Supplementary Information (SI) for Journal of Materials Chemistry C.

Enhanced Output Performance in Paper-Based Piezoelectric Nanogenerators via Polarization-Engineered Schottky Barrier Contacts

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Supplementary Information

1. Experimental section

1.1 Materials and reagents

Fig. S1 illustrates the experimental procedure for fabricating the *CP*-KNN PENGs used in this study. Cellulose was obtained from Hubei Jinhuan New Material Technology Co., Ltd. The solvents and chemicals, including DMAc (99.0%), LiCl (99.0%), PVDF (average Mw ~534,000 g/mol), potassium carbonate (K_2CO_3, 99.0%), sodium carbonate (Na_2CO_3, 99.8%), and niobium pentoxide (Nb_2O_5, 99.5%), were sourced from Sinopharm Chemical Reagents Co., Ltd.

1.2 Preparation of KNN fillers by solidstate method

$K_xNa_{1-x}NbO_3$ (KNN) inorganic nano-ceramics (x=0, 0.2, 0.4, 0.6, 0.8, 1) were manufactured via a conventional solid-state reaction method. Potassium carbonate (K_2CO_3), sodium carbonate (Na_2CO_3), and niobium pentoxide (Nb_2O_5) served as the starting materials, which were precisely weighed according to the stoichiometric ratios of the target compositions. The mixtures were subjected to ball milling in a planetary ball mill for 12 hours, using zirconia balls and anhydrous ethanol as the milling medium. Afterward, the resulting slurry was dried at 80 °C, transferred to an alumina crucible, and calcined at 910 °C for 4 hours with a controlled heating rate of 3 °C/min to produce the nano-ceramic samples.

1.3 Preparation of the cellulose/PVDF-KNN Composite Films

The preparation of cellulose/PVDF-KNN (*CP*-KNN) composite films follows the procedure outlined in our previous work[1]. In brief, a transparent cellulose solution dissolved in DMAc and a PVDF solution in DMAc were mixed at a mass ratio of 4:1 to obtain the RC/PVDF mixture. KNN particles, synthesized via the solid-phase method described earlier, were then incorporated into the mixture at a volume fraction of 1%. The resulting ternary solution was stirred for a minimum of 12 hours to ensure thorough dispersion of the KNN particles. Subsequently, the mixture was subjected to ultrasonic treatment with magnetic stirring for 30 minutes, repeated six times, to produce the cellulose/PVDF-KNN precursor. Finally, composite films were fabricated using the tape-casting method, with the final film thickness controlled at approximately 15 μm.

1.4 Preparation of the piezoelectric nanogenerators (PENGs) (packaging)

A circular specimen (3.2 cm in diameter) was excised from the prepared composite films. Two copper electrodes (3.0 cm in diameter) of corresponding dimensions were affixed to the upper and lower surfaces of the film. For encapsulation, a polydimethylsiloxane (PDMS) mixture was prepared by homogenizing 50 g of the PDMS base agent with 5 g of curing agent (10:1 ratio) using a magnetic stirrer for 10 min. To remove entrapped air bubbles, the PDMS mixture was degassed under vacuum at a reduced pressure of 0.8 mmHg for 30 min in a vacuum drying oven. Subsequently, the electrode-attached film was precisely positioned within a cubic mold measuring 5 cm in length, width, and height, followed by pouring the degassed PDMS mixture to ensure complete encapsulation. Subsequently, the assembly was thermally cured in a drying oven at 80 °C for 4 h. After curing, the piezoelectric nanogenerator was obtained by demolding the encapsulated structure.

1.5 Structural and Property Characterizations

The crystalline structure of the composite films was characterized through X-ray diffraction (XRD, Rigaku D/max-2200PC). The microstructure of the cross-section of the films was observed using a scanning electron microscope (Prisma E SEM, Thermo Fisher Scientific). The morphology of both the KNN particles and cellulose fibers was investigated by field-emission transmission electron microscopy (FE-TEM, JEOL, JEM-F200), and the energy-dispersive X-ray spectroscopy (EDS) attached to the FE-TEM was utilized to obtain the element distribution. The different functional groups of the films were identified by Fourier Transform Infrared Spectroscopy (FTIR, Spotlight 400 & Frontier) within the wavelength range from 4000 cm^{-1} to 500 cm^{-1}. Before electrical measurements, Au electrodes with a diameter of 2 mm were sputtered by a coating system. Both the frequency dependence of the dielectric constant (ε) accompanied by dielectric loss (*tanδ*) and the temperature dependence of ε along with tanδ were obtained from the impedance analyzer (E4980A, Agilent). The mechanical properties were measured using the servo control system universal testing machine (AI-7000-NGD, Gotech Testing Machines), and the surface contact angles of the composite samples were measured by the optical contact angle machine (OCA20, Dataphysics). Finally, the open-circuit voltages and short-circuit currents were measured using the Digital Source Meter (DIGITAL SOURCE METER, Keithley 2450).

Tab. S1 Parameters of the *Rietveld* XRD refinement result and the phase content of the KNN ceramic fillers with different K/Na ratio.

	$NaNbO_3$ (*O*)	$K_{0.2}Na_{0.8}NbO_3$ (*O*)	$K_{0.4}Na_{0.6}NbO_3$ (*O*/*T*)		$K_{0.6}Na_{0.4}NbO_3$ (*O*/*T*)		$K_{0.8}Na_{0.2}NbO_3$ (*T*)	$KNbO_3$ (*T*)
a	3.965	3.979	3.986	3.988	3.991	3.996	3.996	3.998Table
b	4.006	4.007	4.012	3.988	4.006	3.996	3.996	3.998
c	4.006	4.007	4.012	4.015	4.006	4.024	4.031	4.039
chi^2	3.87	3.64	1.84		4.21		4.10	2.98
R_p	3.69	4.56	5.09		3.93		4.25	4.20
R_{wp}	8.01	8.42	6.37		7.98		8.12	7.93
R_{exp}	5.11	5.23	4.69		4.85		5.32	4.78

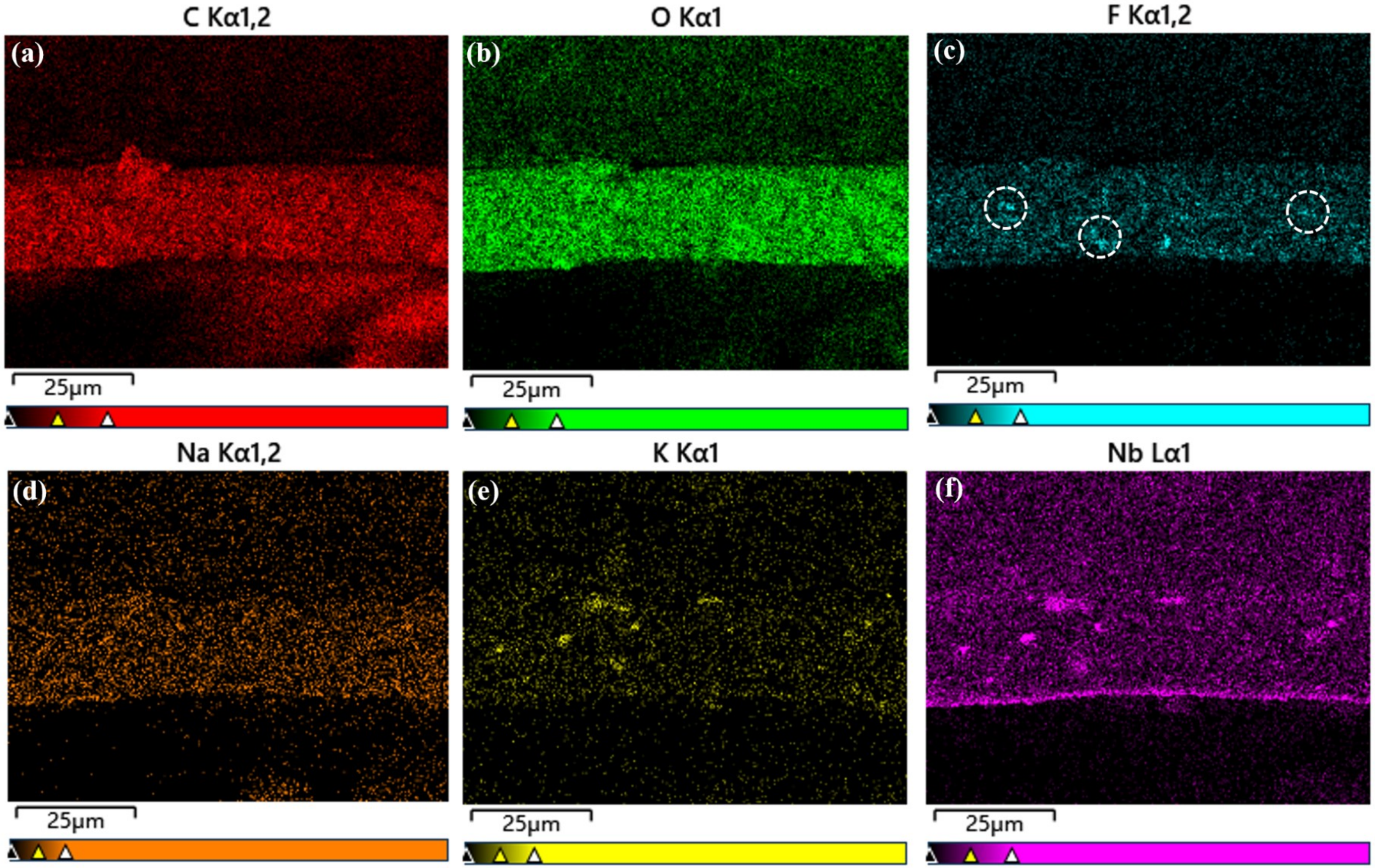

Figure S1 The energy dispersive spectroscopy (EDS) mappings for the C, O, F, Na, K, and Nb elements of Figure 3(a).

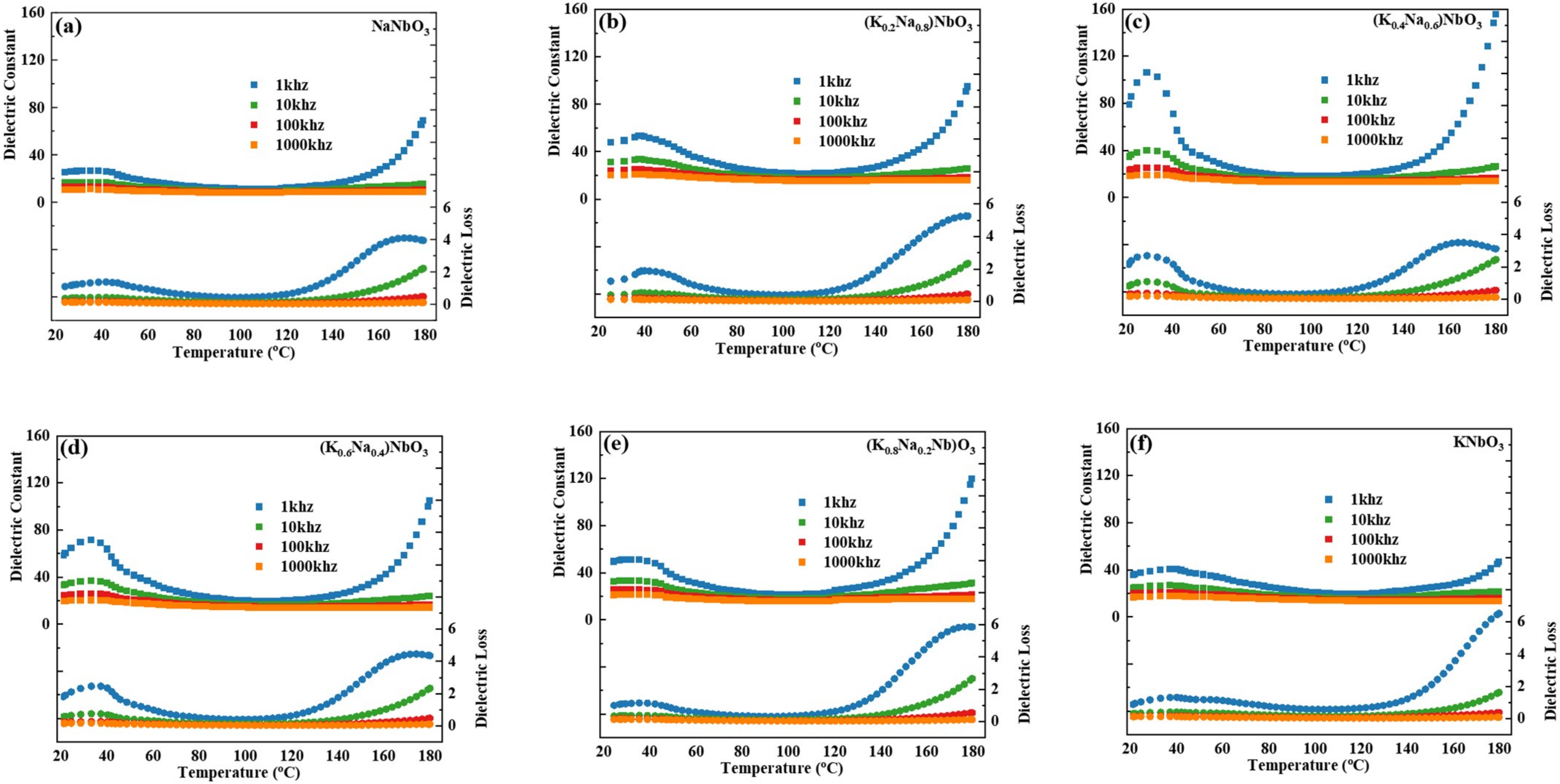

Figure S2 The ε-T curves and tanσ-T curves for all the C8P2-KNN films.

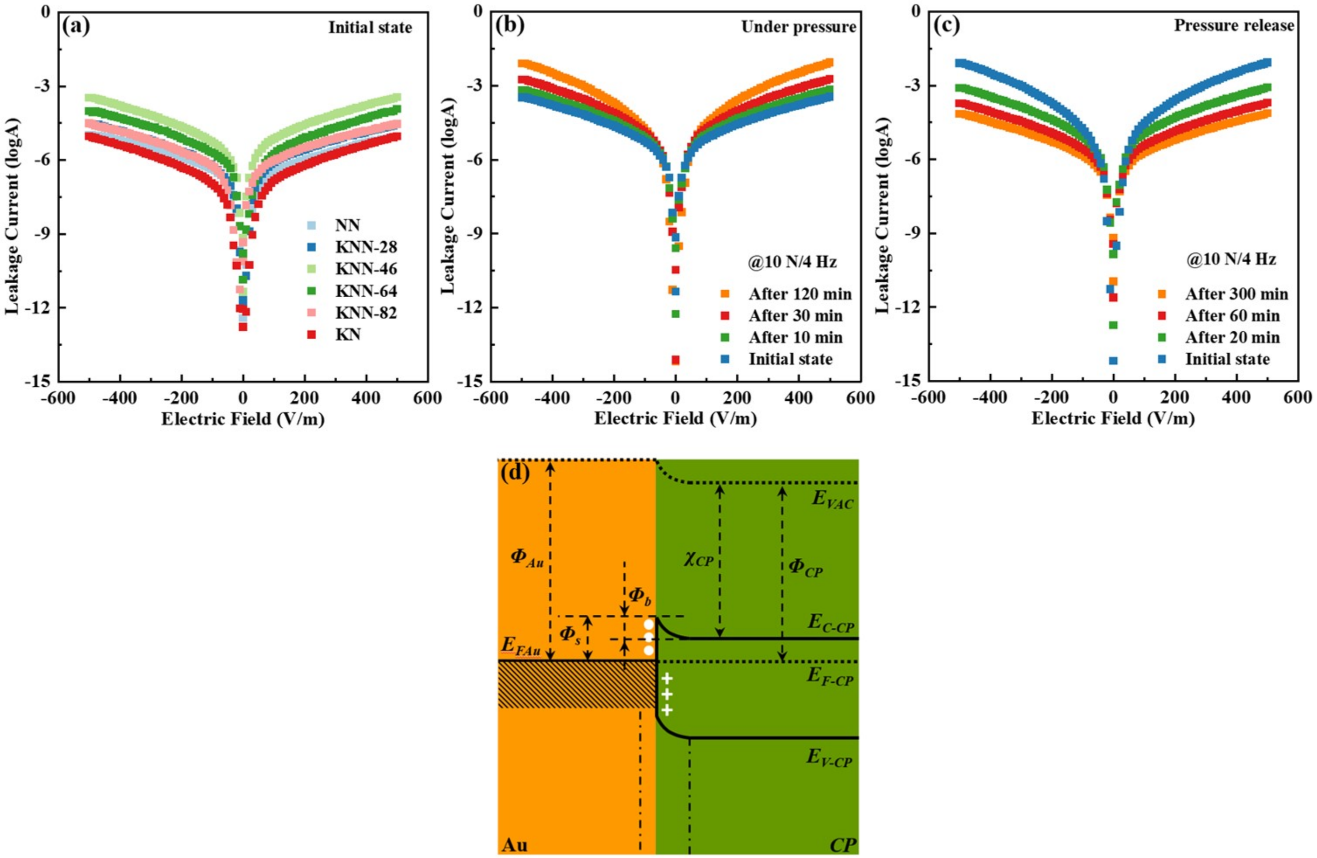

Figure S3 (a) the I-V curvess of all the C8P2-KNN films with different KNN components;(b) the I-V curves of the C8P2-KNN46 film under a mechanical load of 10 N at 4 Hz for different durations; (c) the I-V curves of the C8P2-KNN46 film at different durations after pressure release; (d) the band diagram of the interface between the Au electrode and the pristine C8P2 film.

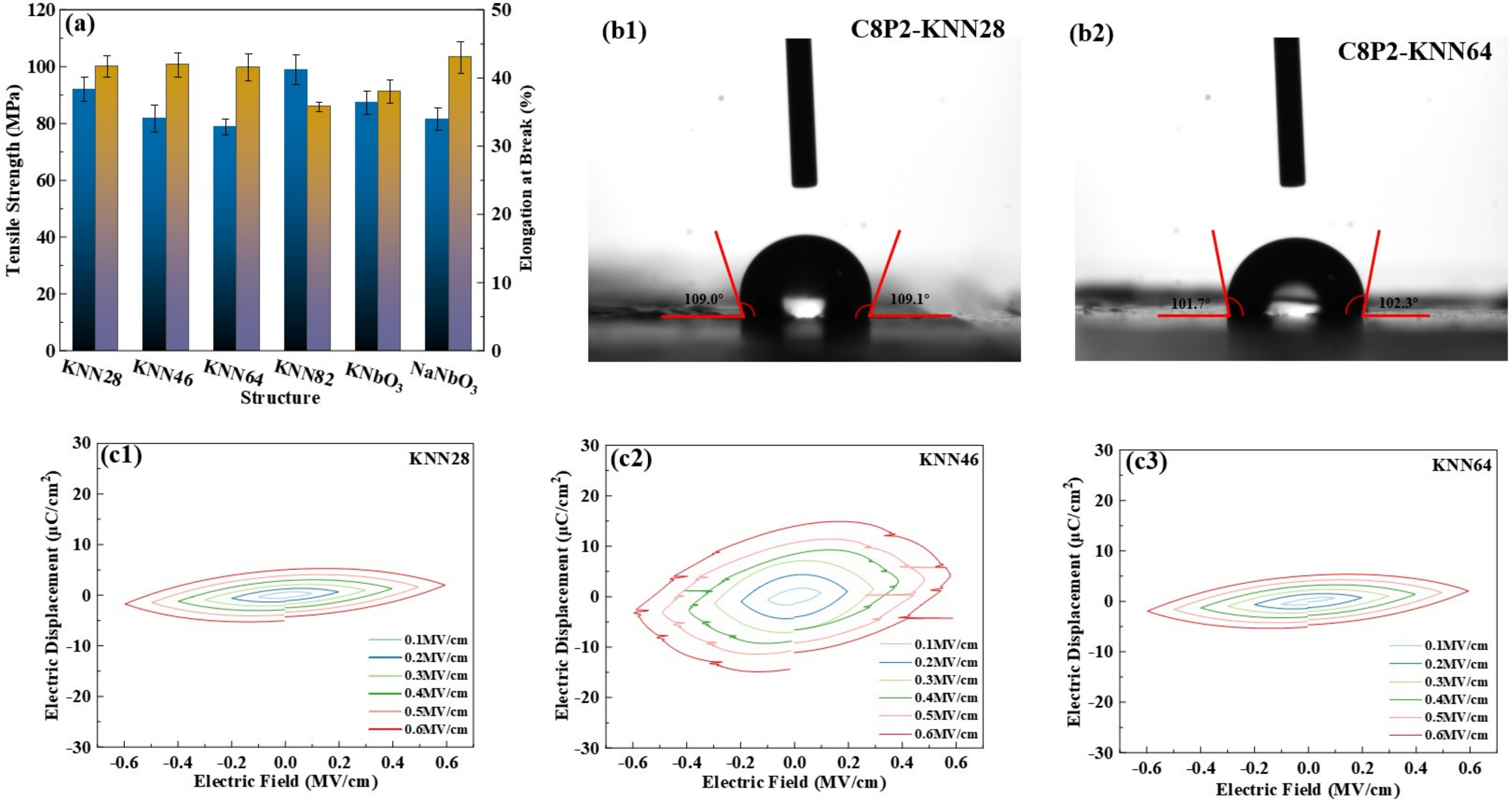

Figure S4(a) the tensile strength and elongation at break of all C8P2-KNN films; The image of the water contact angle of the (b1) C8P2-KNN28; (b2) C8P2-KNN64; the polarization-electric field relationships for the (c1) KNN28, (c2) KNN46, (c3) KNN64 films under different fields.

2. Testing setup and the calculation for piezoelectric output

Fig. 3(h) sketches the work process of the C8P2-KNN PENGs. The as-packaged device is located at the bottom of an electric vibration exciter, and its output parameters can be co-adjusted by the amplifier and the frequency generator. Keithley 2450 source meter was used for data collection, displaying the signal on the screen. The piezoelectric output of the PENGs can be calculated as follows:

$$P_d = \frac{I_S \times V_O}{S} \quad \text{Eq. S1}$$

In which the P_D, I_S, V_O are the power density, short-circuit current and the open-circuit voltage of the device, and the S is the area of the electrode on the PENG.

3. The physical meaning of the abbreviations in the band diagram analyzing

E_{VAC}: the vacuum level

E_{FAu}: the Fermi energy level of Au

$E_{V\text{-}CP}/E_{V\text{-}KNN28}/E_{V\text{-}KNN46}/E_{V\text{-}KNN64}$: the valance band of C8P2/KNN28/KNN46/KNN64

$E_{C\text{-}CP}/E_{C\text{-}KNN28}/E_{C\text{-}KNN46}/E_{C\text{-}KNN64}$: the conducting band of C8P2/KNN28/KNN46/KNN64

$E_{F\text{-}CP}/E_{F\text{-}KNN28}/E_{F\text{-}KNN46}/E_{F\text{-}KNN64}$: the Fermi level of C8P2/KNN28/KNN46/KNN64

Φ_{CP}: the work function of C8P2

χ_{CP}: the electron affinity of C8P2

Φ_{s}: the Schottky barrier height

Φ_{b}: the build-in potential

V_{P}: the voltage generated from the KNN fillers

$R_{d}/R_{d28}/R_{d46}/R_{d64}$: the depletion region of the interface between the film and the Au electrode of pristine C8P2 film/ C8P2-KNN28/ C8P2-KNN46/C8P2-KNN64 when under external force.

References

[1] Z. X. Sun, S. T. Wang, S. B. Zhao, H. S. Wei, G. D. Shen, Y. P. Pu and S. F. Zhang, *J. Mater. Chem. C*, 2024, **12**, 859-867.