Enhanced energy harvesting performance in lead-free multi-layer piezoelectric composites with a highly aligned pore structure

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Abstract

The harvesting of mechanical energy from our living environment via piezoelectric energy harvesters to provide power for next generation wearable electronic devices and sensors has attracted significant interest in recent years. Among the range of available piezoelectric materials, porous piezoelectric ceramics exhibit potential for both sensing and energy harvesting applications due to their reduced relative permittivity and enhanced piezoelectric sensing and energy harvesting figures of merit. Despite these developments, the low output power density and the lack of optimized structural design continues to restrict their application. Here, to overcome these challenges, a lead-free multi-layer porous piezoelectric composite energy harvester with a highly aligned pore structure and three-dimensional intercalation electrodes is proposed, fabricated and characterized. The effect of material structure and multi-layer configuration of the porous piezoelectric ceramic on the dielectric properties, piezoelectric response and energy harvesting performance was investigated in detail. Since the relative permittivity is significantly reduced due to the introduction of aligned porosity within the multi-layer structure, the piezoelectric voltage coefficient, energy harvesting figure of merit and output power are greatly enhanced. The multi-layer porous piezoelectric composite energy harvester is shown to generate a maximum output current of 80 μA, with a peak power density of 209 μW cm^{-2}, which is significantly higher than other porous piezoelectric materials reported to date. Moreover, the generated power can charge a 10 μF capacitor from 0 V to 4.0 V in 150 s. This work therefore provides a new strategy for the design and manufacture of porous piezoelectric materials for piezoelectric sensing and energy harvesting applications.

Key words: multi-layer structure, piezoelectric composite, aligned pore structure, sensing, energy harvesting

1. Introduction

The rapid development of the Internet of Things (IoT) and wearable electronic technologies has led to an increase in the need for sensor networks[1, 2], where the supply of power for such sensor networks has become a serious challenge for our society. The large consumption of fossil fuels and associated environmental pollution have also motivated the development of sustainable and clean energy sources, including heat, wind, vibration and solar energy.[3-6] Mechanical vibrational energy, which is ubiquitous in our living ambient, can be harvested by means of piezoelectric energy harvesters via the *direct piezoelectric effect*.[7-9] As a result, piezoelectric energy harvesters are promising candidates for providing electrical energy to low-power sensor networks and wearable electronic devices.

As a key component of a piezoelectric energy harvester are the piezoelectric materials themselves, which play an important role in determining the output performance of an energy harvester. To assess the ability of a piezoelectric material with respect to sensing and energy harvesting performance, the *piezoelectric voltage coefficient* (g_{ij}) and *piezoelectric energy harvesting figure of merit* (FoM_{ij}) have been developed, respectively. These can be defined by the following two equations when used in classical 33-mode, where the applied force is parallel to the polarization direction:[10, 11]

$$g_{33} = \frac{d_{33}}{\varepsilon_{33}^{T}\varepsilon_0} \quad (1)$$

$$FoM_{33} = \frac{d_{33}^{2}}{\varepsilon_0\varepsilon_{33}^{T}} \quad (2)$$

Where g_{33} is the piezoelectric voltage coefficient, d_{33} is the longitudinal piezoelectric charge coefficient, ε_{33}^{T} is the relative permittivity at constant stress, ε_0

is the permittivity of free space, and FoM_{33} is the energy harvesting figure of merit. It can be concluded from the above two equations that a high piezoelectric charge coefficient and low relative permittivity is beneficial for applications related to both sensing (high g_{33}) and energy harvesting (high FoM_{33}).

While ferroelectric based piezoelectric ceramics, such as barium titanate ($BaTiO_3$)[12] and lead zirconate titanate (PZT)[13], have been widely used for piezoelectric energy harvesting, their high relative permittivity can limit their piezoelectric sensitivity (Eqn. 1) and energy harvesting figures of merit (Eqn. 2). Ferroelectric polymers based on poly(vinylidene fluoride) (PVDF) and its copolymers are attracting interest due to their lightweight nature, excellent mechanical flexibility and biocompatibility.[14-16] However, their low piezoelectric charge coefficient can lead to low output current, which restricts their applications in the field of piezoelectric energy harvesting.[17, 18]

In recent years, porous piezoelectric ceramics and composites have received attention in the piezoelectric sensing and energy harvesting field.[19, 20] It has been demonstrated that the introduction of porosity can significantly reduce the relative permittivity, if the microstructure is designed to maintain a high polarization and high piezoelectric charge coefficient, thereby leading to enhanced piezoelectric sensor sensitivity and a high energy harvesting figure of merit.[21, 22] Shin *et al.* fabricated a porous sandwich structured piezoelectric energy harvester based on $BaZrTiO_3$-$BaCaTiO_3$ (BZCT) ceramics, where a material with a 20 vol% of the porous layer exhibited the highest figure of merit of 4.53 pm^2/N, and was able to generate an output voltage of 3 V.[23] Zhang *et al*. manufactured porous PZT ceramics with aligned porosity and investigated their piezoelectric energy harvesting performance. It was demonstrated that porous PZT ceramics with parallel-connected pores had higher piezoelectric energy harvesting figure of merit compared to porous PZT ceramics with series-connected pores.[24] Moreover, the effect of pore morphology on the piezoelectric energy harvesting performance of a porous BCZT ceramic was evaluated. When compared to porous piezoelectric ceramics with randomly distributed pores, the porous BCZT ceramics with highly aligned pores possessed the highest piezoelectric energy harvesting figures of merit, with a peak power density of 38 μW cm^{-2}.[25] While porous piezoelectric ceramics exhibit superiority with respect to piezoelectric sensing and energy harvesting applications, their low fracture toughness and brittle nature can limit their applications, in particular for high stress or strain applications. Therefore, composites based on porous piezoelectric ceramics have been considered to be promising candidates for piezoelectric energy harvesting applications.[26-28] Hao *et al.* fabricated a flexible piezoelectric energy harvester consisting of a piezoelectric $0.2Pb(Zn_{1/3}Nb_{2/3})O_3$–$0.8Pb(Zr_{1/2}Ti_{1/2})O_3$ (PZN–PZT) skeleton which was infilled with a flexible polydimethylsiloxane (PDMS) polymer. The output voltage and current density were ~25 V and ~170 nA /cm^2, respectively.[29] Subsequently, Yan *et al.* developed a novel flexible pillar-base structured piezoelectric energy harvester based on porous BCZT ceramics containing highly aligned porosity which was impregnated with PDMS. The maximum output voltage and current reached 30.2 V and 13.8 μA, respectively, with a maximum power density of 96.2 μWcm^{-2}, which provided a novel strategy for the design of porous piezoelectric energy harvester.[30]

Despite these exciting developments in porous piezoelectric ceramics and composites, there is a need to optimize the structural design to further improve the piezoelectric output performance. Recently, multi-layer piezoelectric energy harvesters have attracted attention, since piezoelectric elements which are electrically connected in parallel can lead to a significantly enhanced output current.[31-33] Zhou *et al*. produced a multi-layered piezoelectric composite nanogenerator using three-dimensional interdigitated electrodes. The four-unit piezoelectric nanogenerator was able to generate a maximum output voltage of 20 V and a high output current density of 3.75 $\mu A/cm^2$.[34] Yu *et al.* fabricated a multi-layer piezoceramic energy harvester with three-dimensional embedded electrodes via tape casting. The multi-layer piezoelectric energy harvester was used in a cantilever configuration and was able to generate a high output current density of 254 $\mu A/cm^2$.[35] Their encouraging results demonstrate that the construction of multi-layer structure can significantly improve the output performance of piezoelectric energy harvesters.

In this paper, porous piezoelectric $Ba_{0.85}Ca_{0.15}Ti_{0.9}Zr_{0.1}O_3$ (BCZT) ceramics with a highly aligned pore structure were fabricated via a water-based freeze casting method. Porous BCZT ceramics were selected since they are lead-free and environmentally-friendly, where high piezoelectric coefficients have been reported ($d_{33} \sim 620$ pC N^{-1}).[36] Three-dimensional intercalation electrodes were inserted between the porous piezoelectric layers to create a new form of multi-layer porous piezoelectric energy harvester, where the aligned pore structure was infilled with a flexible PDMS polymer into the pore channels to obtain a piezoelectric energy harvester with suitable toughness. The effect of the number of layers and their geometry of the porous piezoelectric ceramics on the dielectric, piezoelectric properties and piezoelectric energy harvesting performance was evaluated in detail. As a result of the multi-layer structure, the piezoelectric energy harvesting figures of merit and output current were significantly enhanced. The four-layer infilled porous piezoelectric energy harvester exhibited a maximum output power density of 209 μW cm^{-2}, and the piezoelectric energy harvester can be used to charge capacitors, illuminate LEDs or supply power for electronic devices. Moreover, the novel design can be used as a sensor to detect force or human motions. This work therefore provides a new strategy to enhance the output performance of piezoelectric energy harvesters based on advanced composites composed of porous piezoelectric materials.

2. Results and discussion

The fabrication process of the multi-layer porous piezoelectric composite is shown in **Fig. 1**a, and detailed information is provided in the Experimental Section. Firstly, a BCZT ceramic suspension with a solid loading of 30 vol.% was prepared, which was composed of deionized water, BCZT ceramic powders and additives, as shown in **Fig. 1**a (i). Then, the suspension was poured into a cuboid PDMS mold and placed on a cold-hot plate, followed by a cooling at a rate of 10 °C/min to -100 °C, as shown in **Fig. 1**a (ii) and (iii). The freezing direction is from the lower section to the upper section of the mold, where aligned ice crystals grow along the thickness direction during the freezing process. Aligned lamellar pore channels were then formed after the sublimination of ice crystals and following sintering process, see **Fig. 1**a (iv) and Fig. S1. Subsequently, the sintered porous BCZT ceramics were cut into 1 mm thickness ceramic wafers, and the wafers were stacked and bonded together with three-dimensional intercalation electrodes to form a multi-layer structure, as shown in **Fig. 1**a (v) and (vi). Finally, PDMS was infiltrated into the aligned pore channels of the multi-layer porous BCZT ceramics and conductive wires were connected to the electrodes to create a multi-layer porous piezoelectric composite based energy harvester; see **Fig. 1**a (vi) and **Fig. 1**b. An optical image of porous BCZT wafer is presented in **Fig. 1**c, and the calculated porosity is approximately 60 vol.% according to the Archimedes' method, with an error of ± 2.0 vol.%. **Fig. 1**d shows the optical image of the four-layer porous piezoelectric composite energy harvester. The microstructure and cross-sectional morphology of the four-layer porous BCZT ceramics are shown in **Fig. 1**e, f and g. Four porous BCZT ceramic layers and silver electrode layers can be clearly observed from **Fig. 1**e. Moreover, the layers were well bonded to each other to form a porous multi-layer structure, with no obvious defects or delaminations observed. Enlarged views of porous BCZT ceramic layer are presented in **Fig. 1** f and g, where a highly aligned pore structure can be seen in each layer of porous BCZT ceramic, which can be attributed to the slower cooling rate during the freezing process.[37] Furthermore, Energy Dispersive Spectroscopy (EDS) mapping of the multi-layer porous BCZT ceramic was used to detect the elemental distribution. It can be seen that the Ba, Ca, Zr, Ti and O elements are enriched and homogeneously distributed in the four porous piezoelectric ceramic layers. Moreover, the Ag element is uniformly distributed in the electrode layer and is not dispersed in the ceramic layer. Fig. S2 shows the morphology of the porous piezoelectric composite, where it can be observed that the PDMS is fully infilled and impregnated into the aligned pore channels due to the low viscosity and high flow behavior of the PDMS prior to curing. The EDS mapping results indicate that Ba, Ca, Zr and Ti elements are homogeneously distributed in the BCZT ceramics, and Si is enriched in the pore channels, demonstrating the successful penetration of PDMS into the aligned pores. A thermogravimetric analysis was conducted to further confirm the content of the BCZT/PDMS composite framework. It can be seen from Fig. S3 that the weight loss is approximately 14.9%, and the calculated volume fraction of the BCZT ceramic is approximately 50 vol.%, while the measured porosity is approximately 60 vol.%. The higher volume fraction of BCZT ceramics obtained by thermogravimetric testing can be ascribed to the incomplete pyrolysis of PDMS polymer; it has been demonstrated that PDMS cannot be fully burnt out, and some silicon-based oxides or carbides can be formed during the pyrolysis process.[38, 39] Therefore, the residual mass is higher than that of the pure BCZT ceramics. The above results demonstrate the successful fabrication of multi-layer porous piezoelectric composite energy harvester.

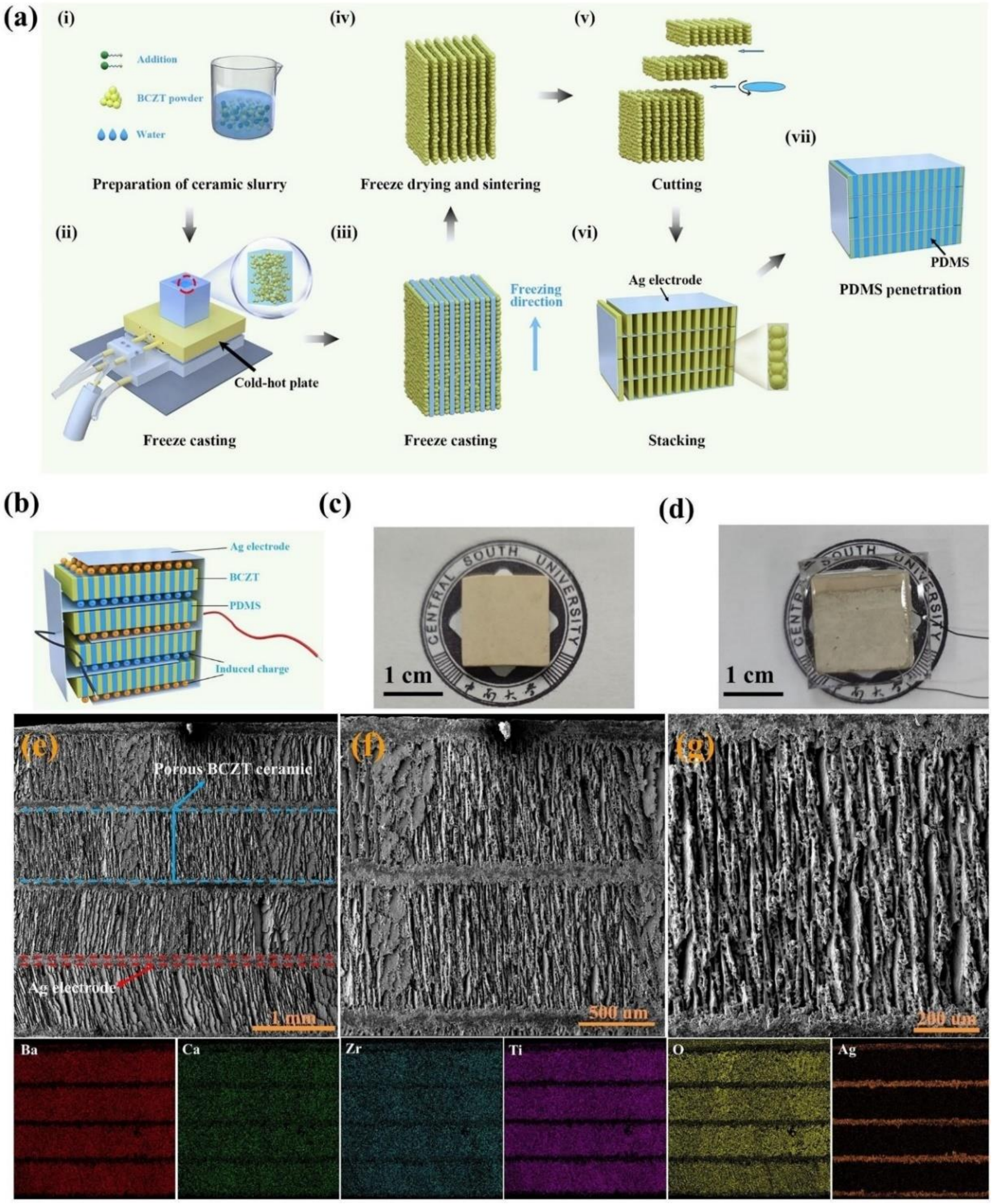

Fig. 1. (a) Illustration for the fabrication process of the multi-layer porous piezoelectric composite. (b) Schematic of the multi-layer piezoelectric energy harvester. Photographs of (c) 1 mm thickness of porous BCZT wafer and (d) four-layer porous piezoelectric composite energy harvester. (e) Morphology of four-layer porous BCZT ceramics. (f) and (g) Enlarged views of porous BCZT ceramic layer and EDS mapping results of the representative elements of four-layer porous BCZT ceramics.

The dielectric properties of the multi-layer porous piezoelectric composites are now characterized. As shown in **Fig. 2**a, the capacitance of the multi-layer porous piezoelectric composites measured at 1 kHz increases almost linearly with an increase of the number of porous ceramic layers. The relative permittivity of a single porous BCZT ceramic layer is approximately 950, which is significantly lower than that of dense BCZT ceramics (~2900), due to the presence of porosity**,** see Fig. S4. The relative permittivity maintains almost unchanged with increasing number of porous ceramic layers, which can be ascribed to the three-dimensional intercalation electrodes forming a parallel connected structure within the multi-layer porous piezoelectric composite. The AC impedance of the multi-layer porous BCZT ceramics is also characterized, where it can be seen from **Fig. 2**b that the impedance of all the samples decreases with an increase of frequency due to the capacitive nature of the material. The impedance decreases from 1.8 MΩ to 350 kΩ with increasing layers of porous ceramic, and the significantly reduced impedance is related to the increase in capacitance of the multi-layer porous BCZT ceramics with number of layers, since $Z=1/(2\pi fC)$, where f is the measurement frequency.[40] The reduced impedance of the multi-layer piezoelectric energy harvester is beneficial to impedance matching in practical applications.[41, 42] The ferroelectric polarization-electric field (P - E) hysteresis loops of a porous BCZT ceramic layer with a porosity of 60 vol.% is shown in Fig. S5. It can be observed that that the shape of hysteresis loops was symmetrical and the maximum polarization could reach 5.5 μC cm^{-2}, demonstrating a good ferroelectric response. As shown in **Fig. 2**c, the effective piezoelectric charge coefficient d^*_{33} almost increases linearly when the porous BCZT ceramic layers increase from 1 to 3, while it increases more slowly with the further increase of porous BCZT ceramic layers. The effective piezoelectric voltage coefficient g^*_{33} also shows the same trend due the increased effective piezoelectric charge coefficient d^*_{33}. Furthermore, it can be seen from **Fig. 2**d that the effective piezoelectric energy harvesting figure of merit (FoM^*_{33}) significantly increases with increasing porous BCZT ceramic layers due to the enhanced piezoelectric charge coefficient and the reduced relative permittivity relative to the dense material. These results demonstrate that the construction of multi-layer porous piezoelectric composite is beneficial for the piezoelectric properties and piezoelectric energy harvesting performance.

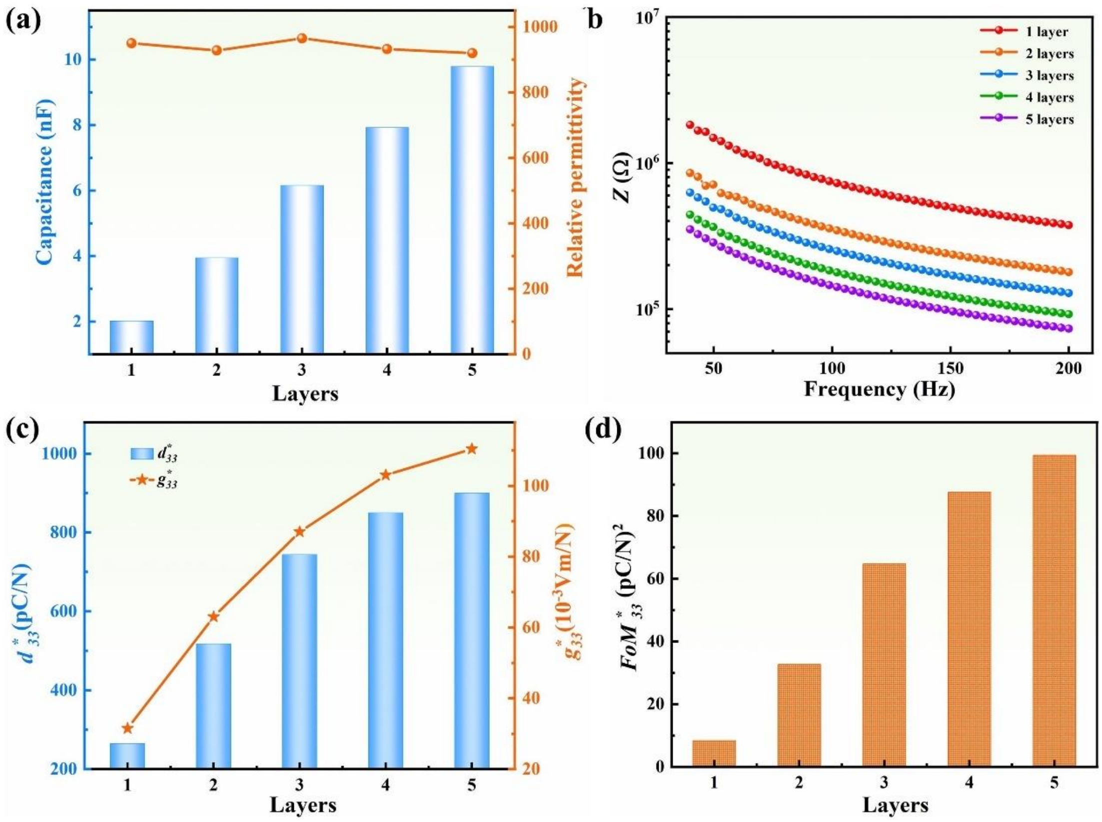

Fig. 2. (a) Capacitance and relative permittivity of multi-layer porous piezoelectric composites. (b) AC impedance measured from 40 to 200 Hz. (c) Effective piezoelectric

charge coefficient d^*_{33} and piezoelectric voltage coefficient g^*_{33}. (d) Effective piezoelectric energy harvesting figures of merit FoM^*_{33}.

The energy harvesting performance of the multi-layer porous piezoelectric composites is now systematically investigated. As shown in **Fig. 3**a, the output voltage measured with a force of 10 N at 2 Hz slightly increases with an increase of porous BCZT ceramic layers and then begins to decrease. The output voltage of the multi-layer porous piezoelectric energy harvester can be described by equation 5. If the force (F) applied to the piezoelectric multi-layer, the generated charge (Q) is given by

$$Q = Nd_{33}F \tag{3}$$

where d_{33} is the piezoelectric charge coefficient of a single-layer porous piezoelectric ceramic and N is the number of layers.

The capacitance of the piezoelectric multi-layer can be expressed as[43]

$$C = \frac{NA\varepsilon_{33}^{T}\varepsilon_0}{t} \tag{4}$$

where ε_{33}^{T} and ε_0 is the relative permittivity and the permittivity of free space, respectively, A is the electrode area of each layer, and t is the thickness of a single layer.

The open-circuit voltage (V_{oc}) of the piezoelectric multi-layer harvester generated from the applied stress can therefore be written by equation (5).

$$V_{oc} = \frac{Q}{C} = \frac{d_{33}t}{A\varepsilon_{33}^{T}\varepsilon_0}F \tag{5}$$

Based on equations (4) and (5), the energy (E) stored in the piezoelectric multi-layer capacitor can be given by

$$E = \frac{1}{2}CV_{oc}^2 = \frac{Ntd_{33}^2}{2A\varepsilon_{33}^{T}\varepsilon_0}F^2 \tag{6}$$

It can be seen that the induced charge Q can be enhanced by N times, where N is number of layers, and the capacitance of the multi-layer piezoelectric energy harvester will also be increased by N times. Since $V = Q / C$, the output voltage will remain unchanged with a change in the number of layers.[44] However, the measured output voltage slightly increases with an increase in the number of layers, which can be attributed to the enhanced surface polarization charges induced by introduction of three-dimensional intercalation electrodes.[45] The output current of multi-layer porous piezoelectric energy harvester is shown in **Fig. 3**b, where it can be observed that the output current increases almost linearly when the porous BCZT ceramic layers increases from $N = 1$ to $N = 4$, then begins to decrease. Since $I = dQ / \mathrm{dt}$, the output current is related to the piezoelectric charge coefficient d_{33} and number of layers, see equation 7 and **Fig. 2**c, where the short circuit current of piezoelectric multi-layer harvester is given by

$$I_{sc} = \frac{Q}{\Delta t} = \frac{Nd_{33}}{\Delta t}F \quad (7)$$

where Δt is the time of induced charge.

Thus, the output current is enhanced due to number of layers and the increased effective piezoelectric coefficient of the multi-layer porous piezoelectric energy harvester.[46] However, the output current of five-layer porous piezoelectric energy harvester slightly decreases, as shown in **Fig. 3**b, which may be ascribed to the external force buffering effect generated by the PDMS polymer and soft silver epoxy electrodes inside the multi-layer piezoelectric energy harvester with an increase of layers.[35, 47] The output voltage and current of the four-layer porous piezoelectric energy harvester under various external force is now evaluated. It can be observed from **Fig. 3**c and **Fig. 3**d that the output voltage and current of the four-layer porous piezoelectric energy harvester increases when the external force increases from 2 N to 10 N, exhibiting a linear trend with increasing force, see Fig. S6. The maximum output voltage and current of the four-layer porous piezoelectric energy harvester could reach 21 V and 80 μA, respectively. The output voltage and current of the 1-laye, 2-layer, 3-layer and 5-layer composites are also presented in **Fig.** S6. All composites show an increasing output voltage and current with an increase of external force, indicating that the output voltage and current are the results of piezoelectric effect rather than a triboelectric effect and this is in agreement with Equations 5 and 7. A polarity-switching test was further conducted to confirm that the output signal is originated from the piezoelectric effect. As shown in **Fig. 3**e, the signal direction of the output voltage was inverted by reversing the electrodes connection, demonstrating that the output signal is due to the piezoelectric effect, which is consistent with previous reports.[48-50] In practical applications, the stability of the piezoelectric energy harvester is also important. A cycling mechanical vibration test was carried out to evaluate the reliability and durability of the four-layer porous piezoelectric energy harvester by applying a cyclic vertical compressive force of 10 N at a frequency of 2 Hz. It can be seen from **Fig. 3**f that the output voltage remains almost stable after 3000 cycles, indicating the excellent mechanical stability and durability.

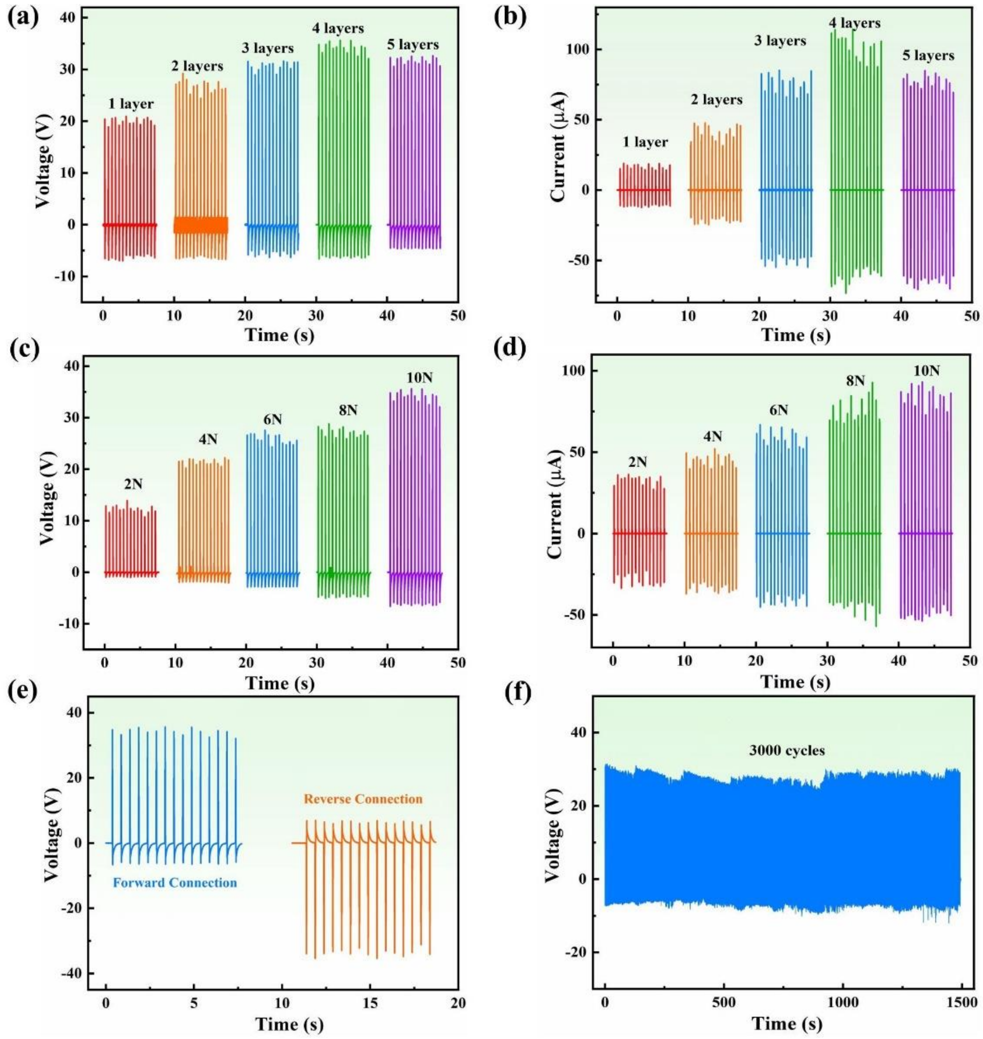

Fig. 3. (a) Output voltage measured under the force of 10 N at 2 Hz. (b) Output current measured under the force of 10 N at 2 Hz. (c) Output voltage of four-layer porous piezoelectric energy harvester. (d) Output current of four-layer porous piezoelectric energy harvester. (e) Output voltage of four-layer porous piezoelectric energy harvester in forward or reverse connection mode. (f) Reliability test of four-layer porous piezoelectric energy harvester within 3000 cycles.

The working mechanism of the multi-layer porous piezoelectric composite energy harvester is illustrated in **Fig. 4**a. It can be seen that the porous piezoelectric ceramic layer is sandwiched by a pair of silver electrodes, and the adjacent infilled porous piezoelectric ceramic layers share the same common electrode. The ferroelectric dipoles are randomly distributed in unpolarized piezoelectric ceramics, and the dipoles tend to align in the direction of applied electric field. Moreover, the electric dipoles are aligned in opposite direction for adjacent porous BCZT ceramic layers due to the construction of three-dimensional intercalation electrodes, see these red and blue arrows in **Fig. 4**a. When an external force is applied to the multi-layer porous piezoelectric energy harvester, the polarization is reduced as the diploes are compressed along the thickness direction and piezoelectric charge is generated which generates a potential difference. As a result, a current is generated in each porous piezoelectric ceramic layer to balance the electric potential difference. The current generated by each porous piezoelectric ceramic layer is combined to form a larger output current due to the parallel structure formed by three-dimensional intercalation electrodes. On removal of the force, the polarization and electrical dipoles return to their original state, and a reversed current is generated in order to maintain the electrical balance. Therefore, a large output current can be generated in the multi-layer porous piezoelectric energy harvester. **Fig. 4**b and **Fig. 4**c show the output voltage and current as a function of load resistance that ranges from 10 kΩ to 100 MΩ. It can be observed that the output voltage increases with increasing load resistance for all the multi-layer porous piezoelectric energy harvesters, while the output current decreases with the increase of load resistance since current flow is restricted. The output power density initially increases with increasing load resistance, and then begins to decrease at a higher load resistance for all the composites. The maximum output power density is obtained at an optimal load resistance where the impedance of the electrical load is matched to that of the harvester; namely the condition $R_{opt}=1/2\pi fC$, where f is the frequency, and C is the capacitance of the multi-layer porous piezoelectric energy harvester. As shown in **Fig. 4**d and **Fig. 4**e, the output power density increases first with increasing layers of porous BCZT ceramic layers then begins to decrease. The four-layer porous piezoelectric energy harvester possesses the maximum power density of 209 $\mu W\ cm^{-2}$, which is seven times higher than that of a single layer porous piezoelectric energy harvester. The corresponding optimal load resistance decreases from 1 MΩ to 300 kΩ, which is consistent with the results of impedance in **Fig. 2**b. These results demonstrate that the construction of multi-layer structure can significantly reduce the resistance of piezoelectric energy harvesters, which is beneficial for their practical applications. Furthermore, the output performance of the multi-layer porous piezoelectric energy harvester was compared with other piezoelectric composite based energy harvesters. As shown in **Table 1**, the output current is higher than other lead-free based piezoelectric composite energy harvesters, and the output power density is also high. Compared with 0-3 type piezoelectric composites, porous piezoelectric composite with aligned pore structure possessed improved piezoelectric properties and stress transfer capability. [30] The output performance is further enhanced due to the design of a multi-layer structure and three-dimensional intercalation electrodes, thereby demonstrating that multi-layer porous piezoelectric composites exhibit significant potential for piezoelectric energy harvesting applications.

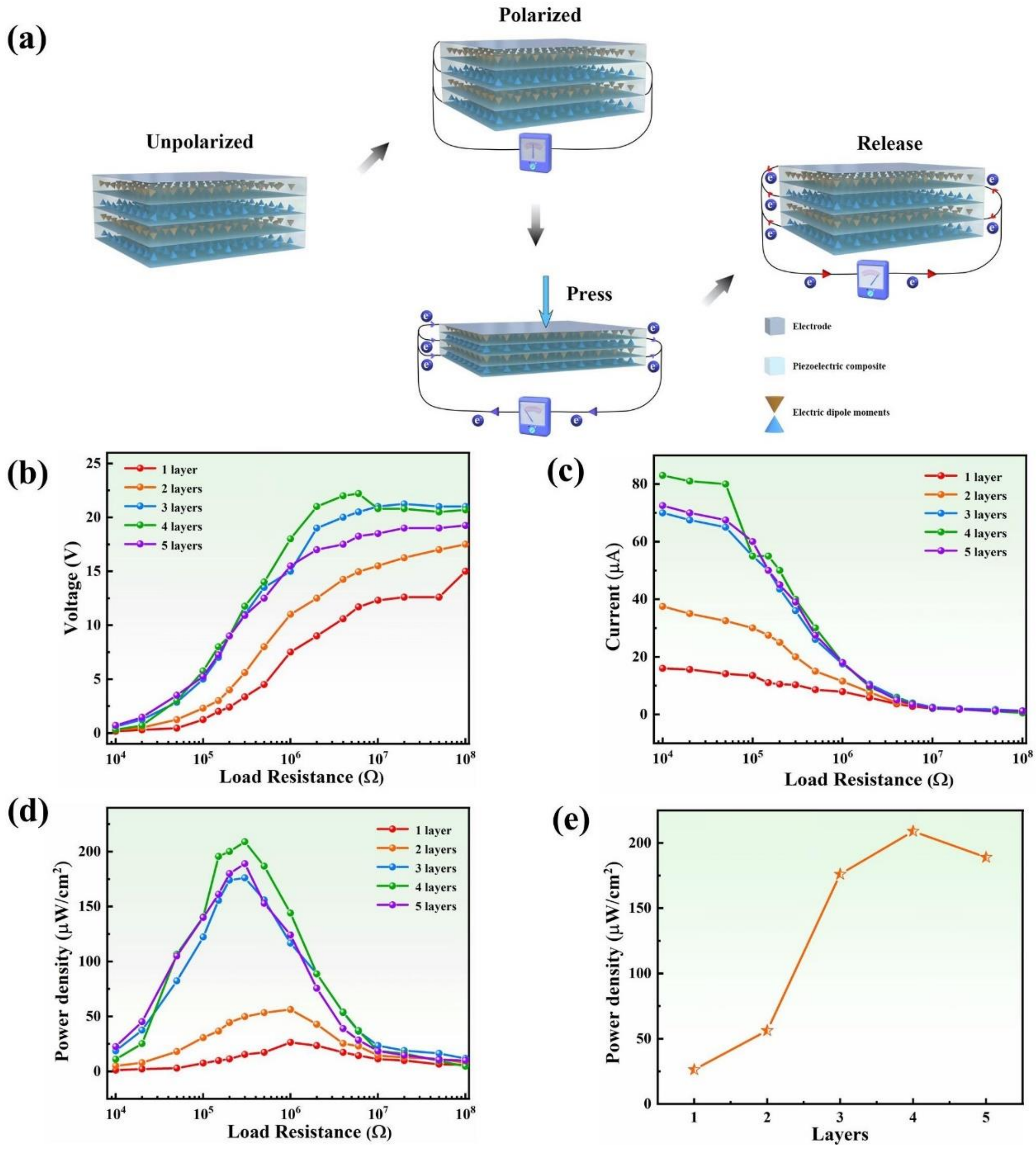

Fig. 4. (a) Working mechanism of multi-layer porous piezoelectric energy harvester. (b) Output voltage with load resistance. (c) Output current with load resistance. (d) Output power density with load resistance. (e) Output power density as a function of porous BCZT ceramic layers.

Table 1. Output performance comparison of piezoelectric composite based energy harvesters

Piezoelectric fillers	Polymer matrix	Voltage (V_{oc}, V)	Current (I_{sc}, μA)	Power density (μW/cm^2)	Refs
BTS-BCT	PDMS	39	2.9	6.1	[51]
BCZT	PDMS	25	0.55	2.6	[26]
BLF-PT	PI	110	0.31	-	[52]
BF	PDMS	16	2.8	3.11	[48]
PMN-PT	PDMS	60	0.85	11.5	[27]
SM-KNN	PVDF	21	22	115.5	[53]
Tb-BCZT	PVDF	48.5	3.35	8.1	[54]
KNN	PDMS	98	3.2	22.5	[55]
$CsPbX_3$	PDLLA	93	65	25.2	[56]
BF-BT	PI	175	0.6	24.6	[57]
BCZT	PDMS	30.2	13.8	96.2	[30]
$FAPbBr_3$	PVDF	26.2	2.1	18.4	[58]
BCZT	**PDMS**	**21**	**80**	**209**	**This work**

Piezoelectric energy harvesters can be used as energy sources to charge capacitors or supply power for low-power electronic devices. As shown in **Fig. 5**a, the AC electrical signal generated by the multi-layer porous piezoelectric energy harvester under an external force of 10 N at 2 Hz can be converted into DC electric signal via a rectifier circuit. The output voltage signal after rectifying can be seen in Fig. S7. The rectified output signal can be used to illuminate LEDs, charge capacitors and be an energy source for low-power electronic devices. The four-layer porous piezoelectric energy harvester was employed to charge a 10 μF capacitor in order to evaluate the charge storing capability. It can be observed from **Fig. 5**b that the charging voltage increases rapidly and then begins to saturate. The 10 μF capacitor can be charged to 4.0 V in 150 s, and the calculated charge rate can reach 400 nC per cycle, see **Fig. 5**c. Moreover, the charging curve of a single layer porous piezoelectric energy harvester charging a 10 μF capacitor is shown Fig. S8. The charging voltage reaches to 0.8 V in 150 s, and the corresponding charging rate is 60 nC per cycle. As a result, the charging rate of a four-layer porous piezoelectric energy harvester is approximately six times faster than that of a single layer porous piezoelectric energy harvester, which can be attributed to the high output current and faster charging rate due to the construction of the three-dimensional intercalation electrodes. Again, an excellent fast-charging rate demonstrates the high potential of multi-layer piezoelectric energy harvester in practical applications.[59] In addition, the multi-layer porous piezoelectric energy harvester can operate low-power electronics after storage in capacitors. **Fig. 5**d shows the charging-discharging curve of a 10 μF capacitor utilized to drive a commercial stopwatch. After charging the 10 μF capacitor for approximately 180 s, the charging voltage can turn on the stopwatch for a period; see Video S1 in the Supporting Information. Moreover, it can be seen from **Fig. 5**e that the multi-layer porous piezoelectric energy harvester can instantaneously illuminate 12 blue LEDs arranged in series. The above results demonstrate that the multi-layer porous piezoelectric energy harvester can supply power for electronic devices in practical applications.

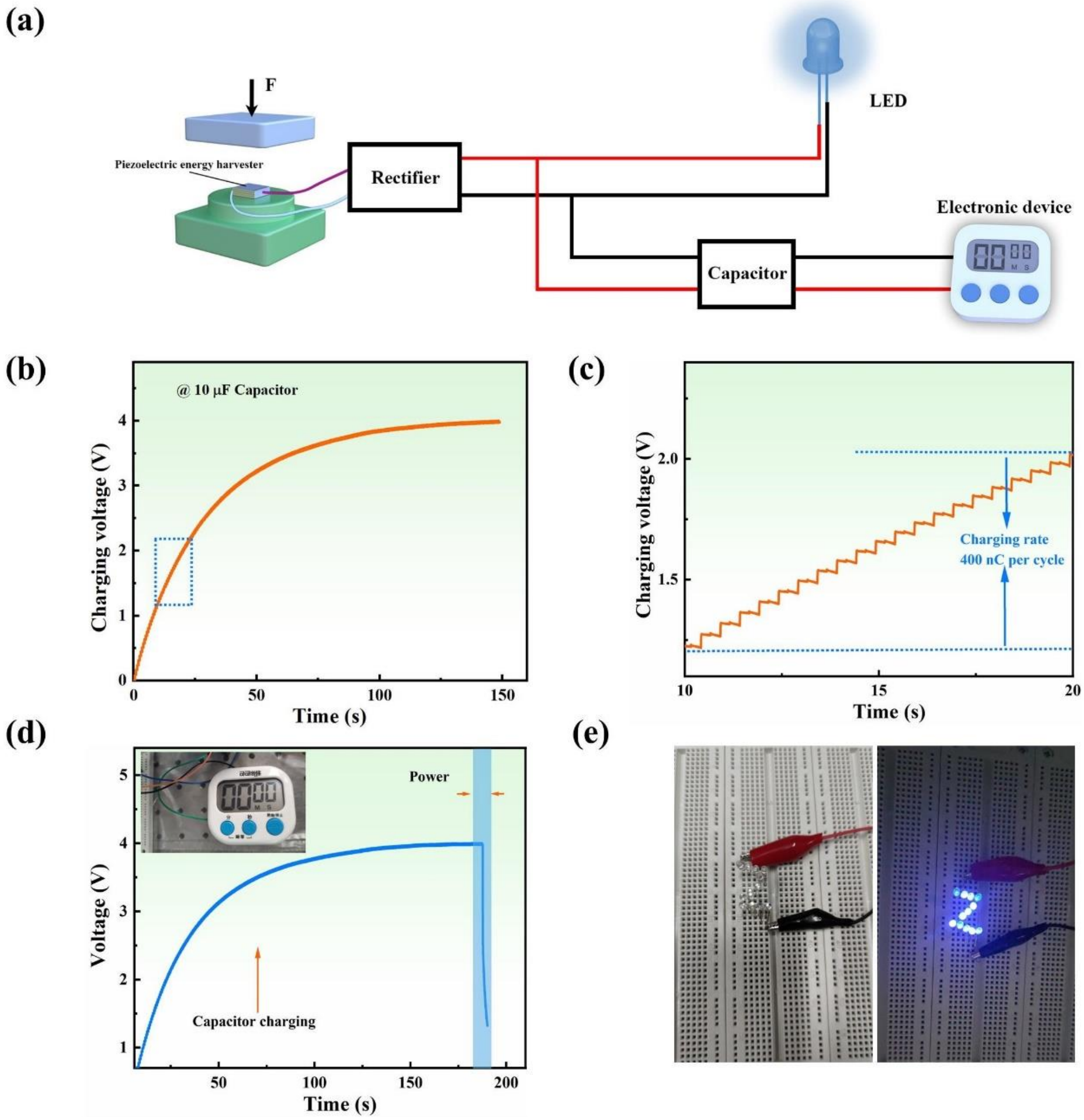

Fig. 5. (a) Schematic of commercial electronics devices and LEDs operated through the energy harvested from the multi-layer porous piezoelectric energy harvester. (b) Time dependent charging curves of four-layer porous piezoelectric energy harvester for the capacitor of 10 μF. (c) Zoomed-in view of the charging curve of 10 μF from 10 s to 20 s. (d) Photograph and the charging-discharging curve of the 10 μF capacitor while operating a stopwatch from the harvested energy of a four-layer porous piezoelectric

energy harvester after storage. (e) Photograph of 12 blue LEDs illuminated by electrical energy generated by four-layer porous piezoelectric energy harvester.

Piezoelectric energy harvesters can harvest mechanical energy from our living environment, such as sound waves, vibration of vehicles and human motions. Moreover, they can also operate as self-powered sensors to detect acceleration, force and strain. Harvesting mechanical energy from human motions or detecting human body movements, such as finger tapping, fist beating and foot stamping, have great potential in practical applications. Piezoelectric energy harvesters can convert various human motions into electric signal; thus, they can be attached to different human parts to detect the associated human movements or harvest mechanical energy, as shown in **Fig. 6**a. **Fig. 6**b shows the output voltage of a four-layer porous piezoelectric energy harvester under slight finger tapping. It can be seen that the measured output voltage could reach about 2.3 V. As shown in **Fig. 6**c, an output voltage of ~ 14 V was generated under human fist beating. Moreover, the four-layer porous piezoelectric energy harvester can be attached to human foot and can produce an output voltage of ~ 20 V under foot stamping, as shown in **Fig. 6**d. These results demonstrate that the multi-layer porous piezoelectric energy harvester can not only be used to harvest mechanical energy from human movements, but also can be used to sense various human motions. Furthermore, the proposed multi-layer porous piezoelectric energy harvester can also be used as a weight sensor by dropping small objects. As shown in **Fig. 6**e, the voltage response of 6.3, 19.1 and 24.4 V was obtained when a 100 g weight falls from the heights of 2, 4 and 6 cm, respectively, demonstrating the potential of working as a pressure sensor. Therefore, the above results clearly confirm that the multil-ayer porous piezoelectric energy harvester can be used to harvest mechanical energy and detect external force.

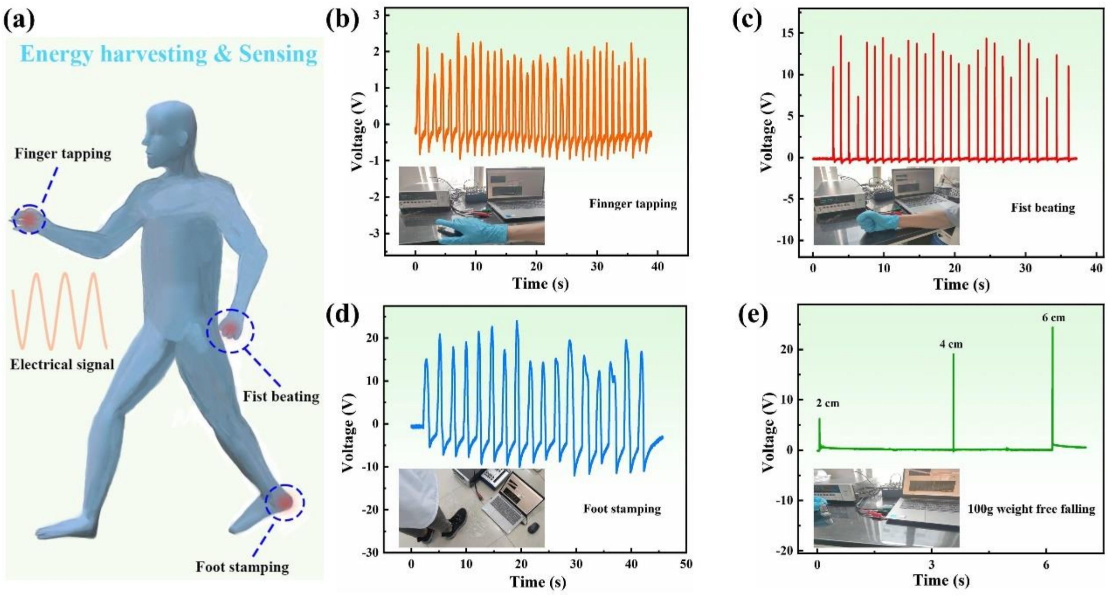

Fig. 6. (a) Schematic showing the application of four-layer porous piezoelectric energy harvester as wearable sensor. (b) Output voltage response by light finger tapping. (c) Output voltage during fist impact. (d) Output voltage response due to foot stamping. (e) Output voltage response of a 100 g weight falls from the heights of 2, 4 and 6 cm.

3. Conclusion

This paper has developed a new form of multi-layer porous piezoelectric energy harvester that is based on porous $BaZrTiO_3$-$BaCaTiO_3$ (BCZT) ceramics, where the pore space is impregnated with a flexible polydimethylsiloxane (PDMS) polymer to provide mechanical toughness. Porous BCZT ceramics with highly aligned pore channels were fabricated by a water-based freeze casting method, with the porosity of 60 vol.%. A multi-layer porous piezoelectric energy harvester then was designed by the introduction of three-dimensional silver intercalation electrodes. The effect of porous BCZT ceramic layers on the dielectric, piezoelectric properties and piezoelectric energy harvesting performance was investigated in detail. The introduction of highly aligned pore structure is shown to significantly reduce the relative permittivity compared to the dense material. The effective piezoelectric charge coefficient increases with an increase in the number of porous ceramic layers, leading to greatly enhanced efficient piezoelectric energy harvesting figures of merit. While the output voltage remains relatively unchanged, the output current increases almost linearly with increasing porous layers. The maximum output voltage and current generated by a four-layer porous piezoelectric energy harvester was 21 V and 80 μA, respectively, with a maximum output power density of 209 μW cm^{-2}; this is significantly higher than other porous piezoelectric materials reported to date. The generated electricity can charge a 10 μF capacitor from 0 V to 4.0 V in 150 s and illuminate 12 blue LEDs. Moreover, the four-layer porous piezoelectric energy harvester is demonstrated to power a stopwatch and the porous piezoelectric energy harvester is also shown to be able to sense and harvest energy from human movements. This work therefore provides a novel design approach to create high-performance piezoelectric energy harvesters based on porous piezoelectric materials.

4. Experimental Section

4.1 *Fabrication of porous BCZT ceramics with highly aligned pore structure*

Porous BCZT ceramics were fabricated via a freeze casting method. BCZT powders (d_{50} =1.0 μm), synthesized by a solid-state reaction technique, were used as raw materials. A ceramic suspension consisting of deionized water, BCZT powders, 1 wt% polyvinyl alcohol (99%, Sinopharm) and 1 wt% ammonium polyacrylate (HydroDisper A160, Shenzhen Highrun Chemical Industry Co. Ltd, P. R. China) was prepared and ball milled for 24 h. After the removal of air bubbles, the suspension was poured into a PDMS mold with dimensions of 2×2×3 cm^3. Then, the PDMS mold with the suspension was placed onto the hot-cold plate (INSTEC, USA) and cooled to -100 °C with a cooling rate of 10 °C/min and maintained at this temperature for 30 min. The frozen samples were freeze-dried under the vacuum of 1 Pa at -25 °C for 48 h to sublimate the ice template and was subsequently sintered at 1350 °C for 3 h to obtain porous BCZT ceramics with an aligned pore structure.

4.2 *Fabrication of multi-layer porous piezoelectric composite energy harvester*

The sintered porous BCZT ceramics were cut into thin wafers with the thickness of 1 mm. Then, the thin wafers were poled under the voltage of 15 kV for 30 min using a corona poling technique. Silver epoxy was selected as the three-dimensional intercalation electrodes, and the porous piezoelectric layers were stacked and bonded by silver epoxy to fabricate multi-layer porous piezoelectric ceramic. Subsequently, a PDMS precursor and curing agent with the weight ratio of 10:1 was prepared and impregnated into the pore channels to form a multi-layer piezoelectric composite energy harvester.

4.3 *Characterization and measurements*

The porosity of porous BCZT ceramics was measured by the Archimedes' method.

The microstructure and surface morphology of porous BCZT ceramics and composite were observed by field emission scanning electron microscopy (FESEM, NovaNanoSEM230, USA). The capacitance and impedance of the porous piezoelectric ceramics with different layers were characterized by Precision Impedance Analyzer (4294A; Agilent Technologies, Santa Clara, USA). The polarization-electric field (*P-E*) loops were measured by a TF Analyzer 3000 (AixACCT systems, Germany). The d_{33} piezoelectric charge coefficient was characterized by a piezoelectric d_{33} meter (ZJ-4AN, Institute of Acoustics, Academic Sinica, China). The piezoelectric energy harvesting performance of the multi-layer porous piezoelectric composite was evaluated by a linear stepping motor testing system. Various periodic compressive stresses of 2, 4, 6, 8 and 10 N at a specific frequency of 2 Hz were applied, and the output voltage and current were measured by a Keithley 7510 electrometer.

CRediT authorship contribution statement

Yan Mingyang: Conceptualization, Experiment, Investigation, Writing - original draft. Liu Shengwen: Experiment, Investigation. Xu Qianqian: Experiment, Software. Xiao Zhida: Investigation, Software. Yuan Xi: Conceptualization. Zhou Kechao: Conceptualization, Supervision. Zhang Dou: Writing - review & editing. Wang Qingping: Conceptualization, Investigation. Chris Bowen: Writing - review & editing. Zhong Junwen: Supervision, Writing - review & editing. Zhang Yan: Supervision, Conceptualization, Writing - review & editing.

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Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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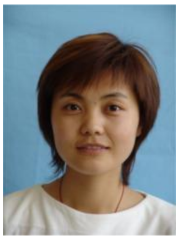

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