Ultrahigh flexoelectricity of 3D interconnected porous PDMS and its application as flexible passive sensors

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ABSTRACT

Non-conductive materials have the property of flexoelectricity, which means they can generate electricity when bent and twisted. However, a small scale irregular shape or a peculiar load has been the necessary condition, and the weight-specific ratios of flexoelectricity are limited. Here, we report the ultrahigh flexoelectric response of porous polydimethylsiloxane (PDMS). The porous PDMS with 3D micron-scale interconnected structures exhibits two orders of magnitude higher weight-specific flexoelectric response than that of solid PDMS. Due to diverse and irregular internal micro-structures, the porous materials can exhibit flexoelectricity under arbitrary loading forms. The flexoelectric signal was found linearly proportional to the applied strain, the microstructural size and the frequency, which makes porous material promising for flexible, ultralight, sensitive and multi-functional passive sensor applications without external applied electric power. Our work highlights the new potential of porous structured materials with remarkable flexoelectric
effect in sensing, actuating, energy harvesting, and biomimetics as light-weight materials.

**Introduction**

Flexoelectricity represents the linear electro-mechanical coupling effect between strain gradient and electric polarization (the direct effect) or electric field gradient and mechanical stress (the converse effect)(1–3). The flexoelectric effect exists in all dielectrics without symmetry requirement(4, 5) and it is proportional to the strain gradient. Therefore, the flexoelectricity is expected to be more significant in nanomaterials compared with macroscopic materials since the strain gradient is inversely proportional to the structure size(6, 7). Significant flexoelectric effect has been observed in ferroelectrics(8, 9), polymers(10, 11), bone mineral(12, 13) and semiconductors(14, 15). The flexoelectricity has demonstrated its broad application prospects in areas of sensing(16, 17), mechanical actuating(18, 19), energy harvesting(20) and high-density data storage(21).

With the extensive applications of flexible electronics and wearable devices, the demand of flexible sensing devices increases fast(22). Flexible polymers have shown their unique advantages in sensing application based on flexoelectric effect due to their softness, flexibility and eco-friendliness. Especially, flexible polymers could realize large elastic deformation, and thus large strain gradients. Hence, lots of researchers have investigated the
flexoelectric effect of flexible polymers, such as the polyurethane (PU)(23), polyethylene terephthalate (PET)(24), polydimethylsiloxane (PDMS)(25) (26) and polyvinylidene fluoride (PVDF)(27), along with flexible polymer/ceramic composites(25). However, the flexoelectric coefficients of flexible polymers are typically three or four orders smaller(23, 28) than those of ferroelectric ceramics like BST(29) and PT(8). Nonetheless, the low density, high flexibility and easiness to fabricate of flexible polymers enable the promising flexoelectricity enhancement through polymer modification(25, 30) or structure design(31, 32).

In most of the researches on flexoelectric effect, the strain gradient is realized by one of the following methods: (1) bending of a thin beam(5, 8); (2) compressing of a truncated pyramid(11, 33); (3) twisting of a cylinder(34); or (4) atomic force microscope probe excitation of a crack(6, 9). Thus, in order to realize the flexoelectric effect of a solid material, one either uses the limited loading form (bending or twisting) or fabricates special geometries to bear various loading forms(35). How to enhance the flexoelectric effect and realize broader applications becomes urgent and essential.

Here, different from the aforementioned traditional structures that have a limited loading form and relatively small strain gradients, the flexible porous PDMS with open pores and ligaments at the length scale at micrometers was utilized for electromechanical coupling measurement
based on flexoelectricity as shown in Fig. 1a and Fig. 1b. This study is inspired by the unique geometry of porous structure, which can bear any loading form and take advantage of its small size effect to enhance the flexoelectric response. The porous structures are composed of a great amount of randomly oriented ligaments, and all kinds of loading forms may produce a considerable strain gradient as schematically illustrated in Fig. 1c. Moreover, the porous structures can be fabricated with a wide range of materials, such as ceramics(36), polymers(22), metals(37) and their corresponding composites(38, 39). Here, the porous PDMS can be cut into any shape macroscopically. When a cubic porous PDMS was compressed to 25% macroscopic strain, it exhibited ca. 100 times larger weight-specific flexoelectric response than a solid truncated pyramid at the specific mass under unit strain. Furthermore, a theoretical flexoelectric effect model of porous microstructure was given for the first time, and the predicted results agree well with the experimental data. This model can be used to design and predict the flexoelectric response of porous materials. And the bending sensors and shock absorption sensors based on porous PDMS were presented, which illustrate great potential for flexible electronic devices. Our findings demonstrate remarkable flexoelectricity enhancement in flexible polymers, which are attractive for flexoelectric device applications.
Results

Porous PDMS sample and its flexoelectricity

The porous PDMS samples with different macroscopic geometries are shown in Fig.1a, which were fabricated by direct templating technique as schematically presented in Fig. S1. Unless otherwise indicated, the macro size of the sample is 2×2×1 mm³. Fig. 1b presents the SEM images of porous PDMS, which illustrates that the samples are consist of 3D interconnected structures with open pores and solid ligaments. Here, two kinds of samples with different pore sizes are named as “large pore” (Fig. 1b, right) and “small pore” (Fig. 1b, left), respectively. The microstructure sizes of the samples are one with pore diameter of 180 μm, ligaments thickness of 50 μm (small pore) and another with pore diameter of 400 μm and ligaments thickness of 75 μm (large pore). Fig. 1c schematically illustrates the majority bending deformation of the internal ligaments when the samples are undergoing various loadings such as tension, compression, bending and torsion. And nonzero net dipole moments (and hence polarization) will be induced due to the relative displacement between the centers of positive and negative charges. The induced flexoelectric polarization along l direction, $P_l$, obeys $P_l = \mu_{ijkl} \frac{d \varepsilon_{ij}}{dx_k}$, where $\mu_{ijkl}$ is the flexoelectric coefficient along l direction of the strain gradient that the elastic strain $\varepsilon_{ij}$ induced along $x_k$ direction. Therefore, regardless of the macro geometry of the sample and the loading form, the remarkable
flexoelectric response can be obtained.

**Ultrahigh flexoelectric response of porous PDMS**

Here, the Gibson-Ashby(41) model was adopted as a unit cell as the left image shown in Fig. 2a, which contains three kinds of beams, namely \( b_1 \) (the beam \( b_1 \) shown in Fig. 2a is half of beam \( b_1 \)), \( b_2 \) and \( b_3 \) with the same dimension (\( L \) and \( \delta \) are the length and width of the beam). In this work, the compressive load was applied on the porous sample as illustrated in the right image of Fig. 2a, in which the displacement analysis of a model with \( 3 \times 3 \times 3 \) unit cells under 15% compression strain using finite element method (FEM) is shown. One can find the large bending deformation of the beams exists in the most top and bottom layers, and thus large strain gradient exists and would contribute to the flexoelectric response. As illustrated in Fig. 2b, the flexoelectric-induced polarization current (left axis) of large pore PDMS and the real-time applied displacement (right axis) display remarkable, repeatable signals, and the current frequency (3 Hz) is highly consistent with that of the applied load. Here, the periodic compression displacement load \( W(t) \) along the vertical direction was applied on the top surface of the cubic sample, which obeys

\[
W(t) = \frac{\lambda_{pp}}{2} - \frac{\lambda_{pp}}{2} \cos 2\pi ft,
\]

where \( \lambda_{pp} \) is the peak to peak displacement value, \( f \) is the frequency and \( t \) represents time. Fig. 2c presents the frequency dependence of the
flexoelectric current of small pore PDMS film (60×15×2.8 mm$^3$) under the applied three point bending macroscopic displacement of 1.5 mm. Similarly as shown in Fig. S2, the flexoelectric output amplitudes increase linearly with the frequency below 3 Hz. Then the output decreases when the frequency is higher than 3 Hz, which behaves similarly to the frequency dependency of ferroelectric ceramic beams(42, 43). This may attribute to the low elastic modulus of porous PDMS since it can hardly follow the high frequency actions. Unless otherwise indicated, periodic applied load of 2 Hz is adopted in this work, and the top and bottom surfaces of the sample are covered with silver conductive electrode. From Fig. 2d one can see that the maximum output current $I_{\text{max}}$ increases linearly with the increasing of the compression strain with both kinds of porous samples, and $I_{\text{max}}$ of small pore PDMS is about 2 times higher than that of the large pore samples. Therefore, as the size of the microstructure decreases, the amplitude of the flexoelectric response increases significantly.

In order to compare the flexoelectric response efficiency of porous PDMS with the bulk PDMS samples, two kinds of truncated pyramid PDMS samples with the same top and bottom square surface ($a_1$=5 mm, $a_2$=10 mm) and different heights (H=6 mm and 8 mm) were fabricated as the inset picture shown in Fig. 3a. A liner relationship can be obtained between the flexoelectric-induced current and the strain gradient of the pyramids samples. The method in Ref. (32) was used to calculate the
longitudinal flexoelectric coefficient $\mu_{1111}$. The measured $\mu_{1111}$ in our experiments is ca. $3.631 \times 10^{-10}$ C/m (the coordinate is the same as that illustrated in Fig. 1c), which agrees with the transverse flexoelectric coefficient $\mu_{1133}=5.3 \times 10^{-10}$ C/m in Ref. (26). This $\mu_{1133}$ value was used in the later numerical analysis. Normally, the PDMS samples might have some electrostatic charges on the surface from the environment during fabrication and storage. The experimental data of the same samples before and after getting rid of the electrostatic charges are shown in Fig. S3, where one can see that those extra charges indeed influence the output results. Thus, an electrostatic eliminator was utilized to get rid of the electrostatic charges before each measurement in this work.

To compare the flexoelectric response efficiency of different kinds of samples, the weight specific effective coefficient ($W_{sec}$) was defined as $W_{sec} = \frac{I_{max}}{m\varepsilon}$, where $I_{max}$, $m$ and $\varepsilon$ represent the maximum induced current, the weight of sample and the applied macroscopic compression strain, respectively. Fig. 3b illustrates $W_{sec}$ of different samples under the applied strain of 25%, and $W_{sec}$ of four different samples at various applied strains are shown in Fig. S4. It can be found that $W_{sec}$ of porous PDMS samples is two orders of magnitude higher than that of the truncated pyramids regardless of the applied strain. And $W_{sec}$ increases when the microstructure size of porous sample decreases.
Theoretical analysis

In order to explore the mechanism of flexoelectric response of porous PDMS and to design the structures with desired flexoelectric polarization, we proposed a theoretical model based on Gibson-Ashby model(41) for porous PDMS as shown in Fig. 2a. The basic element is a beam, which mimics the ligament between two nodes in porous sample with the dimensions as shown in Fig. 1b. There are two major theories for such kind of beam, one is Euler-Bernoulli beam theory and another is Timoshenko beam theory(43). Since the aspect ratio is ca. 4 of the ligament in our samples, Timoshenko beam theory will be utilized here. For the bending beam in Fig. 1c with a concentrated force $F$ on the midpoint, the electric polarization $P$ due to the flexoelectric effect can be calculated as

$$P_y = \mu_{133} \frac{d\varepsilon_{11}}{dz} = \mu_{133} \frac{F \left( \frac{1}{2} - |x| \right)}{EI_y},$$

(1)

where $l$, $b$, $h$ are the length, width and height of the beam, and $E$, $I_y = \frac{bh^3}{12}$ is the Young’s modulus and the moment of inertia of the beam, respectively.

The total electric charge $Q$ is given by

$$Q = \int P_x dS = \frac{3\mu_{133}bF l^2}{32EI_y},$$

(2)

where $S$ is the electrode area. The displacement $w(0)$ at the midpoint of the beam obeys

$$w(0) = \frac{\lambda_{pp}}{2} - \frac{\lambda_{pp}}{2} \cos 2\pi ft,$$

(3)
where $\lambda_{pp}$ is the peak to peak displacement at the midpoint of the beam and $f$ is the frequency of the applied displacement load. The displacement obeys the three point bending equation (Supplementary Note 1):

$$w(0) = -\frac{FL^3}{48EI_y} - \frac{Fl}{4\kappa AG},$$

(4)

where $\kappa = \frac{10(1+\nu)}{12 + 11\nu}$ is the shear correction factor, $\nu$ is Poisson’s ratio, $G$ is shear modulus and $A$ is the cross-sectional area of the beam. From Eqs. (2), (3) and (4), the total charge can be calculated as

$$Q = \frac{-9\mu_{133}b l \kappa G(\lambda_{pp} - \lambda_{pp} \cos 2\pi ft)}{4(l^2 \kappa G + Eh^2)}.$$  

(5)

Finally, the corresponding current of one beam is related to the induced charges as follows (Supplementary Note 2):

$$I = \frac{dQ}{dt} = \frac{-9\mu_{133}b l \kappa G\lambda_{pp} \pi f \sin 2\pi ft}{2(l^2 \kappa G + Eh^2)}.$$  

(6)

Based on the analysis of the beam element, we turned to the flexoelectric calculation of the porous model. Assuming the length, width and height of a porous sample are $2L$, $2L$ and $L$, and the layers of the unit cell in the vertical direction is $n$. Then we have,

$$n(2l + 2\delta) = L.$$  

(7)

Considering the unit cell opposed to the concentrated force $F$ at the end of the outer beam (beam $b_1$) as illustrated in Fig. 2a, the displacements along the vertical direction of the outer and inner vertical beams (beam $b_1$ and beam $b_2$) are defined as
\[ \Delta d_1 = \frac{Fl}{EA} \quad \text{and} \quad \Delta d_2 = \frac{Fl}{2EA}. \]  

(8)

From Eq. (4), the vertical displacement of a unit cell due to the three-point bending of the horizontal beam (beam \( b_3 \)) is

\[ \Delta d_3 = 2w(0) = \frac{Fl^3}{24EI} + \frac{Fl}{2\kappa AG}. \]  

(9)

Thus, the whole vertical displacement \( \Delta d = \Delta d_1 + \Delta d_2 + \Delta d_3 \) of the unit cell obeys

\[ n \cdot \Delta d = W(t). \]  

(10)

Here, two kinds of theoretical models are proposed. The first model is named as \( M_1 \), which considers the compression of the beams \( b_1, b_2 \) and the bending of beam \( b_3 \). And the bending of beam \( b_3 \) in a unit cell contributes most to the flexoelectric polarization (two beams in a single cell), which is (Supplementary Note 3)

\[ Q_i = \frac{\mu_{1133} F \delta^2 (2l - \delta)}{4EI}. \]  

(11)

Since only 15\% or 25\% macroscopic strain loads have been applied on the top surface of porous PDMS and the electrodes lay on the surface of the porous samples, it is reasonable assuming the majority flexoelectric polarization we collected coming from the most top two layers \((2n \times 2n \times 2 \text{ cells in total})\) as the FEM results illustrated in Fig. 2a. Thus, the whole polarized charges can be calculated as

\[ Q_{\text{num}} = 8n^2 Q_i. \]  

(12)

From Eqs. (7) - (12), we can get
\[ Q_{\text{sum}} = \mu_{1133} \frac{12L(2l - \delta)\kappa G\delta^2}{l + \delta} \cdot \lambda_{pp} - \lambda_{pp} \cos 2\pi \frac{ft}{3l\kappa G\delta^2 + \kappa Gl^3 + lE\delta^2}, \tag{13} \]

and the corresponding current is

\[ I = \frac{dQ_{\text{sum}}}{dt} = \mu_{1133} \frac{24L(2l - \delta)\kappa G\delta^2}{l + \delta} \cdot \lambda_{pp} \pi f \sin 2\pi \frac{ft}{3l\kappa G\delta^2 + \kappa Gl^3 + lE\delta^2}. \tag{14} \]

This is also the relationship between the measured current \( I \) and applied displacement \( W(t) \) in the deformation assumption of model \( M_1 \).

In the first model \( M_1 \), only the compression strain was taking into account of the vertical beams. In order to describe the deformation more precisely, the bending of the vertical beams \( b_1 \) and \( b_2 \) was taken into account in the second model (named as \( M_2 \)). A pre-deflection \( \delta_0 = 10 \mu m \) at the midpoint of the vertical beam is assigned, the displacement along \( z \) direction of the unit cell caused by the bending of beam \( b_1 \) and beam \( b_2 \) are defined as (44)

\[ \Delta d_4 = \frac{\pi^2 \delta_0^2}{2l} \frac{F(4P_e - F)}{2(2P_e - F)^2}. \tag{15} \]

and

\[ \Delta d_5 = \frac{\pi^2 \delta_0^2}{2l} \frac{F(P_e - 0.5F)}{(P_e - F)^2}, \tag{16} \]

where \( P_e = \frac{\pi^2 El}{l^2} \).

The total vertical displacement along \( z \) direction of the unit cell can be calculated as

\[ \Delta d = \Delta d_1 + \Delta d_2 + \Delta d_3 + \Delta d_4 + \Delta d_5. \tag{17} \]

The flexoelectric response in model \( M_2 \) consists of both \( Q_1 \) that contribution of the horizontal beam \( b_3 \) considered in \( M_1 \), and also the
contribution of beam \( b_1 \) (named as \( Q_2 \)). However, the contribution of beam \( b_2 \) is not taken into account since it can be hardly collected by the electrode. Similar to the aforementioned calculation method of the three-point bending of beam \( b_3 \), we get \( Q_2 \) as

\[
Q_2 = \mu_{1131} \frac{12\kappa AG\delta^2}{I^2\kappa AG + 12EI} w'(0),
\]

(18)

where \( w'(0) \) is the deflection of the midpoint of beam \( b_1 \). The arc length is approximated by the chord length here to deduce \( w'(0) \) as:

\[
w'(0) = \sqrt{\left(\frac{l}{2}\right)^2 - \left(\frac{l - \Delta d_s}{2}\right)^2}.
\]

(19)

From Eqs. (18) and (19), \( Q_2 \) can be calculated as (Supplementary Note 4)

\[
Q_2 = \mu_{1131} \frac{6\kappa AG\delta^2}{I^2\kappa AG + 12EI} \sqrt{2l\Delta d_s - (\Delta d_s)^2}.
\]

(20)

Thus, the total charges and measured current are

\[
Q_{\text{sum}} = 8n^2 (Q_1 + Q_2),
\]

(21)

and

\[
I = \frac{dQ_{\text{sum}}}{dt}.
\]

(22)

Then the numerical solutions can be obtained.

In the calculation, we assumed \( \mu_{1131} \) and \( \mu_{1133} \) are equal to each other, which can be concluded from the two coefficients given in the literatures such as Refs. (10, 11) and (24). The flexoelectric responses calculated using two theoretical models and also the experimental results under different frequencies and strains are shown in Fig. 4. It can be seen that the
theoretical results calculated by model $M_1$ agrees better with the experimental results of small pore samples than that of model $M_2$, while the results calculated by model $M_2$ agrees better with the experimental results of large pore samples. This may attribute to the much larger pore diameter compared with the small pore, which provides more space for bending of the internal ligaments of large pore samples. Both theoretical models can effectively predict the flexoelectric response of porous PDMS samples.

**Applications as flexible passive bending sensor and shock absorption sensor**

Benefiting from the high flexoelectric response, diverse macrostructures and loading forms, high flexibility and breathability, porous PDMS may enable its applications as wearable sensors. What’s more, it is also a passive sensor since it can generate electrical signals spontaneously without external electric power supply. Therefore, it can greatly simplify the structure of sensor platform and also eliminate the sensing error from power supply precision. Fig. 5 presents the thin porous PDMS films (60 × 15 × 5 mm$^3$) sensing the knuckle bending movement. The porous PDMS with point-like electrode on the midpoint of the film was tied on top of the middle finger by two rubber bands, and both ends of film did not cross the first and the end finger joint as shown in Fig. 5a. Fig. 5b illustrates the
flexoelectric responses of the porous PDMS to different bending angles and modes, where we named the repeated bending and releasing with bending angle of 10°, and the intermittently bending and releasing with the bending angle of 30° as “10° continuous” and “30° intermittent”, respectively. The other bending modes are named in the similar way. One can find that the porous PDMS sensors can measure the knuckle bending angle and action mode accurately and effectively. The excellent liner relationship between the flexoelectric-induced current and bending angles are illustrated in Fig. 5c, which indicates the promising application of porous PDMS in bending sensors based on flexoelectricity.

Since the soft porous structure is naturally perfect protective material, another test was designed to illustrate the possible application of porous PDMS in sensing shock and protection of electronic equipment. A 3D printing polylactic acid ball (7.45 g and the radius is 3 cm) was released at different heights onto the porous PDMS sample (2 × 2 × 0.5 cm³, small pore) as schematically illustrated in Fig. 5d. Firstly, the ball was released at a height of 1 cm and it fell onto the PDMS, then repeated this process twice. Then we lifted the height to 1.5 cm to repeat the same test. The corresponding flexoelectric current of our experiment is shown in Fig. 5d. The flexoelectric signal is generated when the ball touching the surface of porous PDMS sample, and the induced current reaching maximum with the largest deformation of the sample, i.e. the largest displacement of the ball
on PDMS. Then following an oscillation attenuation of the signal till the ball is static. Afterwards, there is a minimum current when the ball was picked up manually. The peak value of the flexoelectric signal increases with the initial falling height, which indicates the high sensitivity of porous PDMS sponges to be a shock sensor and also with the protection functionality.

**Discussion**

The porous PDMS cube or film with 3D-interconnected pores and ligament structures have shown their significant flexoelectric polarized response under compression, which is impossible with a solid PDMS cube or film baring the same load. The weight-specific flexoelectric response ($W_{sec}$) of porous PDMS is two orders of magnitude higher than that of the solid truncated pyramid PDMS.

In this work, only 15% or 25% compression strain has been applied on the porous sample, larger compression strain or other load forms such as tension or torsion should be investigated systematically in future research to explore deeply of the mechanism and possible applications. This finding emphasizes that flexoelectricity is much more significant in porous samples with micron or nano-scale structure size due to not only the large strain gradient but also the more loading forms compared with solid materials. Furthermore, two theoretical models representing the
porous structures based on the well-known Gibson-Ashby model have been proposed, and the calculated and measured results agrees well, which indicates that one can use these models to predict and design the microscopic structure to obtain the desired flexoelectric response. Based on the above performance of the porous PDMS in flexoelectricity, the applications on flexible passive bending and shock sensors with stable responses have been presented.

From a broader perspective, this study highlights the great potential of porous materials in the field of flexoelectric devices (sensing, actuating, energy harvesting and so on) and possible rational micron/nano structure design with various materials to achieve expected flexoelectric response.

**Materials and Methods**

**Sample fabrication**

PDMS prepolymer (Sylgard 184A, Dow Corning) and the thermal curing agent (Sylgard 184B, Dow Corning) was mixed at a weight ratio of 10:1 unless otherwise indicated, which is named as “pre-cured PDMS” here. The commercial sugar cubes (2×2×1 cm³, Taikoo) with particle size of ca. 400-500 μm and salt particles (Macklin) with the size ranging from 150 μm to 200 μm were used as sacrificial templates. The sugar cube was used as template directly, but the salt particles need to be mixed with the pre-cured PDMS as the template. The pre-cured PDMS was mixed with
salt particles at a weight ratio of 4:1, which was filled in a $2 \times 2 \times 1$ cm$^3$ cubic mold tightly to form the PDMS-salt templates\(^{(45)}\). The templates (sugar cubes or PDMS-salt templates) were placed in a Petri dish, and the pre-cured PDMS was poured into the Petri dish until it submerged all of the templates. Then the Petri dish was placed into a vacuum chamber, degassing for 2 h at 80 °C, which allowed the pre-cured PDMS to infiltrate into the pores of the templates with the assist of capillary force and also the polymerization simultaneously. Afterwards, the as-prepared cured PDMS-template cubes were cut off to remove excess PDMS from the surfaces. Then, the PDMS-template cubes were put in water to dissolve the sugar or salt particles at 80 °C for 2 h using ultrasonic cleaner and following ultrapure water cleaning for 5 times. Finally, the 3D interconnected porous PDMS samples with large pores (sugar template) and small pores (salt template) were obtained after drying in a convection oven (Jinghong DHG-9030A) for 2 h at 80 °C. The truncated pyramid was fabricated by filling the pre-cured PDMS into a mold printed by 3D printer (MakerBot PABH65), and then curing for 3 h at 60 °C in a convection oven. Afterwards, truncated PDMS pyramid sample was peeled off from the mold. In order to collect the flexoelectric charge effectively, silver conductive epoxy adhesives (MG chemicals 8330) with high electric conductivity and low stiffness were brushed on the top and bottom surfaces of the samples as electrodes.
**Experimental setup**

The dynamic mechanical analyzer (TA ElectroForce-DMA3200) was used for dynamic uniaxial compression. A low-noise current preamplifier (Stanford Research SR-570) was used to measure and convert the current signal to voltage signal, in which a low noise gain mode and a low-pass filter method were chosen. An electrostatic eliminator (KEYENCE SJ-F036) was used to get rid of the influence of electrostatic charge. The triboelectricity should have no contribution on our measured flexoelectricity as explained in Supplementary Note 5. Finally, the oscilloscope (Tektronix MDO-3034) was used to record the real-time voltage signal.

**Materials characterization**

The microscopic structures were characterized by scanning electron microscope (HITACHI SU8020.), and the ligament and pore sizes were calculated by averaging the values obtained from ImageJ software. The energy dispersive spectroscopy (IXRF ATLAS) was used to check the salt residual. The corresponding spectrum of the small pore PDMS is shown in Fig. S5, where one can conclude that most of the salt particles have been removed.
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**Fig. 1 Porous PDMS sample and its flexoelectricity.** (A) porous PDMS samples with different macroscopic geometries, (B) SEM images of the 3D interconnected structures with open small pores (left) and large pores (right), and (C) schematic diagrams of the strain gradient induced polarization in the bending deformation of the internal ligaments of samples under various loading forms such as tension, compression, bending and torsion.
Fig. 2 Flexoelectric responses of porous PDMS. (A) the Gibson-Ashby model was adopted as unit cell (left) and the displacement analysis of a model with $3 \times 3 \times 3$ unit cells (right) under 15% compression strain by using finite element method (FEM), (B) the flexoelectric-induced current (left axis, red) of large pore PDMS and the real-time applied displacement (right axis, blue) at 3 Hz, (C) the frequency dependence of the flexoelectric current of small pore PDMS film ($60 \times 15 \times 2.8$ mm$^3$) under the applied three point bending macroscopic displacement of 1.5 mm, (D) the maximum output current-compression strain curves of two kinds of porous PDMS samples.

Fig. 3 Comparison of the weight specific effective coefficient, $W_{\text{sec}}$ of porous and bulk PDMS. (A) the maximum current-strain gradient curves of two truncated PDMS pyramids with different height, (B) $W_{\text{sec}}$ of different samples under the applied strain of 25%.
Fig. 4 The flexoelectric response comparison between the experimental and theoretical results under different frequencies and strains. (A) The comparison between experimental and theoretical results of small pore PDMS at different frequencies under 15% and (B) 25% strain; (C) the comparison between experimental and theoretical results of large pore PDMS at different frequencies under 15% and (D) 25% strain; (E) the comparison between the experimental and theoretical results at 2 Hz under different strains of small pore PDMS and (F) large pore PDMS.
Fig. 5 Application as bending sensors and shock absorption sensors. (A) The images of the thin porous PDMS films (60×15×5 mm³) sensing the knuckle bending movement, (B) the flexoelectric responses of porous PDMS to different bending angles and modes, and (C) the liner relationship between the flexoelectric-induced current and bending angles, (D) the flexoelectric-induced current of a shock absorption sensor when a ball released at different heights.

Supplementary Materials

Fig. S1 Schematic diagram of the fabrication method of porous PDMS based on direct templating technique.
Fig. S2 Frequency response of different porous PDMS sponges at different strain with sealed surface and whole electrode. (A) current-frequency curves, (B) weight specific current-frequency curves.

Fig. S3 Comparison of the experimental data of the same samples before and after getting rid of the electrostatic charges.
Pre-tests and determination of experimental parameters

A series of pre-tests have been done to find the suitable electrode area and weight ratio between PDMS prepolymer and curing agent. It can be seen from Fig. S6 that the porous PDMS surface condition (sealed with or without a thin PDMS film) has little effect on the electric signal, so we
sealed the top and bottom surfaces of the sponges to avoid the silver conductive epoxy adhesive infiltrating into the pores. The electrode was brushed all over the top and bottom surfaces with the adhesive to gain as much induced electric signals as possible. Fig. S7 illustrates the relationship between the prepolymer-curing agent ratio (by weight) of 60×15×2.3 mm³ small pore PDMS films and their flexoelectric responses, which indicates that with the increasing of curing agent, the flexoelectric response decrease due to the over crosslinking of the polymer chains. Thus, a typical weight ratio (10:1) recommended by the supplier was adopted in the present study.

![Fig. S6 Maximum current-frequency curves of large pore PDMS sponges with different kinds of surface conditions and electrode areas. At a compression strain of (A) 25% and (B) 15%.](image-url)
Fig. S7 Maximum current-frequency curves of 60×15×2.3 mm$^3$ small pore PDMS films at a peak to peak three point bending displacement of 5 mm with different prepolymer-curing agent ratio (by weight).

**Supplementary Note 1: The derivation of Eq. (4)**

For the bending beam in Fig. S8 with a concentrated force $F$ applying on the midpoint, the electric polarization $P$ due to the flexoelectric effect can be calculated as follows. Because of the symmetry, we only consider half of the beam as a cantilever beam as Fig. S9 shown. Therefore, the displacement $w(l/2)$ of the end of the cantilever beam in Fig. S9 is the same with the displacement $w(0)$ of the midpoint of the beam shown in Fig. S8.

Fig. S8 Typical three point bending beam.
Based on the Timoshenko beam theory, the cantilever beam shown in Fig. S9 obeys

\[ u_x(x, y, z) = -z\varphi(x) \]
\[ u_y(x, y, z) = 0 \]
\[ u_z(x, y) = w(x) \]

where \((x, y, z)\) represents the coordinate of a point on the beam, \(u_x, u_y, u_z\) represent the three dimensional coordinate components of the displacement vector, \(\varphi\) represents the bending angle of the beam’s neutral plane and \(w\) is the displacement of the neutral plane in the \(z\) direction. The control equation of Timoshenko beam is as follows:

\[
\frac{d^2}{dx^2} \left( EI_y \frac{d\varphi}{dx} \right) = q(x,t)
\]
\[
\frac{dw}{dx} = \varphi - \frac{1}{\kappa AG} \frac{d}{dx} \left( EI_y \frac{d\varphi}{dx} \right),
\]

where \(q\) is the distributed load, \(E\) is the elastic modulus, \(G\) is the shear modulus, \(I_y\) is the moment of inertia of the beam, \(A\) is the cross-sectional area, \(\kappa = \frac{10(1+\nu)}{12+11\nu}\) is the shear correction factor and \(\nu\) is the Poisson’s ratio.

The boundary conditions in Fig. S9 are:
where $F$ is the concentrate force at the midpoint of the beam and $M$ is the bending moment.

Combine all the equations above, we obtain the three-point bending control equations as:

$$\varphi(x) = \frac{Fx(x-l)}{4EI}$$
$$w(x) = \frac{Fx^2(2x-3l)}{24EI} - \frac{Fx}{2\kappa AG}.$$

The displacement of the end of the cantilever beam is

$$w\left(\frac{l}{2}\right) = -\frac{Fl^3}{48EI_y} - \frac{Fl}{4\kappa AG}.\quad \text{Therefore, for the beam in Fig. S8, it’s deflection in the midpoint is}\quad w(0) = -\frac{Fl^3}{48EI_y} - \frac{Fl}{4\kappa AG} \quad \text{(Eq. (4)).}$$

**Supplementary Note 2: The derivation of Eqs. (1), (2), (5) and (6)**

For the beam in Fig. S8, the derivation process of Eqs. (1), (2), (5) and (6) is as follows:

$$M(x) = \frac{F}{2}\left(\frac{l}{2} - |x|\right)$$
$$\varepsilon_{x=0}^M \frac{M(x)}{EI_y} \quad \text{and} \quad d\varepsilon_{x=0} = \frac{F}{2}\left(\frac{l}{2} - |x|\right)$$
\[ P_3 = \mu_{113} \frac{d\varepsilon_{11}}{dz} = \mu_{113} \frac{F}{EI} \left( \frac{l}{2} - |x| \right) \]

\[ Q = \int P_3 dS = \frac{3\mu_{113}bF z^2}{32EI_y} , \]

where \( \varepsilon \) is the strain, \( \mu \) is flexoelectric coefficient, \( P \) is polarization, \( Q \) is the induced charge, and \( S \) is the electrode area. The deflection

\[ w(0) = -\frac{Fl^3}{48EI_y} - \frac{Fl}{4\kappa AG} \]

obeys

\[ w(0) = \frac{\lambda_{pp}}{2} - \frac{\lambda_{pp}}{2} \cos 2\pi f t , \]

so we get

\[ F = -\frac{48EI\kappa AGw(0)}{l^3\kappa AG + 12El} = -\frac{24EI\kappa AG(\lambda_{pp} - \lambda_{pp} \cos 2\pi ft)}{l^3\kappa AG + 12El} . \]

And thus

\[ Q = -\frac{9\mu_{113}bG(\lambda_{pp} - \lambda_{pp} \cos 2\pi ft)}{4(l^2\kappa G + Eh^2)} \]

\[ I = \frac{dQ}{dt} = -\frac{9\mu_{113}bG\lambda_{pp} \pi f \sin 2\pi ft}{2(l^2\kappa G + Eh^2)} . \]

**Supplementary Note 3: The derivation of Eq. (11)**

\[ M(x) = \frac{F}{2} \left( \frac{l}{2} - |x| \right) \]

\[ \varepsilon_{11_{\text{max}}} = \frac{M(x)}{EI} \left. \frac{d\varepsilon_{11}}{dz} \right|_{z=\frac{\delta}{2}} = \frac{F}{2} \left( \frac{l}{2} - |x| \right) \left. \frac{d\varepsilon_{11}}{dz} \right|_{EI} , \]

\[ P_3 = \mu_{113} \frac{d\varepsilon_{11}}{dz} \]

\[ Q_1 = 2 \int_{S_2} P_3 dS_2 = \frac{\mu_{113}F \delta^2 (2l - \delta)}{4EI} , \]

where \( S_2 \) is the area of the contact part of the beam \( b_1 \) and beam \( b_3 \).

**Supplementary Note 4: The derivation of Eqs. (18), (19) and (20)**

For beam \( b_1 \), its deformation is estimated as shown in Fig. S10, in
which \( w'(0) = \sqrt{\left(\frac{l}{2}\right)^2 - \left(\frac{l - \Delta d}{2}\right)^2} \) (Eq. 19).

Fig. S10 Deformation of beam \( b_1 \).

Assuming a concentrate force \( F_2 \) at the middle point of the beam \( b_1 \) leads to the bending of \( b_1 \), so the charge \( Q \) induced in beam \( b_1 \) is derived as follows:

\[
M(x) = \frac{F_2}{2} \left(\frac{l}{2} - |x|\right)
\]

\[
\varepsilon_{11,\text{max}} = \frac{M(x)z}{EI} \left|_{x = \frac{l}{2}} \right. = \frac{d\varepsilon_{11}}{dz} = \frac{F_2}{2} \left(\frac{l}{2} - |x|\right)
\]

\[
P_1 = \mu_{131} \frac{d\varepsilon_{11}}{dz} = \mu_{131} \frac{F_2}{2} \left(\frac{l}{2} - |x|\right)
\]

\[
Q = \int P_1 dA = P_1 \delta^2 = \frac{\mu_{131} F_2 \delta^2}{8EI}
\]

There are two beams \( b_1 \) in the unit cell, so the whole induced charges of beam \( b_1 \) in the unit cell is \( Q_2 = 2Q = \frac{\mu_{131} F_2 \delta^2}{4EI} \). While \( F_2 = -\frac{48EI \kappa A G w'(0)}{l^3 \kappa A G + 12EI} \) (as deduced in the Supplementary Note 2), so \( Q_2 = \frac{12\kappa A G \delta^2}{l^2 \kappa A G + 12EI} w'(0) \) and \( Q_2 = \frac{6\kappa A G \delta^2}{l^2 \kappa A G + 12EI} \sqrt{2l\Delta d - (\Delta d)^2} \) (Eqs. (18) and (20)).
Supplementary Note 5: Exclusion of triboelectric effect

Here, the contribution of triboelectric effect can be excluded in the present study. Firstly, there exists almost none triboelectric charge in the pore surface of our porous PDMS since the friction between PDMS can hardly produce triboelectric charge. Secondly, we assume that the triboelectric charge is most likely to be occurred in the friction between the push rod/sample holder (PVC) and electrodes (silver) on the surface of porous PDMS during the repeated compression. However, the push rod/sample holder, PDMS, and the silver electrode on the surface of the sample could not constitute a typical triboelectric generator. There is no electrode on the push rod/sample holder, and the triboelectric induced charge should be saturation on both PVC surface of the push rod/sample holder. Thus, there is no extra potential difference to drive charge transfer(46). Thirdly, the abilities of PDMS and PVC to gain/loss electrons are almost the same(46). Thus, the triboelectricity between PVC on the push rod/sample holder and porous PDMS surface with point-like electrode can be ignored. Fourthly, the pre-compression displacement (ca. 0.5mm) has been set before each measurement, so there is no longitudinal separation and lateral displacement between the push rod/sample holder and the sample surfaces during the experiment. Therefore, there exists no condition from triboelectricity.
Besides, from the point of view of the output signal: Firstly, the induced electric signal we obtained (Fig. 2b) remains highly consistent with the displacement load. There exists no AC pulse signal, which is a typical characteristic of the triboelectric current. Secondly, the electrical outputs of porous PDMS samples with different surface conditions (sealed or not) remain almost the same (Fig. S6), indicating the induced electric signal have nearly no triboelectricity component since the surface roughness will seriously influence the triboelectric output.