# Supplementary Information

# Flexible composite-nanofiber based piezo-triboelectric nanogenerators for wearable electronics

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# 1. Synthesis of BCZT particles and BP-based NF

## (1) Solid-state reaction method (SS method)

BaCO<sub>3</sub> (100 nm), CaCO<sub>3</sub> (10 nm), TiO<sub>2</sub> (25 nm), and ZrO<sub>2</sub> (20 nm) were used as the raw materials to prepare nano-BCZT precursor powders. In accordance with the typical procedure, requisite quantities of raw materials were mixed in stoichiometric ratios and stirred for 24 h with the addition of ethanol. After drying at 100 °C for 12 h, the mixtures were calcined at 1000 °C for 2 h and then sintered at 1200 °C for 2 h to obtain pure perovskite-structure BCZT particles.



Fig. S1. Synthesis procedure schematic of BCZT-SS particles.

## (2) Hydrothermal method (HT method)

Initially, materials including  $BaCl_2 H_2O$ ,  $ZrCl_2O \cdot 8H_2O$ ,  $CaCl_2$  and  $TiO_2$  (25 nm) were added to DI water and stirred at 25 °C for 12 h. Afterwards, 10 M NaOH was added to the mixture and stirred for another 12 h. The obtained solution was poured into a Teflonlined stainless steel autoclave and heated at 240 °C for 20 h. After being centrifuged and washed for four times, the product was dried in an oven at 100 °C for 12 h.



Fig. S2. Synthesis procedure schematic of BCZT-HT particles.

#### (3) Sol-gel method (SG method)

First, requisite quantities of EtOH, HAc, and Hacac were first mixed. TBOT,  $Ba(Ac)_2$ ,  $Ca(Ac)_2$ , and zirconium acetylacetonate ( $C_{20}H_{28}ZrO_8$ ) were then sequentially added in stoichiometric ratios and continuously stirred at 25 °C for 4 h. Later, PVP-K30 was dissolved into the above mixture and stirred at 50 °C for 9 h. After aging for 72 h, a transparent yellow gel was formed. Finally, the gel was sintered at 650 °C for 2 h.



Fig. S3. Synthesis procedure schematic of BCZT-SG particles.

# (4) Synthesis procedure of BP-based NF



Fig. S4. Synthesis procedure schematic of BP-based NF.

# 2. Physical properties of BP-based NF

Sample	PVDF-HFP NF	BP-SS NF	BP-HT NF	BP-SG NF
Phase	α(100), <b>β(110)</b>	α(100), <b>α(110)</b>	α(110), <b>β(110)</b>	α(110), <b>β(110)</b>

 Table S1. Phases of PVDF-HFP in different NF

\*Note: Overstriking words represent the main phases in the NF.



Fig. S5. SEM images of BP-based NF under (a-c) ETD Mode and (d-f) BSED Mode.

# 3. Output performance of BP-SG NF



Fig. S6. Effect of (a, b) contact frequency and (c, d) gap distance between on the open-circuit voltage ( $V_{OC}$ ) and short-circuit current ( $I_{SC}$ ) of BP-SG PTNG.

#### 4. Assembly and working mechanism of BP-SG S-TPNG

#### (1) Assembly of BP-SG S-TPNG

The BP-SG S-TPNG in **Fig. S7** includes three parts that forms a sandwich structure: a BP-SG-NF film (2\*2 cm<sup>2</sup>) with an Ag/Ni tape connection, and two bottom and top PDMS films (3\*3 cm<sup>2</sup>) as substrate and negative triboelectric materials, respectively.

#### (2) Working Mechanism of BP-SG S-TPNG

The working mechanism of BP-SG S-TPNG under the contact-separation mode is illustrated in **Fig. S7(b-e)**. As human skin is more triboelectrically positive than PDMS according to the triboelectric series, skin and PDMS generate positive and negative charges, respectively. In the initial state, no electric potential between skin and BP-SG S-TPNG is generated. As seen in **Fig. S7(b)**, triboelectric charges flow between skin and PDMS upon contact with each other, where skin is positively charged and PDMS is negatively charged. Simultaneously, piezoelectric charges are also generated with the deformation of PDMS. Electrical potential difference in **Fig. S7(c)** is then established due to the electrostatic induction effect and the recovery of PDMS as soon as skin moves away from PDMS. In this case, electrons flow from Ag/Ni tape to the ground and a charge signal is produced. When skin is totally separated from the device, all the ions and charges maintain an electrostatic equilibrium state (**Fig. S7(d)**). Once skin touches PDMS again, an opposite current signal is generated, resulting from electrons transferring back from the ground to BP-SG NF in **Fig. S7(e)**.



Fig. S7. Working mechanism of BP-SG S-PTNG.