

Highly Transparent and Adhesive Poly(vinylidene difluoride) Films for Self-Powered Piezoelectric Touch Sensors

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Electronic Supplementary Information

Abstract With the rapid development of internet of things, self-powered touch sensors made of piezoelectric fluorinated polymers have attracted significant interest because they can constantly convert mechanical energy into electrical energy without external power supply. However, it is still challenging to fabricate fluorinated polymer films with good adhesion and high output performance with a large-scale and low-cost method while maintaining high transparency, which are extremely important for simultaneous optical detection and electromechanical transduction. In this work, we demonstrate that the incorporation of a molecular ferroelectric-dabcoHReO₄ (DH) into poly(vinylidene difluoride) (PVDF) solution enables high-throughput and low-temperature processing of flexible and transparent piezoelectric films by scalable processing method. The effects of multiaxial DH are multiple. First, DH can trigger the phase transition of PVDF from α - to β -phase and realize the orderly orientation of PVDF, which guarantees higher piezoelectric performance without any additional electrical poling process. Second, the hydrophilic nature of DH can improve the adhesion properties of PVDF, which in turn improve the stability and durability of the devices. By optimizing the fabrication processes, the transmittance of the piezoelectric touch sensors based on PVDF films and Ag nanowires coated poly(ethylene terephthalate) electrodes can be higher than 94%. The piezoelectric voltage constant g_{33} of the transparent films can reach to 1.2 V·m·N⁻¹, which is at least three times higher than the commercially available PVDF films obtained by stretching. These results indicate that the flexible piezoelectric sensors have potential applications in transparent electronic devices for mechanical sensing and energy harvesting.

Keywords PVDF; Transparent; Adhesive; Large scale; Piezoelectric sensor

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INTRODUCTION

Flexible pressure sensors are required for applications in fields such as health monitoring, robotics, and human-machine interaction, which stimulate the development of portable electronic devices and electronic skin.^[1–3] To date, the transduction mechanisms of flexible pressure sensors are mainly based on force-induced changes in capacitance, resistivity, polarization, and static electricity.^[4–7] Among these aspects, self-powered or battery-free sensors based piezoelectricity are most widely used for pressure sensing or energy harvesting, because the surface polarization level can be reliably changed when a piezoelectric material is subjected to a stress.^[8–11]

The perpetual goal for portable electronic devices is to possess high level of flexibility and transparency for visual imper-

ceptions and electrical-mechanical sensing. Highly transparent piezoelectric touch sensors (PTSs) can be applied in portable electronic devices without interfering with visibility, resulting that they are more popular than low-transparent PTSs.^[12–14] To date, tremendous efforts and continuous progress have been made to enhance the performance of piezoelectric sensing or energy harvesting in terms of material development, surface engineering, and device designs.^[12,13] However, piezoelectric films with flexible and transparent configurations are still difficult to fabricated, although integration of these characteristics in self-powered piezoelectric pressure sensors enables simultaneous optical detection and force sensing.^[4,14–16] The pivotal challenge for the transparent PTSs is to select proper sensor materials with flexibility and transparency which can be fabricated by a low-cost and high throughput manufacturing process. Inorganic piezoelectric materials have excellent piezoelectric properties, but the inherent brittleness of them may lead to accidental breakage during handling.^[17,18] In order to meet the requirement of

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flexibility for inorganic piezoelectric materials, the inorganic nanostructures such as barium titanate (BaTiO_3),^[18,19] lead zirconate titanate (PZT),^[20] and zinc oxide (ZnO)^[21] can be incorporated into flexible polymer matrix by making nanocomposite piezoelectric materials, which have been used for self-powered flexible piezoelectric sensors.^[22] However, to maintain the transparency of the flexible self-powered sensors, the inorganic nanostructures have to be aligned on the substrates or in the matrix, making it difficult to fabricate the transparent and flexible self-powered sensors with a simple, efficient, and scalable processing method.^[15,19,20]

Solution processable flexible fluorinated piezoelectric polymers such as poly(vinylidene difluoride) (PVDF) present a multifunctional material platform for fabricating various electronic devices due to its combined ferro-, piezo- and pyroelectric properties with flexibility and easy processability.^[21,23] However, realization of transparent fluorinated polymers-based piezoelectric touch sensors with a low cost and large scale method is not straightforward and there are at least three critical issues associated with the fluorinated polymers in touch panels that have not been well addressed until now. First, the valuable spontaneous polarization and piezoelectric performance are influenced by the crystal orientation and sufficient polar β -phase content of PVDF. In order to obtain the desired crystal orientation and β -phase for PVDF, several post processing methods such as mechanical stretching, nanoconfinement, epitaxial growth and electrically poling, have been applied to PVDF-based films obtained by melt or solution crystallization.^[24–27] The sophisticated fabrication process hampers the large-scale fabrication and film uniformity of PVDF films. Numerous studies have proven that incorporation of nano-fillers such as piezoelectric ceramics (BaTiO_3 , ZnO , and PZT, etc.) and carbon materials (carbon nanotubes and graphene) into PVDF matrix can provide the easiest and lowest cost method for large scale fabrication of β -phase PVDF films for sensing and harvesting applications without external treatment.^[19,21,28] However, the nanocomposite films suffer the problem in terms of transparency. Second, the interfacial interactions between polymeric film and electrode is of prime importance. The electrode must adhere to the polymer film and withstand repeated deformations over the lifetime of a device. Due to the absence of functional groups in PVDF or P(VDF-TrFE), however, there only exists weak van der Waals interactions between the polymeric film and the metal electrodes.^[29,30] This is another big limitation in successful use of piezoelectric-based touch interactivity. Third, flexible and transparent electrodes have to be used for maintaining the transparency and flexibility of PVDF-based devices. In this aspect, graphene is typically used for PVDF-based touch sensors.^[31,32] For instance, Bae *et al.* fabricated flexible and transparent nanogenerators based on graphene/P(VDF-TrFE)/graphene multilayer films and demonstrated its possibility for flexible applications.^[31] Alternatively, Vuorinen *et al.* used commercially available PVDF films and sprayed graphene-based ink onto both sides of the PVDF film to fabricate transparent piezoelectric touch panels. However, to our best knowledge, only a maximum transparency of 74.1% have been achieved with the graphene electrodes.^[32]

In this work, we demonstrate transparent and flexible

piezoelectric touch sensor devices based on piezoelectric films fabricated by a low cost and large scale method. We incorporate the commercially available Ag nanowires (NWs) coated poly(ethylene terephthalate) (PET) as the transparent electrode and solution processed PVDF-dabcoHReO₄ (DH) composites as the piezoelectric layers. The hydrogen bonding interaction between multiaxial molecular ferroelectric DH and PVDF can trigger the phase transition of PVDF from α - to β -phase and realize the orderly orientation of PVDF, which guarantees higher piezoelectric output performance of PVDF without any external treatment. Moreover, the hydrophilic nature of DH can improve the adhesion properties of PVDF-DH nanocomposites, which improves the stability and durability of the devices. The solution processability and adhesive properties of PVDF-DH composites annealed at relatively low temperature enable the high-throughput and low-cost fabrications with a doctor blade method. Further, when the DH particles are dissolved by water, the transmittance of the PVDF-based films with a piezoelectric voltage constant (g_{33}) of $1.2 \text{ V}\cdot\text{m}\cdot\text{N}^{-1}$ increases from 85% to above 94% at a light wavelength of 450 nm. The transparent PVDF-based film shows good piezoelectric output performance under various deformations such as pressing and bending. Combining the self-powered piezoelectric structures with good transmission and mechanical properties, the reported sensors can be integrated in transparent touch panels and portable electronic devices with sensing and energy harvesting properties.

EXPERIMENTAL

Fabrication of the PVDF-based Films and Piezoelectric Sensors

PVDF powder ($M_w=5.34\times 10^5 \text{ g/mol}$), 1,4-diazabicyclo[2.2.2]octane (dabco) and HReO₄ were all purchased from Sigma Aldrich, USA. The dabco powders and HReO₄ were mixed in ultrapure water or ethanol at a molar ratio of 1:1, and DH can be obtained after the reaction.^[33,34] PVDF powders were dissolved in a mixed solvent of *N,N*-dimethylformamide (DMF, Sinopharm Chemical Reagent Co., Ltd.) and acetone (Ac, Sinopharm Chemical Reagent Co., Ltd.) (DMF:Ac=1:1). After a clear solution was obtained, DH was added to the solution by mechanical agitation in the mass ratio of 8:92 (DH:PVDF). The transparent Ag NWs-coated PET substrates were provided by Gu's Nano Technology Co., Ltd., and used as received without any further treatment. By depositing the solutions onto the Ag NWs-coated PET substrates with a doctor blade method, wet thin films were obtained. The wet films were then dried and annealed in a vacuum oven to evaporate the solvent at different temperatures for 4 h. If needed, the DH on the surfaces of PVDF-DH composites can be dissolved by immersing the PVDF-DH composites into ultrapure water. Finally, another piece of Ag NWs-coated PET was covered on the piezoelectric films. The two copper wires were connected to the electrodes *via* silver paste. For the PTS devices, transparent Ag NWs act as the top and bottom electrodes.

Characterization and Measurements

Fourier transform infrared spectroscopy (FTIR) (Vertex 70v, Bruker) was recorded in an ATR mode with a resolution of 2 cm^{-1} . Wide-angle X-ray diffraction (WAXD) measurements were

carried out to characterize the crystalline phase of samples by using X-ray diffractometer (PANalytical, Holland) with a Cu-K α radiation source ($\lambda=0.154$ nm). The surface morphological analysis of samples was carried out by atomic force microscope (AFM) (MFP-3D, Asylum Research) and field-emission scanning electron microscope (FE-SEM, S-4700, Hitachi). The transparency of samples was obtained by measuring the transmittance with a UV-visible absorption spectrometer (UV-3600, SHIMADZU). Adhesion properties were characterized by the D3359 ASTM standard test method. The piezoelectric constant (d_{33}) was measured by a d_{33} meter (SA1303A, Shiao Technology Co., Ltd.) The piezoelectric outputs from the devices were recorded by a digital oscilloscope (TDS 2024B, Tektronix, internal input impedance 10 M Ω). The applied force was provided by an electromechanical vibrator exciter (SINOCERA PIEZOTRONICS, INC.) and calibrated with a piezoelectric force transducer (DFT 5100, Yangzhou Chuanglian Measurement and Control Equipment Co., Ltd.). The touched area was about 1 cm². The bending mode was controlled by a linear motor (SINOCERA PIEZOTRONICS, INC.).

RESULTS AND DISCUSSION

Fig. 1 illustrates the flow diagram of fabrication process of transparent PVDF-based piezoelectric films. Briefly, the PVDF-DH solution was deposited onto Ag NWs-coated PET substrates at room temperature with a doctor blade. After deposition, the samples were thermally annealed in an oven at different temperatures ranging from 50 °C to 110 °C. For simplicity, we labelled the PVDF-DH films annealed at different temperatures ranging from 50 °C to 110 °C for every 10 °C increase as C-50, C-

60, C-70, C-80, C-90, C-100, and C-110, respectively. If the DH particles were subsequently dissolved with ultrapure water, we labelled the corresponding samples as W-50, W-60, W-70, W-80, W-90, and W-100, respectively. The transparent PTS devices have three layers, in which the piezoelectric thin film is sandwiched between two Ag NWs-coated PET films. SEM image of Ag NWs on PET substrate is shown in Fig. S1 (in the electronic supplementary information, ESI).

Transparency

We estimated the transparency of the PVDF-based films by measuring the transmittance with a UV-visible spectrometer. Fig. 2(a) shows the transmittance of the composite films (the C series of samples), which were obtained by annealing the PVDF-DH composite films supported by Ag-NWs coated PET films at the temperature range of 50 °C to 100 °C. We find that the transmittance of the PVDF-DH coated PET films slightly depends on the annealing temperatures. For instance, C-50 just exhibits a transmittance of 77% at light wavelength of 450 nm. However, by increasing the annealing temperature to 100 °C, the transmittance is obviously increased to 86%. Considering that the DH particles in the composite films may cause light scattering which would result in the lower transparency of the composites, we immersed the samples into ultrapure water to dissolve the DH particles. Surprisingly, it can be seen from the curve of the films after dissolving the DH particles (the W series of samples) in Fig. 2(b), the transmittances of all the W series of samples are higher than the C series of samples. For example, when light wavelength is 450 nm, the transmittance of C-80 is increased from 85% to 94% (W-80). The photographs shown in Fig. 2(b) exhibit the transparency of the W-80 intuitively. The

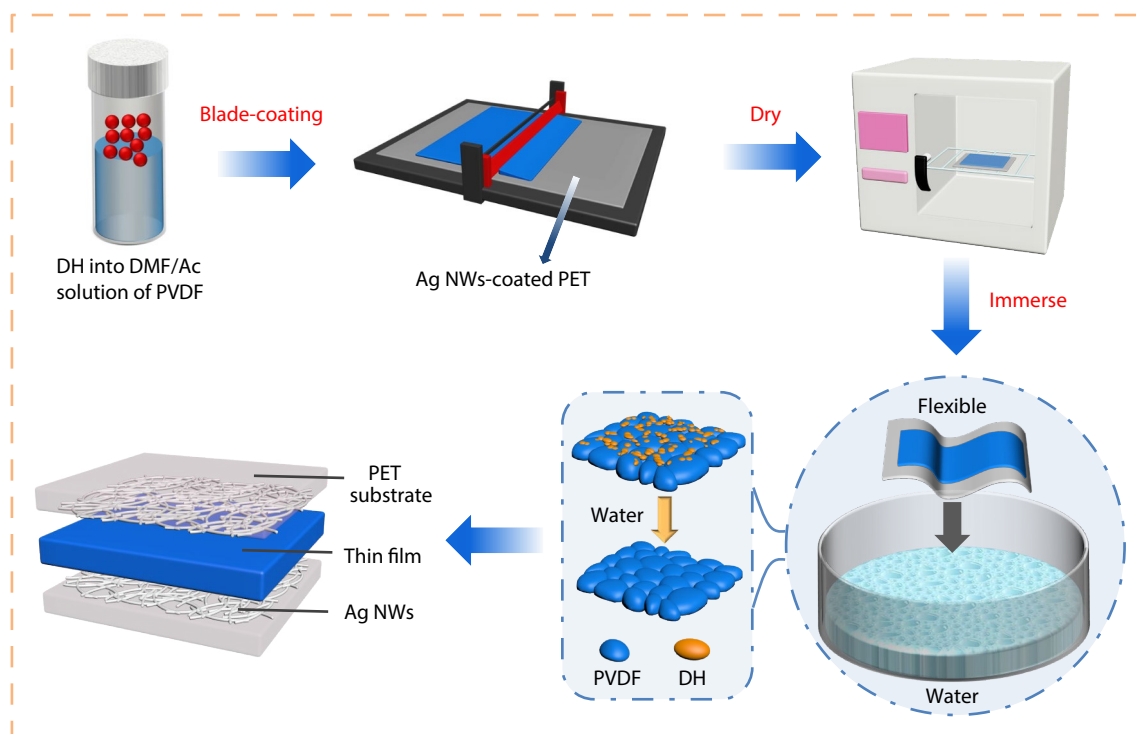


Fig. 1 Schematic illustration of the preparation process and the architecture of the transparent and flexible PTS devices. The fabrication process including deposition PVDF-DH films by a doctor blade, thermal annealing and dissolving DH particles with ultrapure water.

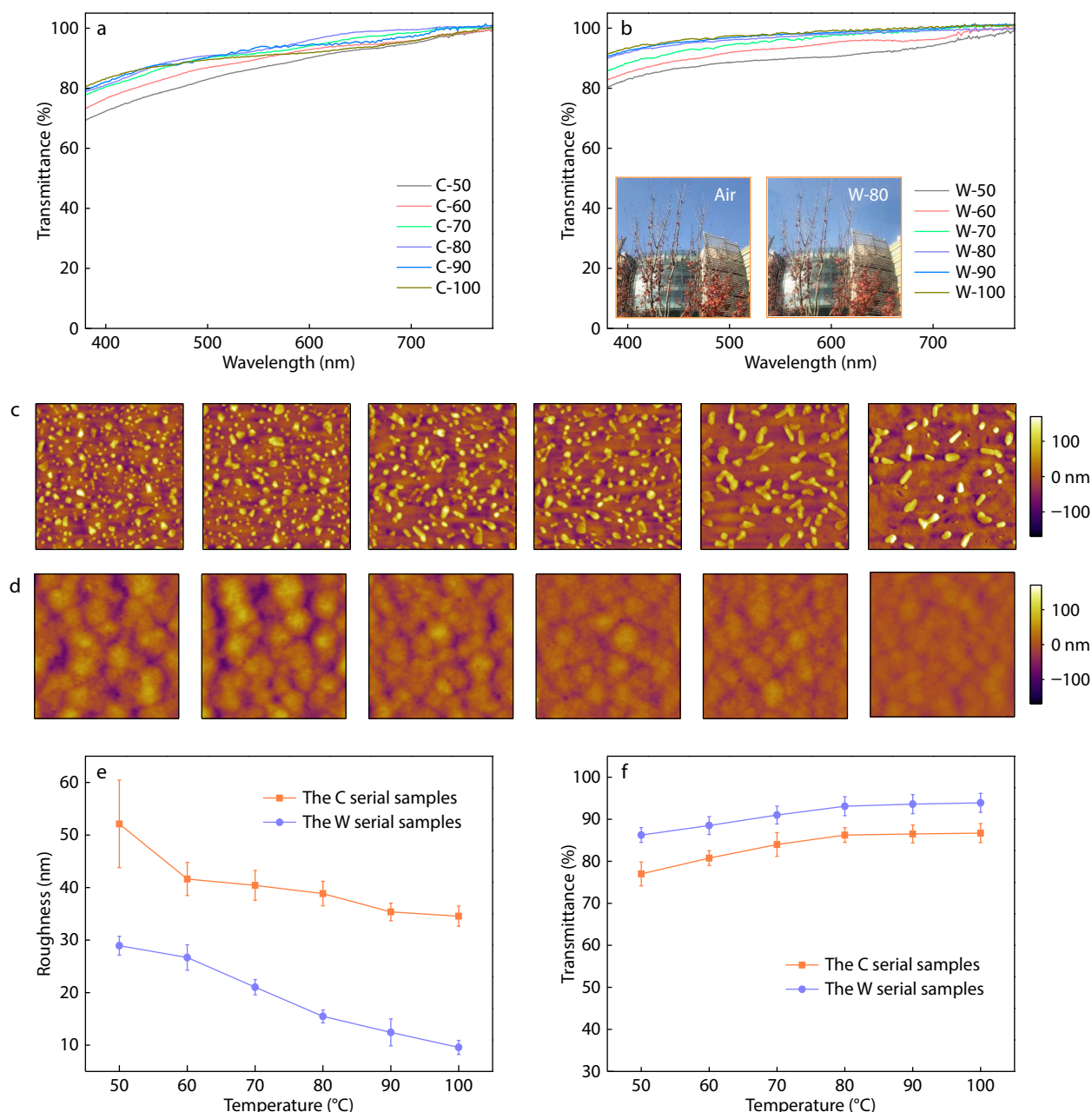


Fig. 2 Transmittance of (a) C series of samples and (b) W series of samples measured by UV-visible absorption spectra. The photographs in (b) show digital photograph of W-80 film where the library at Soochow University is selected as the background. Examples of AFM topographic images of (c) the C series of samples and (d) the W series of samples. The annealing temperatures from the left to the right are 50, 60, 70, 80, 90, and 100 °C, respectively. The imaging scale is $10\ \mu\text{m} \times 10\ \mu\text{m}$. (e) Evolution of the rms roughness of the C and W serial samples upon variation in annealing temperature between 50 and 100 °C. (f) The transmittance of the films when the light wavelength is 450 nm.

background can be observed clearly when looking through the W-80 films.

In order to understand the changes of transparency, we have probed the surface morphology of the C and W series of samples with atomic force microscope (AFM). Fig. 2(c) shows the typical AFM topographical images of the C series of samples which were annealed in the temperature range of 50 °C to 100 °C. We note here that these images were obtained at a $10\ \mu\text{m} \times 10\ \mu\text{m}$ scale. Judging from mass ratio of DH particles with respect to PVDF (8:92), we attributed the

particles dispersed on the surfaces of films to DH. As seen from Fig. 2(c), the DH particles change from granular- to rod-like shapes with increasing annealing temperature. Meanwhile, their dimensions became larger and amounts became less. The surface of PVDF matrix, however, keeps relatively smooth. In order to better probe the surface morphologies of PVDF matrix, we zoomed in the regions between the DH particles by scanning at $1\ \mu\text{m} \times 1\ \mu\text{m}$ scale. As shown in Fig. S2 (in ESI), the PVDF matrix is mainly composed of granular- or rod-like crystals when the annealing temperature ranges

between 50 and 100 °C, which is typical of β -phase PVDF crystallites as reported in previous reports.^[21,25] In addition, the shape and size of PVDF crystals do not strongly depend on the annealing temperature. However, if the annealing temperature is increased to 110 °C or above, the lamellar crystals of PVDF in the composite films grow into the typical morphologies of α -phase (Fig. S3 in ESI).^[21,25] By immersing the samples into water, we expected that the DH particles distributed on the surface of PVDF matrix can be removed due to the solubility of DH in water. As seen in Fig. 2(d) and Fig. S4 (in ESI), the DH particles were indeed removed by water and the surface topography of the W series of samples became smoother as compared to the C series of samples. In addition, it is revealed that the W series of samples are mainly composed of nanoscale grains which aggregate into microscale domains. The appearance of microscale domains indicates that the DH particles in the grain boundaries are simultaneously dissolved by the water washing process. As the annealing temperature increases, the PVDF unit cells gradually aggregate resulting in a slight difference in surface morphology (Fig. 2d).

It is known that the transparency of thin films is mainly related to light scattering resulted from surface roughness. The scattering coefficient (α_{sc}) is related to the root mean square surface roughness (σ_{rms}) as follows:

$$\alpha_{sc} = \frac{1}{d} \left(\frac{2\pi(n_f - n_a)\sigma_{rms}}{\lambda} \right)^2 \quad (1)$$

where d is the film thickness, n_f and n_a are the refractive indices of the films and the ambient, and λ is the wavelength of incident light.^[35,36] Therefore, we quantitatively estimated the surface roughness of the samples before and after water washing by AFM images shown in Figs. 2(c) and 2(d). As shown in Fig. 2(e), the σ_{rms} values of the C-series of samples typically lie in the range of 33–58 nm. The exact σ_{rms} values can be slightly decreased by increasing the annealing temperature. For instance, the σ_{rms} is 46–58 nm for C-50. When the annealing temperature is increased to 100 °C, σ_{rms} of the C-100 is decreased to 33–36 nm. Under a certain annealing temperature range and the proper condition of supersaturating and undercooling, the crystal nucleus is formed in the initial stage. Subsequently, the reduction in the surface free energy as the driving force promotes further crystal growth. In general, the growth rate of PVDF crystals increases with increasing annealing temperature. Films grown at low temperatures have more voids, resulting in the rough and porous surface morphologies. As the annealing temperature increases, the PVDF unit cells will coalesce to form much denser and more uniform films.^[35] For example, when the temperature is lower than 50 °C, the surface of the PVDF-DH composite film is rough with more pores, as shown in Fig. S5 (in ESI). When the annealing temperature is higher than about 50 °C, the relatively homogeneous and smooth films are obtained. As the annealing temperature increases, the film becomes much smoother, the σ_{rms} values become much smaller (Fig. 2e). If the DH particles are removed by water, the σ_{rms} can be further decreased. Typically, the σ_{rms} value decreases to the range of 9–30 nm, which still slightly depends on the annealing temperatures before dissolving the DH particles. The smaller the roughness, the smaller the probability of light scattering, and the transparency of the film

will become higher. We plotted the transmittance of the C-series and W-series of samples at light wavelength of 450 nm in Fig. 2(f). As seen, both the changing trends of transmittance as a function of annealing temperature and the differences of transmittance between C and W series of samples agree with the measured roughness presented in Fig. 2(e).

Structural Analysis

Because the electrical performances of the transparent PTS devices may strongly depend on the content of β -phase of PVDF, we characterized the samples with FTIR spectroscopy and WAXD, and presented the results in Fig. 3. Typically, absorption bands at 840 and 1279 cm^{-1} , which evidence the presence of β -phase of PVDF,^[37,38] can be clearly observed in the FTIR spectra of the C- and W-series of the samples annealed at the temperature range of 50 °C to 100 °C, as shown in Figs. 3(a) and 3(b). Meanwhile, the absorption bands at wavenumbers such as 766, 796 and 1380 cm^{-1} which belong to α -phase of PVDF,^[37,38] can also be observed in the FTIR spectra of the films annealed at 110 °C. These phenomena indicate that the PVDF matrix in the C- and W-series of samples annealed at the temperature range of 50 °C to 100 °C is mainly dominated by β -phase. When the temperature is increased to above 110 °C, the PVDF matrix is mainly composed of mixture of α - and β -phases. We calculated the relative fraction of β -phase (F_β) in the films using the following equation:

$$F_\beta = \frac{A_\beta}{1.26A_\alpha + A_\beta} \quad (2)$$

where A_β (β -phase) and A_α (α -phase) are the absorption band intensities at 840 and 766 cm^{-1} , respectively.^[37,38] As shown in Fig. 3(c), the fraction of β -phase is higher than 90% when the annealing temperature lies in the range of 50–80 °C. In addition, the exact values of F_β can be slightly increased from 91% to 96% when the annealing temperature is increased from 50 °C to 80 °C. The fractions of β -phase are comparable to the values achieved by other methods in the previous reports.^[27,28,39,40] However, if the annealing temperature is higher than 80 °C, the content of β -phase starts to decrease with further increasing the annealing temperature. As previously reported,^[34] the phase transition of PVDF from α to β -phase is mainly triggered by the intermolecular hydrogen bonding interactions between PVDF and DH during crystallization process. The phenomena of slightly increasing of β -phase content when the annealing temperature is lower than 80 °C may be owing to the increased chain mobility of PVDF with the increased annealed temperature. If the annealing temperature is higher than 80 °C the bonding energy of hydrogen bonds between PVDF and DH is weakened and thus the content of β -phase starts to decrease. When the temperature is further increased to above 110 °C, the intermolecular hydrogen bonding interaction is destroyed, so the β -phase content drops sharply. For comparison, the FTIR spectra of the PVDF film annealed at 50 °C to 110 °C are shown in Fig. S6 (in ESI). When the annealing temperature is 80 °C (PVDF-80), the β -phase content of PVDF film is about 42%, which is much lower than C-80 and W-80. We further compared the phase structure and crystallinity of the samples through WAXD images. As observed by WAXD patterns shown in the Fig. 3(d), characteristic peaks of β -phase PVDF at $2\theta=20.6^\circ$ ^[34,40] were observed in both C-80 and W-80. Due to the presence of

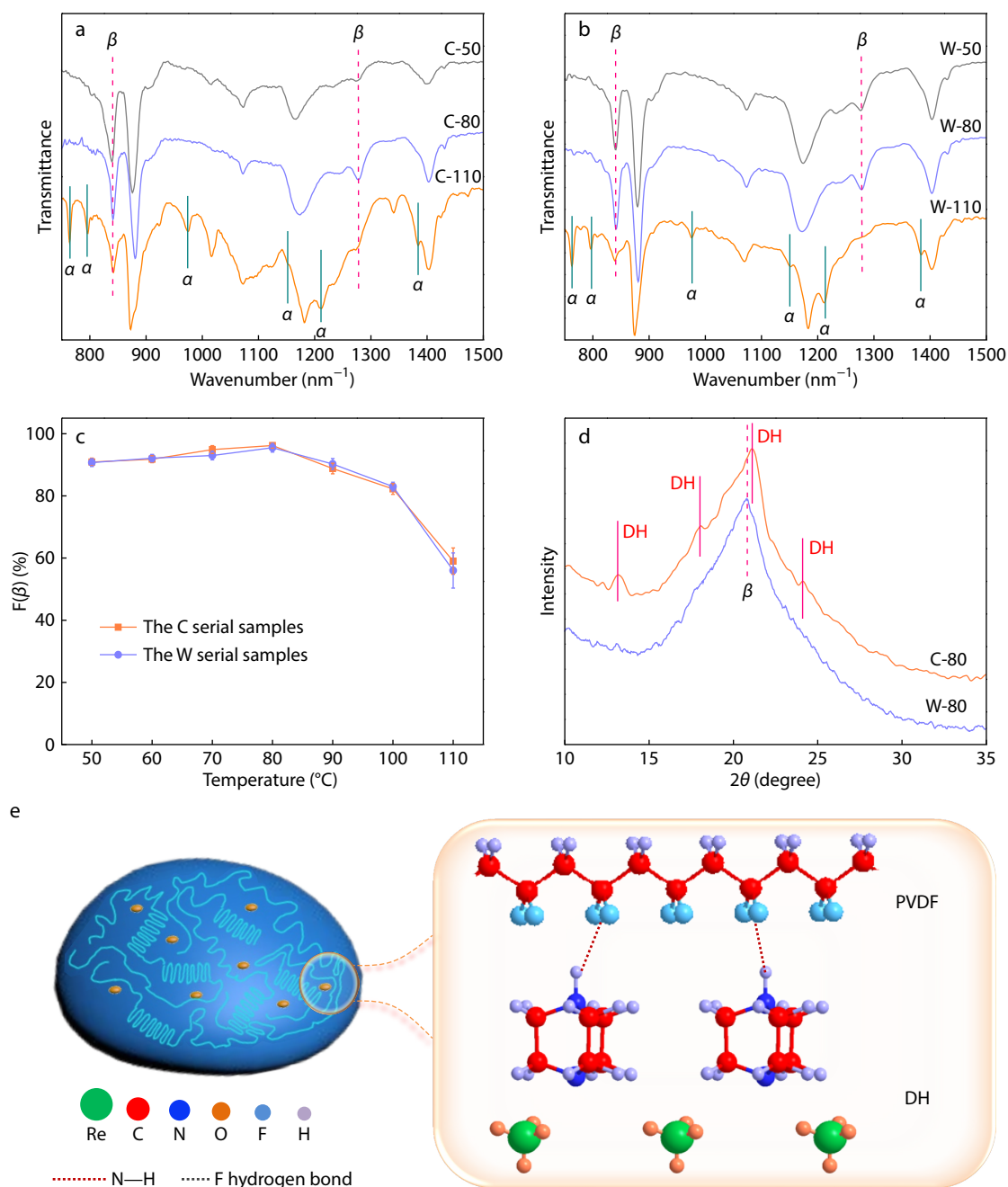


Fig. 3 FTIR spectra of (a) C-series of samples and (b) W-series of samples. (c) The fraction of β -phase PVDF of these films. (d) WAXD patterns of C-80 and W-80. (e) The schematic diagram of the hydrogen bonding interaction between PVDF and DH.

DH, characteristic peaks belonging to DH at $2\theta=13.2^\circ$, 17.8° , 21.0° and 24.1° are also observed in C-80.^[34] As observed in Figs. 3(c) and 3(d), both the relative fraction of β -phase and the crystallinity of PVDF are not changed obviously by the water washing processes. In order to understand the hydrogen bonding interaction more intuitively, we show the schematic diagram in Fig. 3(e).

The excellent piezoelectric properties of PVDF-based films also depend on the orientation of PVDF. Piezo-response force microscopy (PFM) is an effective characterization tool for studying polarization switching in the nanoscale ferroelectric

domain.^[33,41] Here, local PFM spectroscopic experiments were performed to identify the orientation of lamellar crystals, the evolution of domain structure and domain dynamics in PVDF-based W-80 film. We scanned the PFM signal of the sample in an area of $1\ \mu\text{m} \times 1\ \mu\text{m}$ (Figs. 4a–4c), and counted the phase degree at the red line (Figs. 4d–4f). The phase images of the un-poled W-80 are shown in Figs. 4(a) and 4(d). In order to visualize the switching process of the ferroelectric domain, we first applied a DC voltage ($-8\ \text{V}$) between the conductive tip and the conductive substrate to perform a local switching test. After the first polarization, significant reversals of phase contrasts ($\sim 180^\circ$) appear in the polarized area (the square

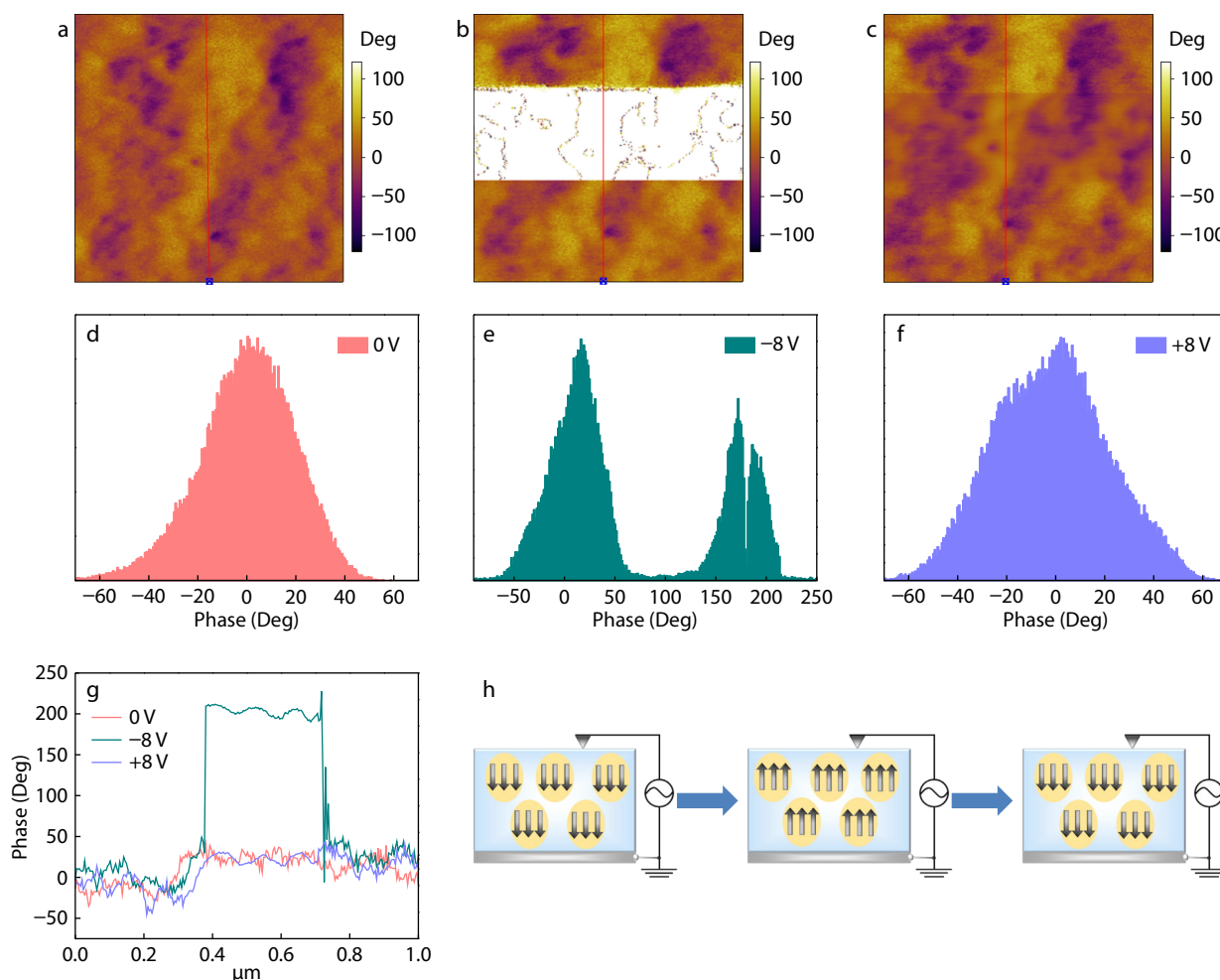


Fig. 4 (a) Phase images for the $1 \mu\text{m} \times 1 \mu\text{m}$ area of the W-80, which was taken (a) in the origin state and taken after applying tip biases of (b) -8 V and (c) $+8 \text{ V}$ in the central region. Phase degree at the red line for the W-80, which was taken (d) in the origin state and taken after applying tip biases of (e) -8 V and (f) $+8 \text{ V}$. (g) The phase degree statistics of (d)–(f). (h) Schematic diagram of dipole arrangement during polarization.

area in the middle of the PFM image) (Figs. 4b and 4e). After continuing to apply the reverse DC bias ($+8 \text{ V}$), the phase of the polarized region returns to the original state (Figs. 4c and 4f). There is no obvious trace of deformation in the polarized area during the switching of ferroelectric domains. The phase change of the sample before and after polarization is shown in Fig. 4(g).

Assuming that the direction of the dipole in an ordered PVDF crystal is shown in Fig. 4(h1), after applying a voltage, the dipole is reversed Fig. 4(h2). After applying a reverse voltage to the sample again, the dipole returns to its original direction, as shown in Fig. 4(h3). The above results provide evidence that the existence of aligned dipoles in the β -phase PVDF of W-80. The switchable polarization also suggests the ferroelectric properties of W-80 and shows the potential application in non-volatile ferroelectric random access memory (FeRAM).^[33,41]

Piezoelectric Output Performance

Flexible piezoelectric materials have attractive potential and play increasingly important roles in flexible piezoelectric devices. Next, we explore the piezoelectric response of PVDF-

based films to demonstrate their applications in piezoelectric sensing, and energy harvesting, etc. First, the piezoelectric response under pressing mode of the transparent PTS devices was evaluated with a vibration exciter which can apply a controlled pulse force with different magnitudes and frequencies to the films supported on a hard stage. The data collector with force transducer can accurately measure the amount of force applied to the samples in real time. The electrical signals generated by the samples are collected by the oscilloscope. The schematic diagram of the measurement setup is shown in Fig. 5(a). Fig. 5(b) shows the voltage outputs of the C-series of samples which was repeatedly impacted by a force of 25.5 kPa with a frequency of 8 Hz , we find that the voltage peak values can be slightly enhanced by increasing the annealing temperature from $50 \text{ }^{\circ}\text{C}$ to $80 \text{ }^{\circ}\text{C}$. The highest value of 1.23 V is recorded for the C-80. As discussed in the above sections, the content of β -phase PVDF and the ordered orientation of PVDF, which are the origin of piezoelectric properties of PVDF, can be slightly increased by increasing the annealing temperature between $50 \text{ }^{\circ}\text{C}$ to $80 \text{ }^{\circ}\text{C}$. Therefore, the enhanced voltage outputs observed in Fig. 5(b) should be caused by the increased

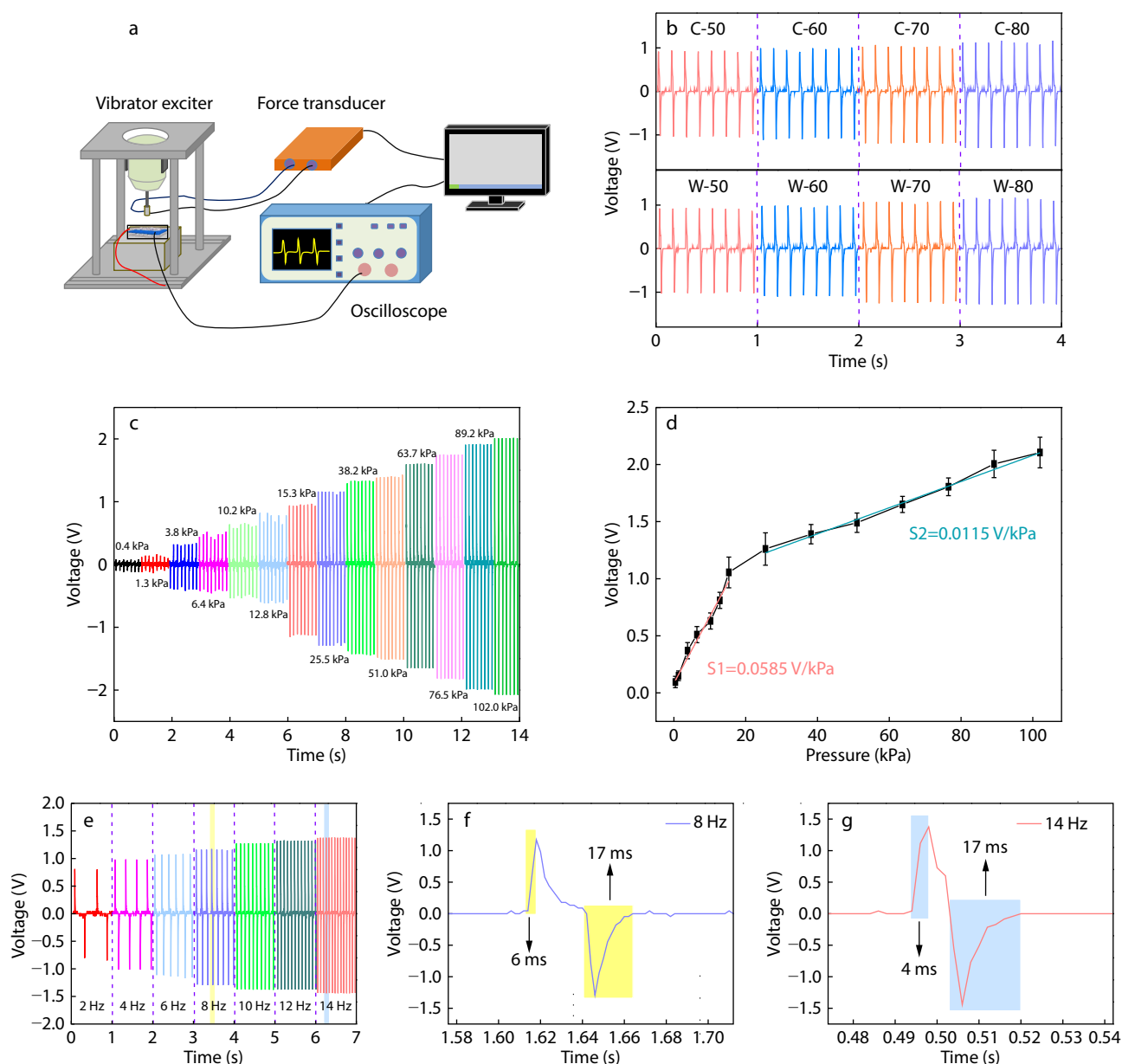


Fig. 5 Piezoelectric response under the pressing deformations of the C series of samples and the W series of samples. (a) Schematic diagram of the measurement setup. (b) The output voltage of the C series of samples and the W series of samples (25.5 kPa, 8 Hz). (c) The output voltage of W-80 under different applied pressures (8 Hz). (d) The trend of applied pressure versus output voltage. (e) The output voltage of W-80 under various frequencies (25.5 kPa). The response time and the recovery time of W-80 under (f) 8 Hz and (g) 14 Hz.

content of β -phase PVDF. Since the samples which were originally annealed at a temperature higher than 80 °C displayed a descending content of β -phase, the piezoelectric performance of them are not presented here. The W series of samples were also investigated in the same conditions. Again, the highest voltage outputs were recorded in W-80, which was originally annealed at 80 °C and demonstrated the maximum content of β -phase PVDF. When comparing the voltage outputs of W serial samples to those of C serials, we found that their values are almost identical, in agreement with the similar content of β -phase PVDF. The dipoles in the β -phase PVDF molecules are in the same direction, resulting larger piezoelectric output signals under the action of external forces

than the α -phase PVDF film annealed at 80 °C (Fig. S7 in ESI). Piezoelectric constant (d_{33}) is a key parameter to measure the strength of piezoelectric effect, and it is related to the electrical output performance and sensitivity of piezoelectric materials. We tested the piezoelectric constant value of the W series of samples and found that with the increase of annealing temperature, the piezoelectric constant first increased and then decreased, reaching a peak value (-29 pC/N) in the W-80 sample (Fig. S8 in ESI), which is comparable to the value in other literatures.^[42]

The piezoelectric voltage constant g_{33} also indicates the piezoelectric performance of the PTS devices, was calculated the values of g_{33} according to the following equation:

$$V = g_{33} \cdot T \cdot F/A \quad (3)$$

where V is the voltage output, T is the thickness of piezoelectric film (50 μm), F is the applied force, A is the touched area of the films, and F/A is the applied pressure.^[15,43] For W-80, the g_{33} is found to be $1.2 \text{ V}\cdot\text{m}\cdot\text{N}^{-1}$. It is worthy to note here that the g_{33} is about three times higher than the commercially available PVDF films which are obtained by stretching and electrically poling.^[44] In addition, the output performance is related to the thickness of the films. The output voltage value has a linear relationship with the thickness of the film, the details are described in Fig. S9 (in ESI).

Fig. 5(c) shows the voltage outputs of W-80 under different pressures at a frequency of 8 Hz. Clearly, the voltage outputs increase in accordance with the increase of the applied pressure. When the applied pressure is gradually increased from 0.4 kPa to 102.0 kPa, the values of output voltage are gradually increased from 0.09 V to 2.12 V, as shown in Figs. 5(c) and 5(d). We evaluate the sensitivity of the sensor by calculating the slope of the voltage-pressure curve.^[45] The device shows a sensitivity of 0.0585 and $0.0115 \text{ V}\cdot\text{kPa}^{-1}$ in the areas below and above 15.3 kPa, respectively. Obviously, W-80 can be

used as a self-powered piezoelectric sensor for force detection, especially in a relatively low pressure range. The sample can even detect the electrical signal generated under the applied pressure of 0.4 kPa. In addition, we characterized the output voltages of W-80 at a constant pressure (25.5 kPa) with different frequencies and presented the result in Fig. 5(e). Clearly, the resulted output voltages slightly depend on the frequency of applied forces when the PTS are impacted at low frequency (lower than 10 Hz). For instance, the output voltage increases from 0.83 V at 2 Hz to 1.35 V at 10 Hz. However, when the frequency of applied forces is higher than 10 Hz, the output voltage is saturated at about 1.45 V. The increased output voltage with increasing the applied frequency may be caused by the decreased impedance with the increasing of applied frequency.^[46] Randomly select two output voltage curves under different frequencies (8 Hz, 14 Hz) as the representatives for detailed analysis (Figs. 5f and 5g). W-80 can quickly respond to external mechanical stimuli and quickly return to its original state. As the frequency increases from 8 Hz to 14 Hz, the response time decreases from 6 ms to 4 ms. The recovery time is slightly longer than the response time and

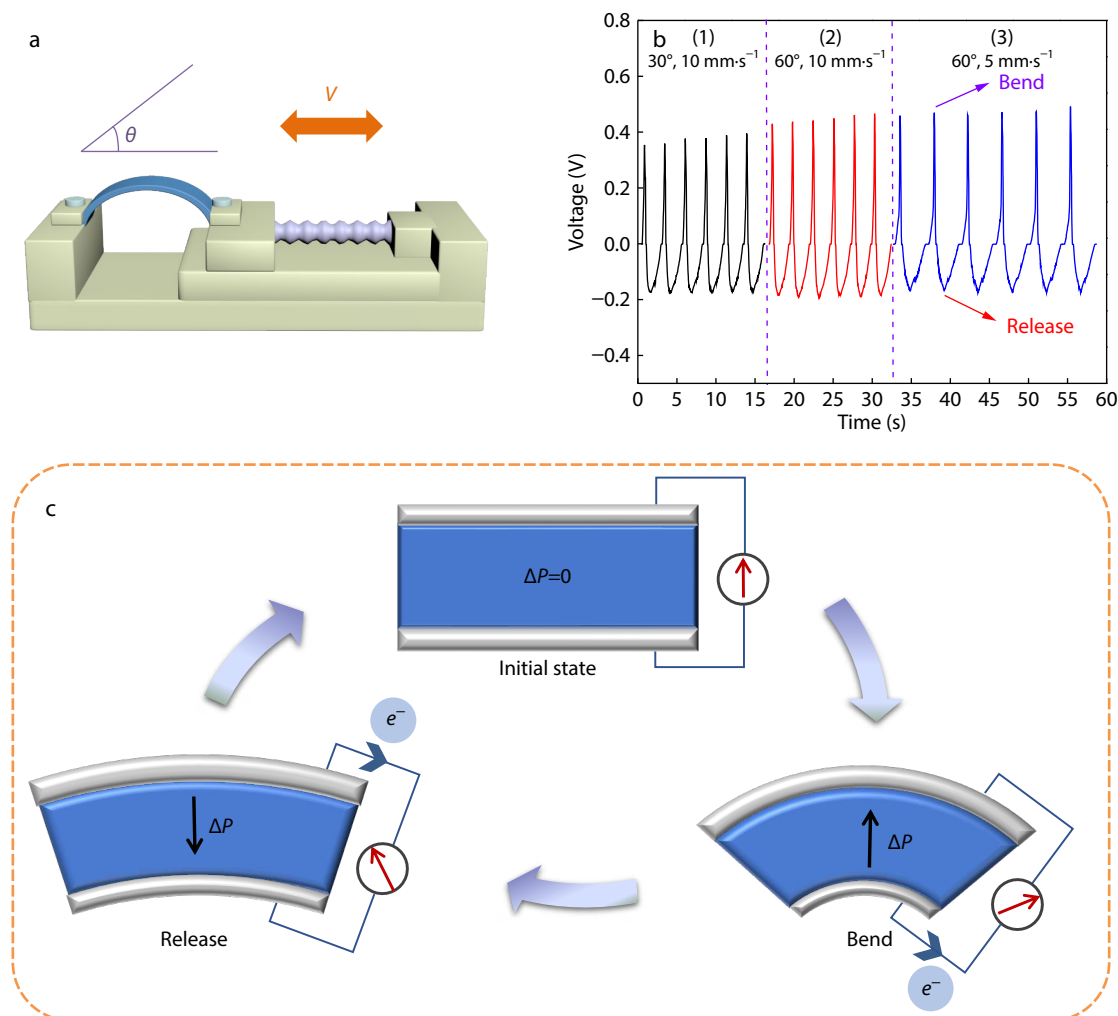


Fig. 6 Piezoelectric response under the bending deformations of the W-80. (a) The schematic illustration of measurement setup. (b) The output voltage of the W-80 under different bending angles (30° and 60°) and different average releasing rates (5 and $10 \text{ mm}\cdot\text{s}^{-1}$). (c) The schematic illustration of the piezoelectric signals generating through dynamic bending and releasing process.

hardly changes with the frequency (17 ms). The possible reason is that the slow decrease of the residual charges on the film surface leads to a longer recovery time.^[45]

In addition to the applied pressing forces, the W-80 can be accustomed to detect the output signals under the bending deformations. Bending angle and average releasing rate can be controlled by a linear motor, the schematic diagram is shown in Fig. 6(a). Figs. 6(b1) and 6(b2) present the response curve under different bending angle (30°, 60°) with average releasing rate of 10 mm·s⁻¹, the output voltage values are increased from 0.4 V to 0.47 V, respectively. When the bending angle is constant (60°) and the releasing rate is decreased to 5 mm·s⁻¹, the response curve changes, as shown in Fig. 6(b3). Under bending deformation, the schematic diagram of the piezoelectric signal generated through the piezoelectric sensor is shown in Fig. 6(c). In the original state, the net dipole moment of the film is zero, so no piezoelectric signal is generated. Under bending deformation, the net dipole moment of the film is no longer zero, and a piezoelectric signal is generated. In the process of releasing to the original state, the charge accumulated on the electrode is transferred in the reverse direction, generating a piezoelectric signal in the opposite direction.^[47,48] These results indicate that these transparent sensors can detect mechanical deformation under different conditions, and demonstrate their potential in practical applications.

To evaluate the effective output power of the PTS devices, we connected the W-80 samples to external loads with differ-

ent electric resistances. As illustrated in Fig. S10(a) (in ESI), the output voltage gradually increases and saturates to the open-circuit voltage with increasing the resistance from 10⁵ Ω to 10⁸ Ω. Meanwhile, the output current gradually decreases and saturates by increasing the resistance. Accordingly, the output power (*W*) can be calculated according to the following equation:

$$W = \frac{V^2}{R} \quad (4)$$

where *V* is the output peak voltage and *R* is the loaded resistance.^[38,49] As presented in Fig. S10(b) (in ESI), *W* reaches a maximum value of about 146.4 nW at a load resistance of about 10⁷ Ω. At the same voltage level, the short-circuit current and output power of the W-80 sample are comparable to some reports.^[26,38,50] This indicates that the 10⁷ Ω load resistance is the perfect load matching resistance to the W-80 device for achieving the maximum power to drive low-power electronic devices.

Lifetime and Adhesive Properties

To ensure good lifetime of the PTS devices, the piezoelectric films should adhere to the substrates or metal electrodes and must sustain repeated deformations. Therefore, we measured the adhesion properties of C-80 and W-80 samples which display high transparency and the best electric output performances among the samples using the D3359 STM standard test method.^[29] For comparison, pure PVDF films which was obtained by deposition under the same conditions of C-80, was also tested. As shown in Fig. 7(a), neat PVDF films can

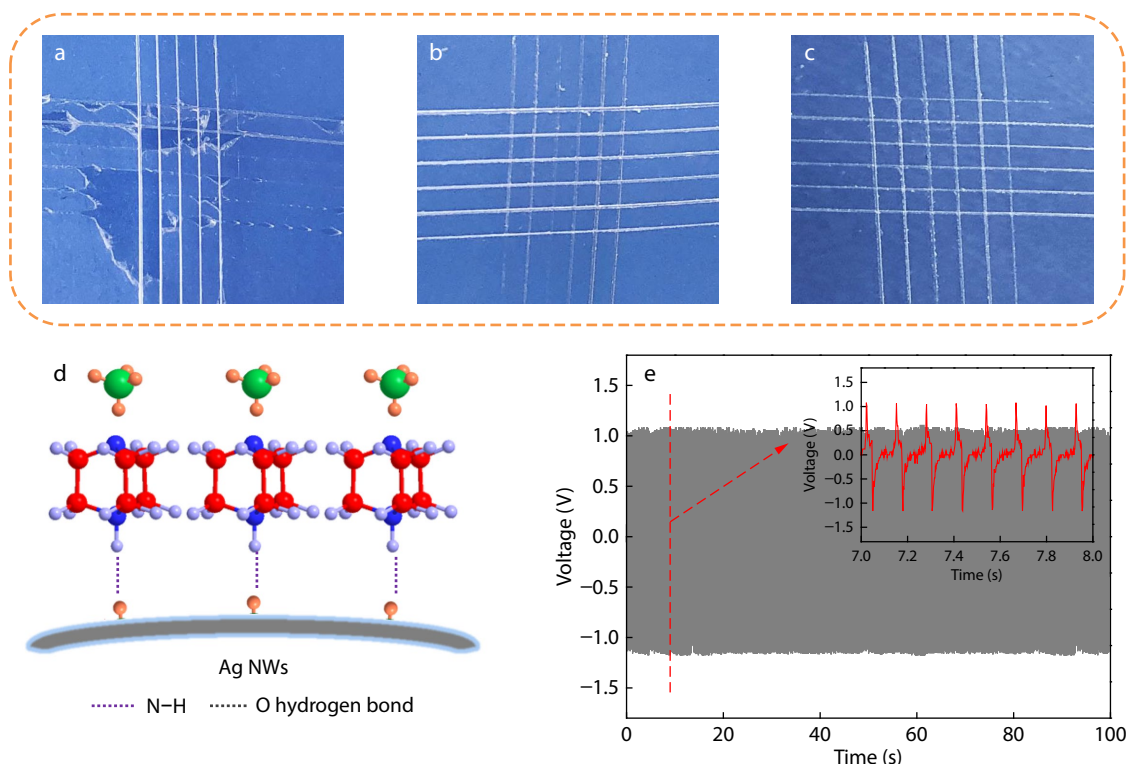


Fig. 7 Photographs of (a) neat PVDF film annealed at 80 °C, (b) C-80, and (c) W-80, whose adhesion properties were characterized by the D3359 tape test method; (d) The schematic diagram of the hydrogen bonding interactions between DH and the oxygen-containing functional groups on the surface of the Ag NWs; (e) Stability test of W-80. The photograph inside is the magnified view of the output signals highlighted in (e).

be easily peeled off from the Ag NWs-coated PET substrates. However, the PVDF-DH composite films can adhere strongly to the substrates (Fig. 7b). In addition, even if the DH particles are removed from the composite films, the adhesion property of these films is not essentially changed, as shown in Fig. 7(c). The possible reason is that the water only washed away the DH on the PVDF surface and the PVDF grain boundary edges, and part of DH contacting the substrate remained. The enhanced adhesion of PVDF-DH films should be resulted from the hydrogen bonding interactions because there are N—H groups in DH and oxygen-containing functional groups on the surfaces of Ag NWs (Fig. 7d). Benefitted from the good adhesion between piezoelectric films and Ag NWs-coated PET substrates, the PTS devices exhibit high stability and mechanical endurance under repeated mechanical impacts. Fig. 7(e) displays the output voltage-time curves of the W-80 device under a dynamic pressing compression force of 25.5 kPa and a frequency of 8 Hz. The output voltage is almost constant without any significant degradation even after 8000 measured cycles, indicating the long-term stability and durability of the PTS devices.

CONCLUSIONS

In summary, we fabricated piezoelectric touch sensors based on solution processable PVDF-dabcoHReO₄ composite materials by a low cost and large scale method. The incorporation of the multiaxial molecular ferroelectrics-dabcoHReO₄ can not only induce the phase transition of PVDF from α - to β -phase at relatively low annealing temperatures (below 100 °C) and the crystal orientation, but also improve the adhesion properties of PVDF-based films due to the hydrophilic nature of dabcoHReO₄. Therefore, PVDF-dabcoHReO₄ films can be easily deposited on flexible, transparent and conductive substrates, which can be integrated to self-powered transparent screens, interactive interface, etc. When the dabcoHReO₄ particles on the surfaces of films are removed by ultrapure water, the transmittance to visible light can be further increased to a value higher than 94%, and the crystal form and crystallinity of PVDF are not changed obviously while maintaining the electromechanical properties. These excellent characteristics of the as-prepared transparent thin films make the corresponding devices have good piezoelectric output performance, stability and durability, and show their potential applications in touch panels with sensing and energy harvesting capabilities.

NOTES

The authors declare no competing financial interest.

Electronic Supplementary Information

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