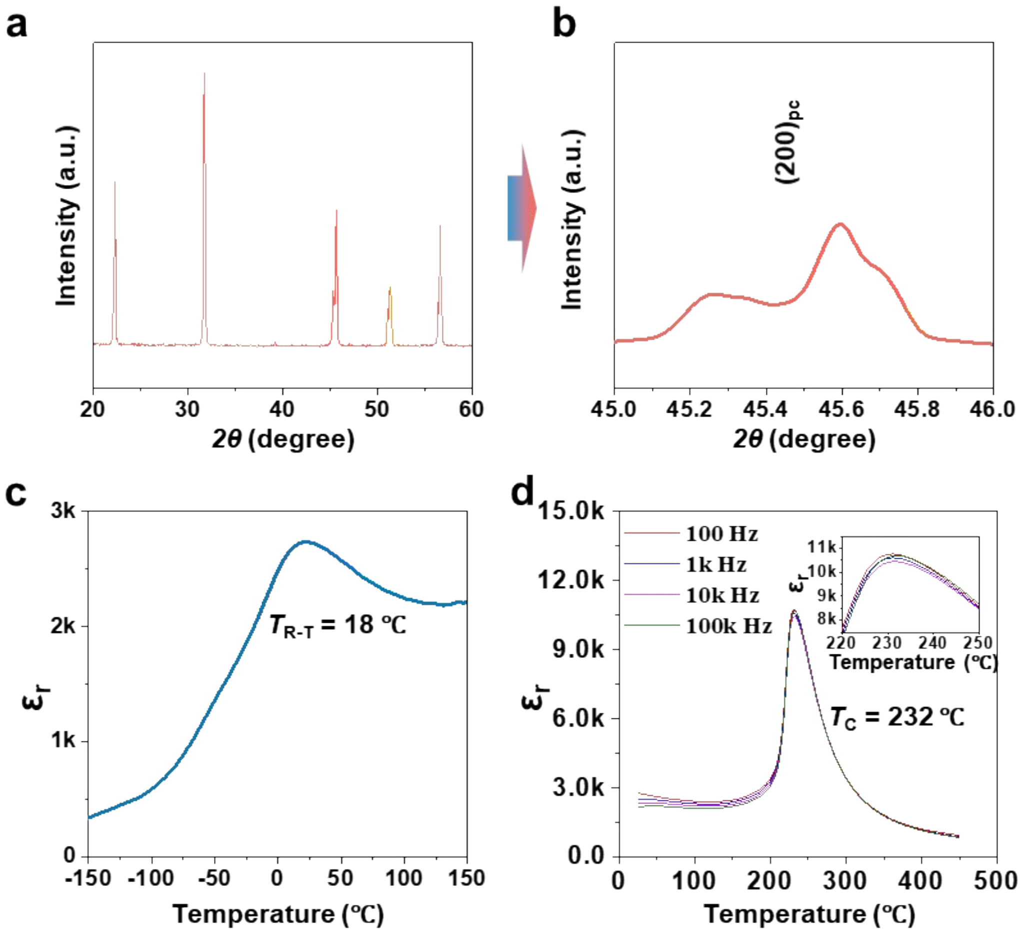

Fig. S3 Structural characterization of the synthesized KNN ceramic. (a) XRD pattern (20°-60°) of the synthesized KNN ceramic. (b) Enlarged XRD pattern (45°-46°) of the synthesized KNN ceramic. (c,d) ε_r-T curves of the synthesized KNN ceramic in the temperature range of -150-150 ℃ and 25-450 ℃. The sintered ceramic exhibits a typical room temperature rhombohedral-tetragonal (R-T) phase boundary, thus enhancing the piezoelectric properties of the ceramic.

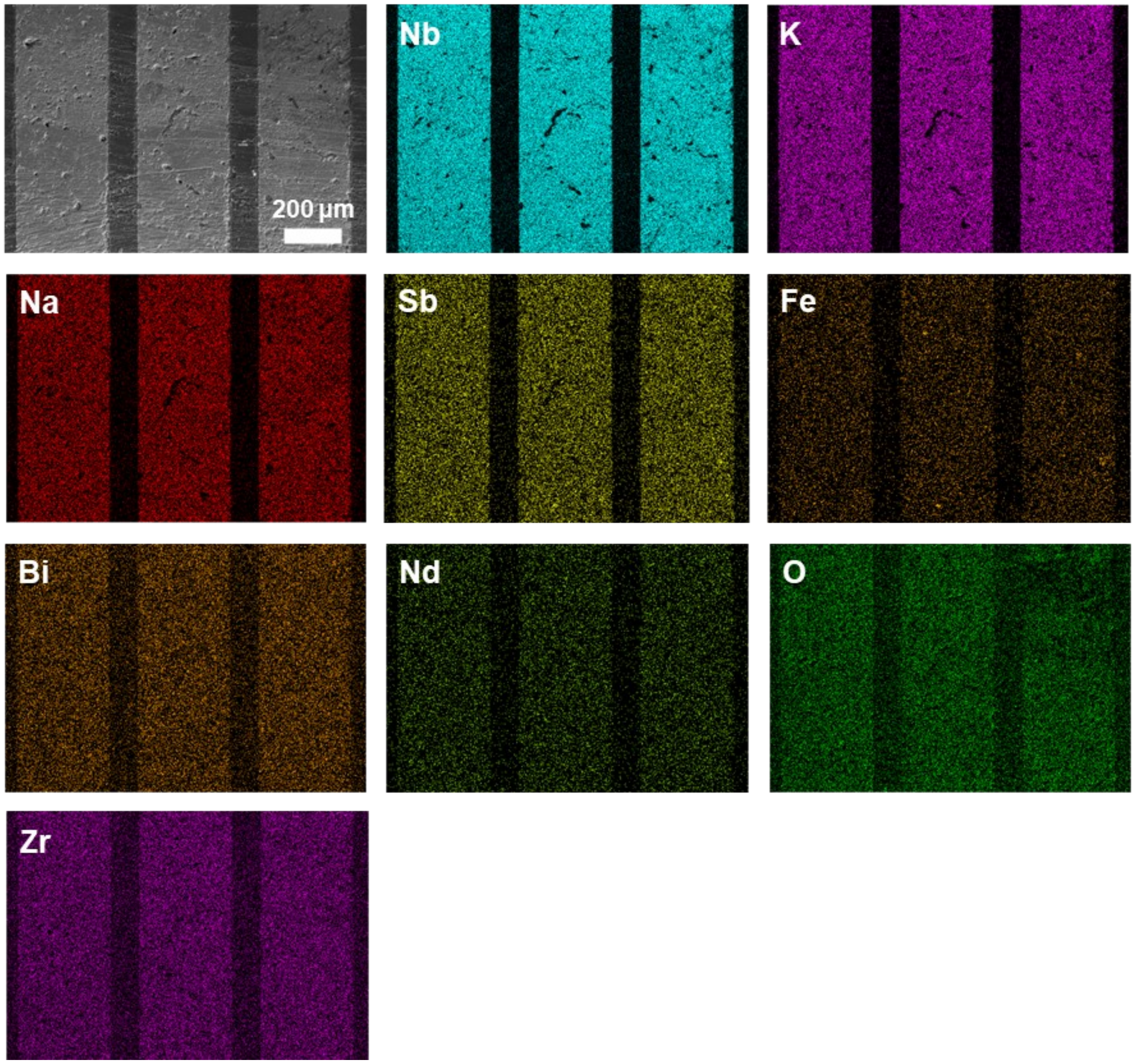

Fig. S4 EDS mapping of the KNN-based composite framework along the longitudinal direction.

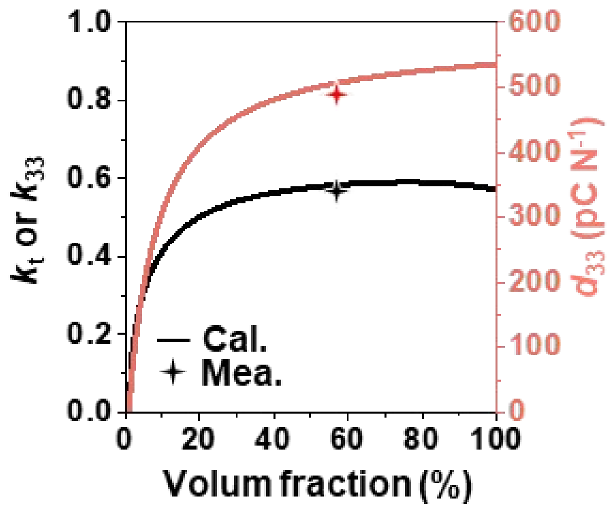

Fig. S5 Electromechanical coupling factor (k_t or k_{33}) and piezoelectric coefficient (d_{33}) of the composites as a function of KNN-based ceramic volume fraction (lines: calculated results; symbols: measured results).

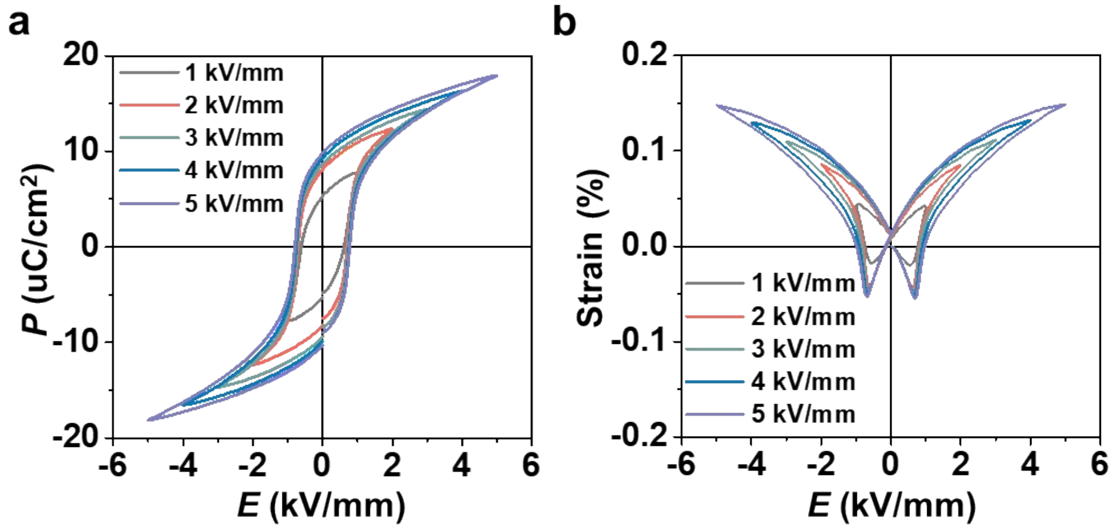

Fig. S6 Polarization hysteresis loops (a) and strain curves (b) of the fabricated 1-3 piezo-unit.

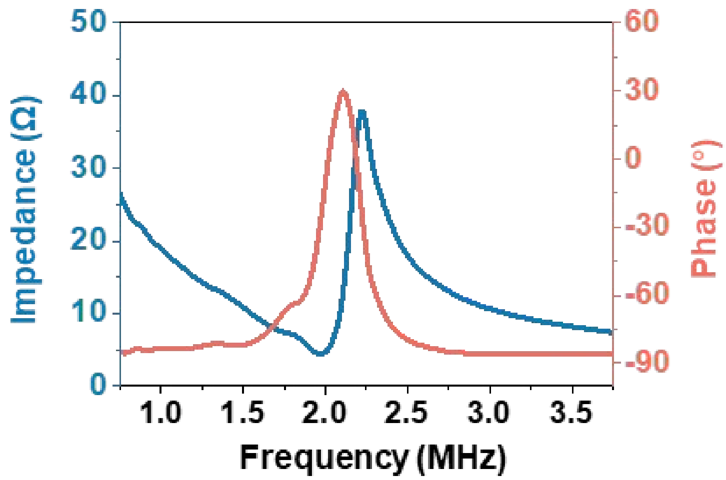

Fig. S7 Impedance and phase angle spectra of the flat ultrasound transmitter. The result shows a resonant frequency near 2 MHz.

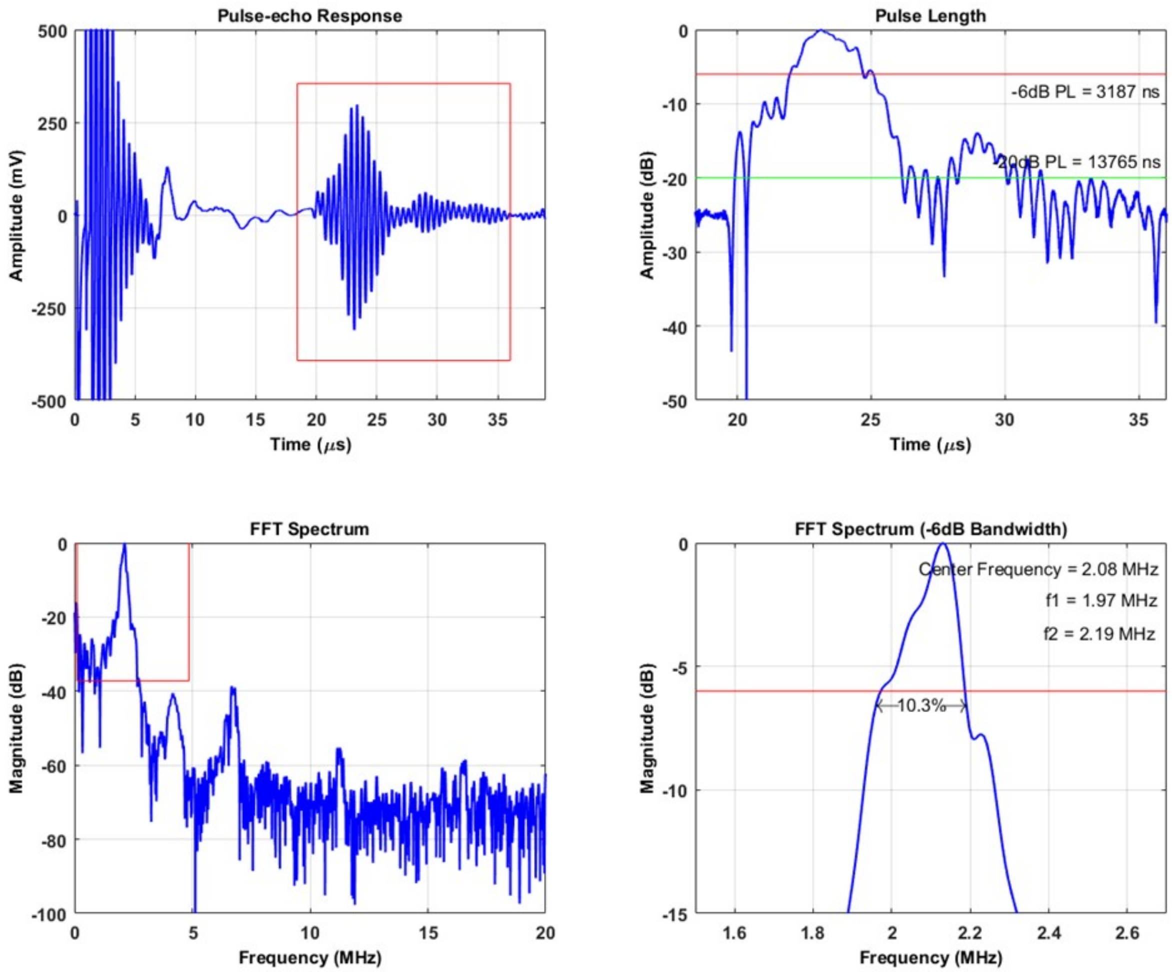

Fig. S8 Pulse-echo measurement of the ultrasound transmitter. Here, the quartz crystal as a target was placed in front of the transmitter. A 2.08-MHz center frequency was obtained from its frequency domain.

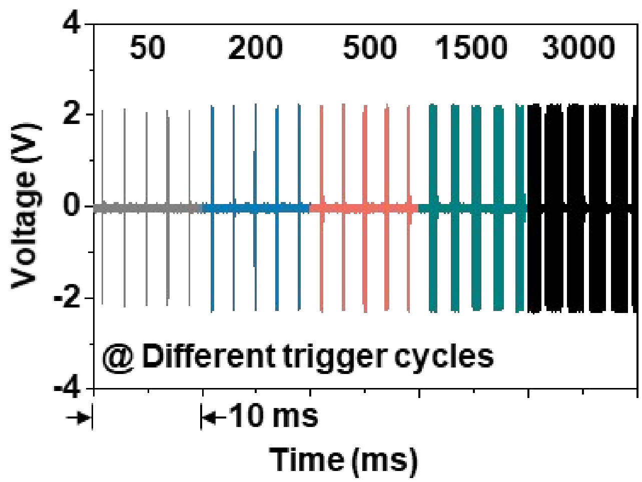

Fig. S9 Output voltages of the f-LFPA depending on the trigger cycles (from 50 to 3000) of sine waves. Ultrasound-induced energy transmission can be regulated by setting trigger cycles.

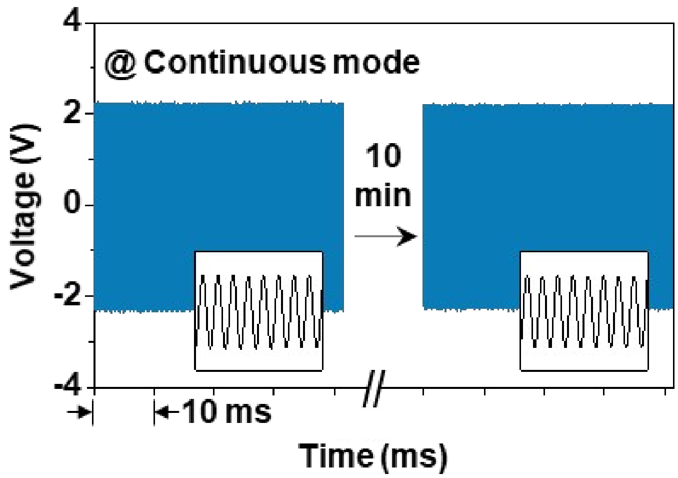

Fig. S10 Output voltage of the f-LFPA under continuous mode. The output voltage amplitude of the K-UEH does not show obvious attenuation after ultrasonic excitation for more than 10 minutes, indicating the stability of ultrasonic energy transmission.

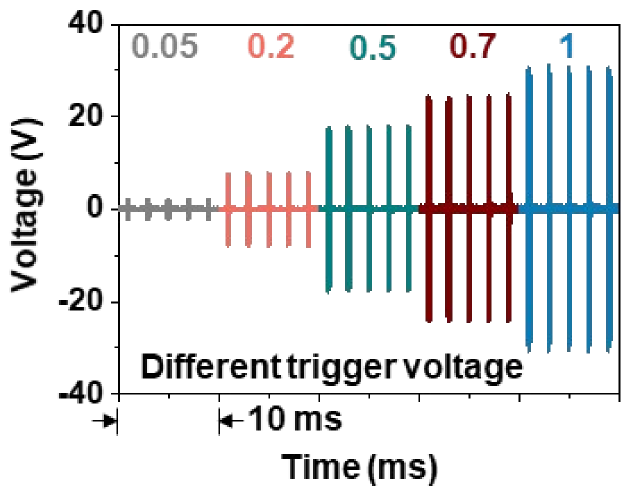

Fig. S11 Unrectified output voltage of the f-LFPA under different trigger voltage (× 316 Vpp).

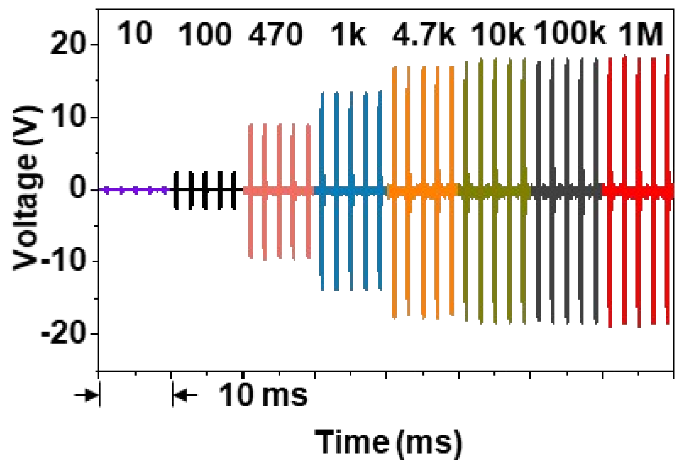

Fig. S12 Unrectified output voltage of the f-LFPA connected to different load resistance. The trigger voltage is 0.5 × 316 Vpp.

4. Supporting References

1. Z. Y. Shen, J. F. Li, R. M. Chen, Q. F. Zhou and K. K. Shung, *J. Am. Ceram. Soc.*, 2011, **94**, 1346-1349.
2. Q. Zhou, K. H. Lam, H. Zheng, W. Qiu and K. K. Shung, *Prog. Mater. Sci.*, 2014, **66,** 87-111.
3. H. C. Song, S. W. Kim, H. S. Kim, D. G. Lee, C. Y. Kang and S. Nahm, *Adv. Mater.*, 2020, **32**, 2002208.