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Supporting Information

Energy Scavenging Luminescent Piezo Fabrics: Small Silicon Dots Enable Big Electrical Outputs

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Experimental Section

Materials and Reagents: PVDF-TrFE copolymer with a molar ratio of 8:2 was supplied by Arkema Inc., France. (3-Aminopropyl) trimethoxysilane (APTES, 98%) and sodium ascorbate (SA) were purchased from Aladdin Chemical Reagent Co., Ltd, Shanghai, China. Analytical grade acetone and N-N dimethyl amide (DMF) were provided by Kelon Chemical Co., Ltd, Chengdu, China.

Synthesis of luminescent SiDs: 0.5 g of SA was dissolved in 10 mL of deionized water. Then 7.5 mL of SA solution and 2 mL of APTES were added into 25 mL of deionized water, and stirred thoroughly at room temperature for 20 min. A hydrothermal method was used for the synthesis of SiDs. The above precursor solution was put into a 50 mL Teflon-lined stainless steel autoclave, and reacted at 200 ℃ for 24 h before cooling to room temperature. The resulting SiDs colloidal solution was further purified for 24 h using a dialysis bag with a molecular weight cut-off of 1 kDa. Finally, the as synthesized SiDs were extracted from aqueous solution with the utilization of a freeze dryer, and the SiDs in powder form were obtained for later use.

Electrospinning of SiDs/PVDF-TrFE hybrid fabrics: A schematic illustration of the manufacturing process of an electrospun SiDs/PVDF-TrFE fibrous fabric is shown in Figure 1a. First, SiDs and PVDF-TrFE were dissolved in a mixed solvent of DMF and acetone (4:6, v/v) at room temperature to generate a transparent solution with a concentration of 160 mg mL^{-1}. Next, the uniformly mixed electrospinning solution was injected into a 10 mL syringe connected to a spinneret with an inner diameter of 0.7 mm. After that, the electrospinning was carried out at a voltage of 15 kV and an outflow speed of 80 μL min^{-1}. The ejected fibers were collected by using a rotating drum, with a receiving distance of 16.5 cm and a rotating speed of 500 rpm. Last, the electrospun fabric was peeled off the drum after electrospinning.

Characterization of Materials: TEM was performed using a JEOL JEM-2100F apparatus. PL spectra were recorded on a FLS980 spectrometer equipped with a 450 W xenon lamp. The 1931 CIE (International Commission on Illumination) system was used to calculate the chromaticity coordinates. The absolute PL QYs were measured using a calibrated integrating sphere attached to the spectrometer. Fluorescence microscopy images

were acquired on an Olympus IX51 microscope. SEM images were obtained using a JSM-6330F apparatus. The images were analyzed with ImageJ software to identify the distribution of fiber diameters. DSC was performed using a TA-Q20 instrument. XRD data were collected on a PANalytical X'pert PRO diffractometer. Attenuated total reflectance Fourier transform infrared (ATR-FTIR) spectra were acquired using a Nicolet iS20 spectrometer.

Fabrication of PNGs: The detailed fabrication process of SiDs/PVDF-TrFE fabric (SiD-x) based PNGs are shown schematically in Figure S1, Supporting Information. The composite structure of the flexible PNG device is a sandwich structure composed of SiD-x fabric, aluminium (Al) electrode and polyurethane (PU) tape. First，two aluminium films were attached to the upper and lower sides of the electrospun SiD-x hybrid fabric. They were used as electrodes to derive piezoelectric signals. Next, the aluminium electrodes were encapsulated using polyurethane tape. Finally, the PNG device was fixed to the acrylic plates to ensure a smooth impact during subsequent piezoelectric measurements. The impact head of the measurement system was also made of the same acrylic resin to eliminate the possible interference of triboelectric charges.

Test of Devices: After being integrated as a flexible PNG device, a reciprocating impact test was carried out to evaluate the piezoelectric outputs of electrospun fabrics. The schematic diagram of the measurement system and the structure assembly of the tested samples are shown in Figure 1b. A NTIAG HS01-37×166 linear motor was utilized as the impact source. The output voltage signals were collected by a Keithley 6514 system electrometer. The output current signals were measured by a Stanford Research SR570 low-noise current preamplifier. To confirm the electrical output came from SiD-x fabric rather than from aluminium electrode and acrylic plate, the blank device without fabric and the PNG device with SiD-x fabric were tested under the same conditions for comparison (Figure S2, Supporting Information). The electrical output of the blank device without fabric mostly came from noise and was negligible if compared to that of SiD-x fabric based PNG device. A switching polarity test was also conducted to verify the output signals came directly from the piezo responses of PNG device, rather than from the influence of measurement system

or environment (Figure 5b) [1, 2].The relevant biological signals involved in this article were collected from volunteers, and informed consent was obtained prior to the research. The relevant experiments involving human subjects conformed to the local ethical requirements.

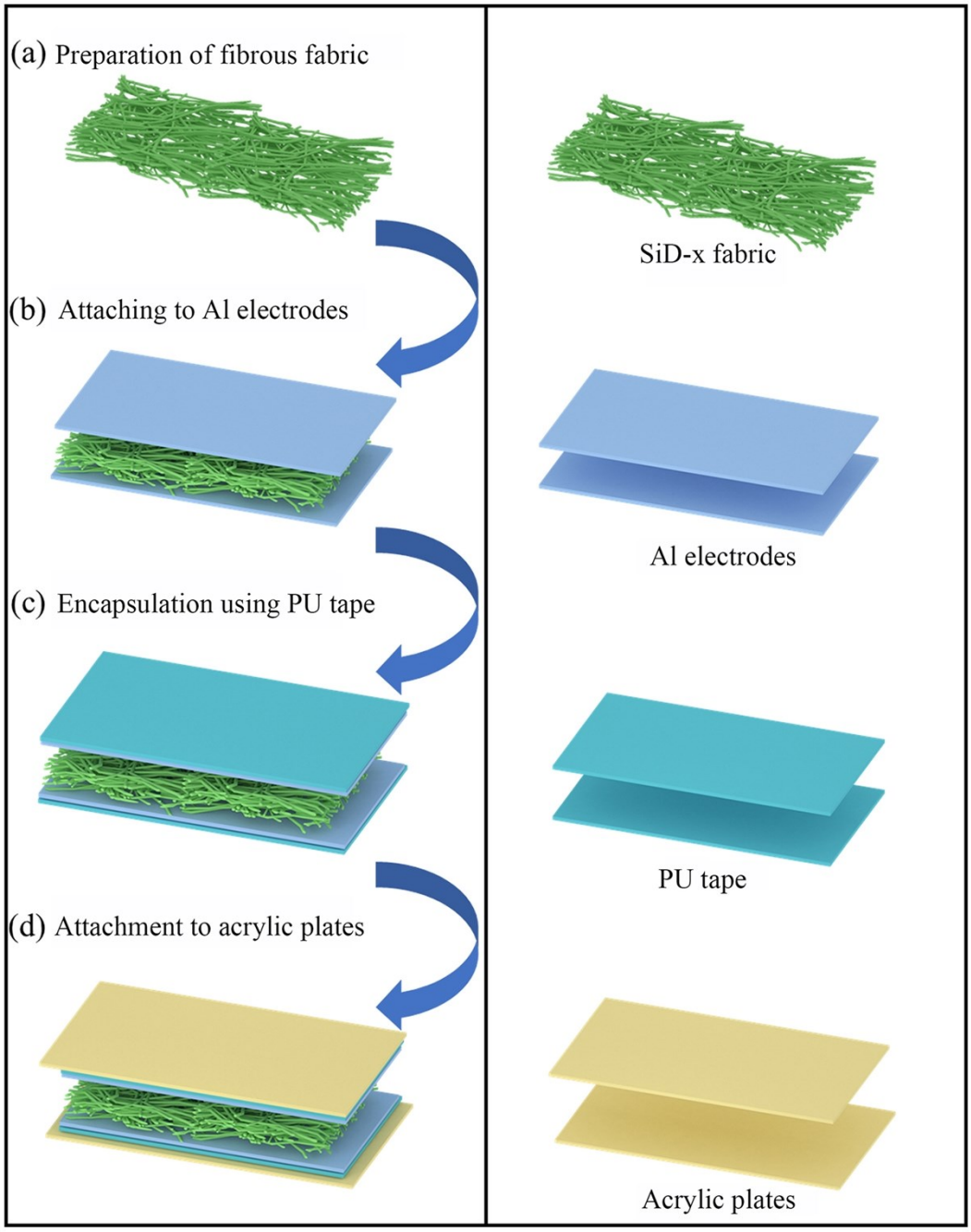

Figure S1. Schematic diagram of the fabrication process of SiD-x fabric based PNGs.

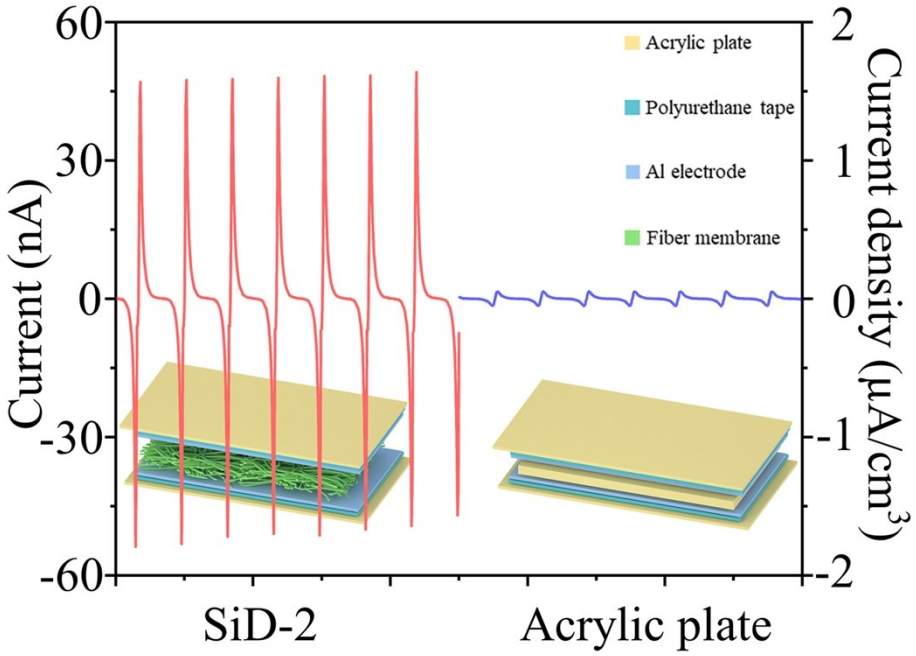

Figure S2. A comparison of short-circuit current outputs of SiD-2 fabric and acrylic plate, generated at a stimulation frequency of 1.5 Hz and an applied force of 4.5 N. The insets show the structural assembly of SiD-2 fabric based PNG (left) and acrylic plate based device (right), respectively. Aluminum is used as electrode material for both types of devices. SiD-2 fabric size: 20 mm×20 mm×0.080 mm.

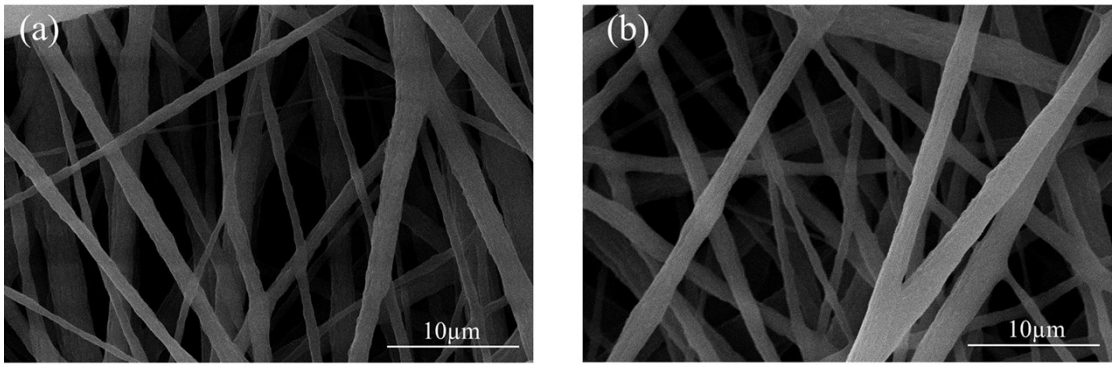

Figure S3. SEM of a) SiD-1 and b) SiD-4 fibers, fabricated by electrospinning at an applied voltage of 15 kV.

Table S1. DSC data of SiDs/PVDF-TrFE hybrid fibers, fabricated by electrospinning at an applied voltage of 15 kV.

Sample	SiDs (%)	T_m [a] (^oC)	ΔH_m [b] (J/g)	X_c [c] (%)
SiD-0	0.0	156.8	43.71	41.78
SiD-1	0.1	156.3	47.17	45.14
SiD-2	0.2	156.3	48.39	46.35
SiD-4	0.4	158.5	49.38	47.40

[a] T_m: melting point; [b] ΔH_m: melting enthalpy; [c] X_c: crystallinity.

The crystallinity X_c was calculated from the melting enthalpy ΔH_m by means of the following equation:

$$X_c = \frac{\Delta H_m}{(1-\varphi)\Delta H_m^0} \times 100\% \quad (1)$$

where φ is the mass fraction of SiDs in hybrid fibers, and ΔH_m^0, assumed to be 104.6 J/g, is the melting enthalpy of ideal PVDF crystal [3].

Table S2. Relative content of crystalline α, β and γ forms in SiDs/PVDF-TrFE hybrid fibers electrospun at an applied voltage of 15 kV, calculated from Equations (2)-(5).

Sample	SiDs (%)	α (%)	β (%)	γ (%)
SiD-0	0.0	17.81	36.87	45.32
SiD-1	0.1	17.12	41.40	41.48
SiD-2	0.2	12.27	70.08	32.48
SiD-4	0.4	14.19	49.64	36.17

The fractions of α, β and γ form crystals in electrospun SiDs/PVDF-TrFE fibers were quantified by using the following equations [2, 4, 5]:

$$F_{(\beta,\gamma)} = \frac{A_{840}}{A_{840} + 1.26 \times A_{764}} \times X_c \tag{2}$$

$$F_{(\beta)} = \frac{A_{1280}}{A_{1280} + A_{1230}} \times F_{(\beta,\gamma)} \tag{3}$$

$$F_{(\gamma)} = F_{(\beta,\gamma)} - F_{(\beta)} \tag{4}$$

$$F_{(\alpha)} = X_c - F_{(\beta,\gamma)} \tag{5}$$

where A_{840}, A_{764}, A_{1280} and A_{1230} represent peak areas at 764 cm^{-1}(α phase), 840 cm^{-1} (β and γ phase), 1280 cm^{-1} (β phase) and 1230 cm^{-1} (γ phase) in FTIR spectrum, respectively; and X_c is the crystallinity of the sample.

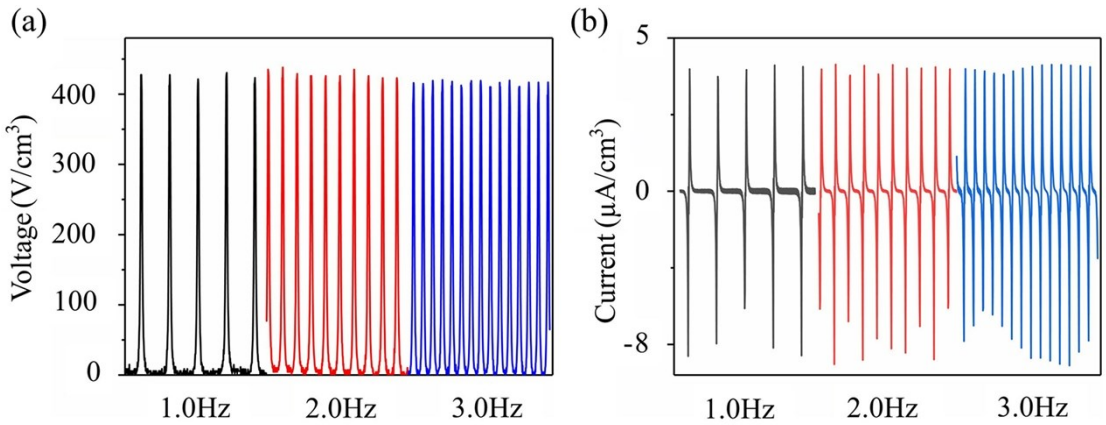

Figure S4. a) Open-circuit voltage and b) short-circuit current outputs of electrospun SiD-2 fibers stimulated at different frequency and a fixed force of 13.5 N.

References

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