

High-performance flexible piezoelectric sensor assisted by machine learning for human motion and physiological signal monitoring

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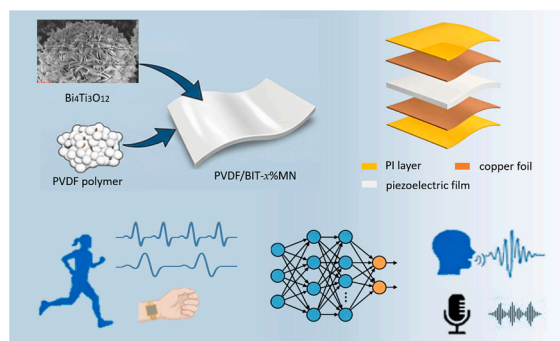
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GRAPHICAL ABSTRACT

This work develops PVDF-based piezoelectric sensors using modified Bi₄Ti₃O₁₂ fillers to enhance β -phase content and piezoelectric performance. Integrating with machine learning, the piezoelectric sensor is used to monitor human motion and weak physiological signals.



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ABSTRACT

Achieving a high polar β -phase fraction in fluoropolymer piezoelectric sensors is essential for optimizing the piezoelectric coefficient (d_{33}) and sensitivity, both of which are pivotal for the monitoring of weak human physiological signals and human-machine interaction. However, traditional methods for increasing the β -phase fraction mainly rely on hydrogen bonding interactions, which necessitate complex surface modification for inorganic components. In response to this challenge, we propose chemical modulation of the interfacial ion-dipole interaction, enabling effective enhancement of the polar β -phase fraction and obtaining high sensitivity of poly(vinylidene fluoride) (PVDF)-based sensors. Herein, PVDF-based piezoelectric composites were

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successfully fabricated by employing metal-modified $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) as the filler. Experimental results show that the piezoelectric coefficient (d_{33}) of PVDF/BIT-25%MN is $47 \text{ pC}\cdot\text{N}^{-1}$. This is mainly due to the interfacial ion-dipole interactions between the variable-valence ions/defects and the polymer chains, which promote the β -phase fraction. Furthermore, this piezoelectric sensor exhibits a high power density of $1580 \text{ nW}/\text{cm}^2$ for energy harvesting and a high sensitivity of $1.83 \text{ V}\cdot\text{kPa}^{-1}$ for sensing. Owing to its high sensitivity and excellent dynamic response, the sensor reliably monitors weak physiological signals, such as pulse and throat vibrations. Furthermore, by integrating machine learning algorithms, the system enables intelligent classification and precise recognition of complex human motion signals, facilitating the development of next-generation self-powered intelligent monitoring systems with multifunctionality.

1. Introduction

Although multifunctional flexible and wearable electronics have advanced remarkably, they remain largely reliant on traditional power sources such as lithium-ion batteries. The rigid, non-stretchable nature of these sources, coupled with periodic maintenance requirements, poses a significant bottleneck to integration with implantable devices. To overcome these challenges, self-powered flexible sensors have emerged as the preferred paradigm for next-generation miniaturized electronics. Accordingly, the design of lightweight and sustainable self-powered sensing systems has become a central focus of contemporary research [1–3]. Among the numerous energy harvesting strategies available, flexible piezoelectric generators have attracted widespread interest for their capacity to harvest environmental mechanical energy (human movements and weak vibrations) and convert it into electricity [4,5]. Given its superior mechanical flexibility, chemical resistance, and processability, poly(vinylidene fluoride) (PVDF) is widely regarded as the primary matrix for developing high-performance flexible piezoelectric generators. PVDF primarily consists of α , β , and γ crystalline phases, with the α -phase being nonpolar and the γ -phase exhibiting weak polarity. It is well known that the β -phase features an all-trans (TTTT) conformation. In the β -phase, the negative ends of dipoles (from C—F bonds) and the positive ends (from C—H bonds) are oriented in opposite directions, resulting in the unidirectional alignment of molecular dipole moments. This alignment induces spontaneous polarization and a significant piezoelectric/ferroelectric response [6]. Nevertheless, the fraction of the electroactive β -phase and piezoelectric coefficient d_{33} ($7\text{--}28 \text{ pC}\cdot\text{N}^{-1}$) of pure PVDF remain limited [7–9], thereby significantly restricting its potential for high-efficiency electromechanical coupling in sensing, actuation, and energy harvesting.

Notably, the piezoelectric coefficient and sensitivity of fluoropolymer sensors are highly dependent on the construction and enrichment of the polar β -phase. Therefore, achieving superior piezoelectric performance in PVDF-based materials requires promoting the formation of this electroactive β -phase within the crystalline structure. Although various fabrication strategies have been reported, extensive research efforts to date have focused on molecular-scale structural design, including chemical modification [10] and compositional tuning [11,12]. Among these, incorporating inorganic fillers with high piezoelectric activity into the PVDF matrix to form composites has been recognized as one of the most effective strategies to increase the β -phase fraction [13]. For instance, Gu et al. reported that the addition of HfO_2 and Cu nanoparticles enhances the crystallinity of the β -phase in PVDF piezoelectric materials, leading to improved dielectric properties and significantly enhanced electromechanical performance [14]. Fu et al. fabricated high-sensitivity flexible piezoelectric energy harvesters by incorporating aligned BaTi_2O_5 nanorods into the PVDF matrix. They employed a combination of hot-pressing and subsequent high-voltage polarization, which increased the β -phase fraction of the composite from 42% to 54% [15]. Additionally, as previously reported, flexible polymer-inorganic composite films were successfully fabricated by embedding carboxyl-functionalized VSe_2 monolayers into the PVDF matrix. The carboxyl groups on the VSe_2 surface not only inhibit nanosheets aggregation but also induce the formation of the

electroactive β -phase in PVDF via O—H...F hydrogen bonding. This co-crystallization strategy facilitates the formation of an ultra-flat hybrid structure, thereby significantly enhancing the efficiency of strain and polarization transfer between the two phases [16]. Although some progress has been made in incorporating nanomaterials into PVDF, the increase in polar phase either relies on high-cost, complex modification of inorganic fillers, focuses on interfacial hydrogen bonding interactions, or remains insufficiently understood.

Here, we propose that the interfacial ion-dipole interactions induced by valence reconstruction and defects are an effective strategy to enhance the polar phase. Among various inorganic fillers, we employed a metal-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) filler. BIT has a layered perovskite structure and holds significant potential due to its high Curie temperature and unique ferroelectric characteristics [17]. Previous studies have demonstrated that doping with metal elements can modulate oxygen vacancy concentrations, optimize electrical properties and polarization strength, and consequently enhance the piezoelectric activity of the material. For instance, the synergistic substitution of Ti^{4+} ions by high-valence Ta^{5+} and low-valence Mn ions reduces the concentration of oxygen vacancy defects in BITMT ceramics, thereby increasing the piezoelectric coefficient d_{33} [18]. Similarly, Bai et al. reported co-doping $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ with Cr and Nb not only endows stronger piezoelectric performance but also promotes spectral absorption [19]. Indeed, even minor alterations to the pristine properties of the filler can significantly influence the composite. Moreover, the composition and micromorphology of the fillers play a crucial role in determining the overall performance of the resulting composites [20,21].

In this study, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ was successfully modified by synergistic co-doping with donor Nb and acceptor Mn to substitute for Ti, resulting in the formation of hierarchical nanoflower structures. These nanopowders, denoted as $\text{Bi}_4(\text{Mn}_{1/2}\text{Nb}_{1/2})_y\text{Ti}_{3-y}\text{O}_{12}$ ($y = 0, 0.1, 0.2, 0.3, 0.4, 0.5$) and abbreviated as BIT- $x\%$ MN ($x = 0, 5, 10, 15, 20, 25$, and $2x\% = y$), offer distinct structural advantages. At the macroscopic level, the hierarchical flower-like structures exhibit rougher surfaces and significantly larger specific surface areas compared to traditional spherical particles. This morphology not only enhances stress transfer through improved mechanical interlocking, but also provides abundant interfacial nucleation sites, thereby strengthening the interfacial interaction between the fillers and the polymer matrix. At the microscopic level, the optimization of charge distribution through compositional modification leads to the formation of localized charged centers arising from charge imbalance. These further enhance the ion-dipole or dipole-dipole interactions, thereby inducing the conformational transition of PVDF molecular chains from random coils to an all-trans (TTTT) configuration. This process destabilizes the α -phase while concurrently increasing the β -phase fraction, thereby fundamentally enhancing the piezoelectric properties of the composite. Consequently, flexible devices fabricated from this material not only enable efficient mechanical energy harvesting but also demonstrate high sensitivity and rapid response times in monitoring large-scale human movements and detecting subtle physiological signals (such as pulse and laryngeal vibrations). This work offers a novel material solution for next-generation self-powered health monitoring systems, as illustrated in Fig. 1. Furthermore, machine learning was used to evaluate recognition accuracy.

2. Results and discussion

As illustrated in Fig. 2a, $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT) exhibits a perovskite-like structure, characterized by $[\text{Bi}_2\text{O}_2]$ layers sandwiched between triple layers of $[\text{TiO}_6]$ octahedra [22]. In this study, BIT nano powders were synthesized via a facile hydrothermal method. The microscopic morphology consists of nanoflowers assembled from numerous nanosheets [23], as confirmed by the scanning electron microscopy (SEM) image in Fig. 2b. As anticipated, the thickness and width of the constituent nanosheets vary with doping concentration of Mn and Nb, as shown in Fig. S1. Furthermore, energy dispersive X-ray spectroscopy (EDS) elemental mapping confirms the uniform distribution of Bi, Mn, Ti, Nb, and O elements throughout the nanoflowers (Figs. 2b and S2). The powder X-ray diffraction (PXRD) patterns of pure BIT and the BIT- $x\%$ MN ($x = 0, 5, 10, 15, 20, 25$) systems, measured in the 2θ range from 10° to 70° , are presented in Fig. 2c. The results indicate that all hydrothermally synthesized nano powders exhibit an orthorhombic crystal structure. All diffraction peaks are consistent with previously reported data [24], and no impurity phases were detected. This indicates that Mn and Nb co-doping preserves the phase purity of all samples without inducing any observable secondary phases. It has been reported that the ionic radii of Nb^{5+} (0.64 Å) and Mn^{2+} (0.80 Å) are larger than those of Ti^{4+} (0.605 Å) [25]. As shown in the XRD (Fig. S3), the main peaks exhibit a slight shift toward lower angles, indicating an expansion of the unit cell and an increase in the interplanar spacing d . This trend is consistent with the expectation that larger-radius ions substitute for Ti at the B-sites of the perovskite structure. To further characterize the structural features of the nano powders, Fourier-transform infrared (FT-IR) spectroscopy was performed (Fig. S4). The absorption bands at 530 cm^{-1} and 823 cm^{-1} are attributed to the stretching vibrations of the Bi—O and Ti—O bonds in BIT, respectively [26]. The peaks at approximately 3400 cm^{-1} and 1600 cm^{-1} correspond to the bending vibrations of O—H bonds from adsorbed water molecules [27]. Notably, the optical absorption intensity of the doped nanoflowers is significantly enhanced in both the visible and near-infrared regions (Fig. S5), which directly indicates that the electronic structure has been modified.

Since Mn and Nb doping may induce charge imbalance, X-ray

photoelectron spectroscopy (XPS) was employed to investigate the valence states of the constituent elements. Based on the XPS results for the pure BIT and BIT-25%Mn powders (Fig. S6, S7), Nb was found to exist in a +5 state and Bi in a +3 state, while Ti exhibits a coexistence of +3 and +4 oxidation states [28,29]. Deconvolution of the Mn 2p XPS spectrum suggests the coexistence of Mn^{2+} , Mn^{3+} , and Mn^{4+} species (Fig. 2d), with the satellite peak at 647 eV confirming the presence of Mn^{2+} [30]. These observations indicate that the mixed-valence states detected by XPS are likely accompanied by the formation of local defects. Regarding oxygen species in the nanomaterials, the deconvoluted O 1s spectra in Fig. 2e reveal that the oxygen species consist primarily of lattice oxygen and oxygen vacancies, along with a minor amount of adsorbed oxygen [31,32]. Fig. S8, S9 reveals a clear and systematic positive shift in the F 1s binding energy: from 686.8 eV in pure PVDF to 687.2 eV in the optimally doped PVDF/BIT-25%Mn sample. This +0.4 eV shift indicates a measurable depletion of electron density around the fluorine atoms, consistent with the withdrawal of lone-pair electrons by the strongly Lewis acidic Mn^{3+} sites. Notably, the magnitude of this shift increases with the Mn doping concentration, establishing a direct correlation between the Lewis acid strength and the extent of interfacial interaction. This trend strongly supports the proposed mechanism: stronger ion–dipole interactions at higher Mn^{3+} content destabilize the nonpolar α -phase and promote the all-trans (TTTT) conformation characteristic of the β -phase.

As we all know that the piezoelectricity of PVDF primarily originates from its internal polar β -phase. The presence of defects, including charge defects and oxygen vacancies, strengthens the electrostatic interactions between the fillers and fluorine atoms on the polymer chains, thereby effectively enhancing the β -phase fraction. Therefore, it is meaningful to conduct this research. Fig. 3a illustrates the complete synthesis process of the ferroelectric PVDF/BIT- $x\%$ Mn composite piezoelectric films. Detailed procedures are provided in the Experimental section. To investigate the morphology of the PVDF matrix filled with BIT- $x\%$ Mn particles, SEM was employed to characterize the films. As presented in Fig. 3b, the pure PVDF film exhibits a dense and continuous interwoven microstructure. This specific architecture endows the film with favorable mechanical flexibility and structural

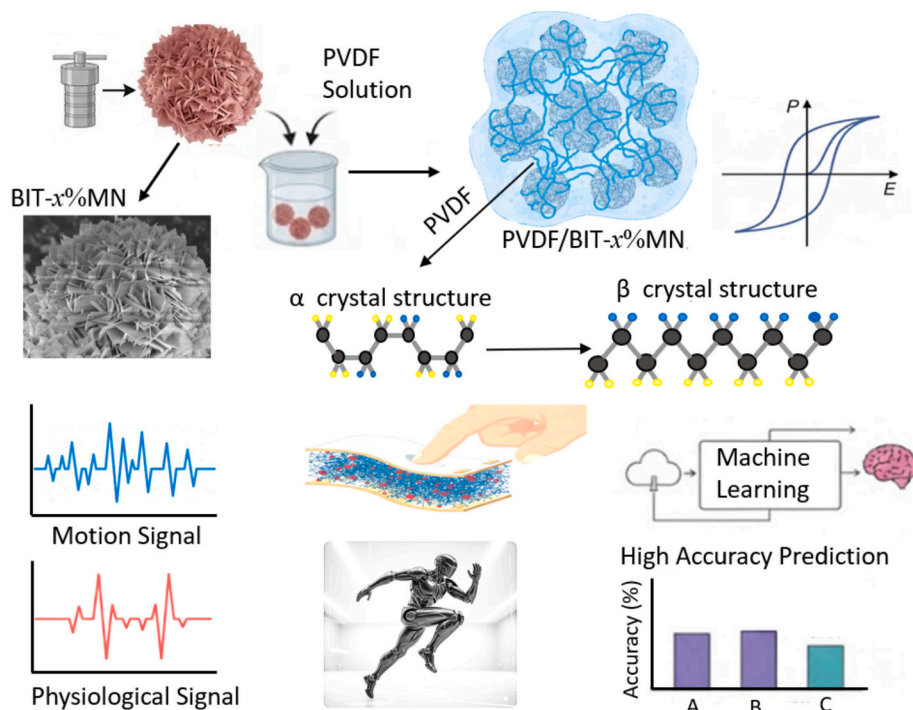


Fig. 1. Schematic illustration of the synthesis process, piezoelectric response, and machine learning framework.

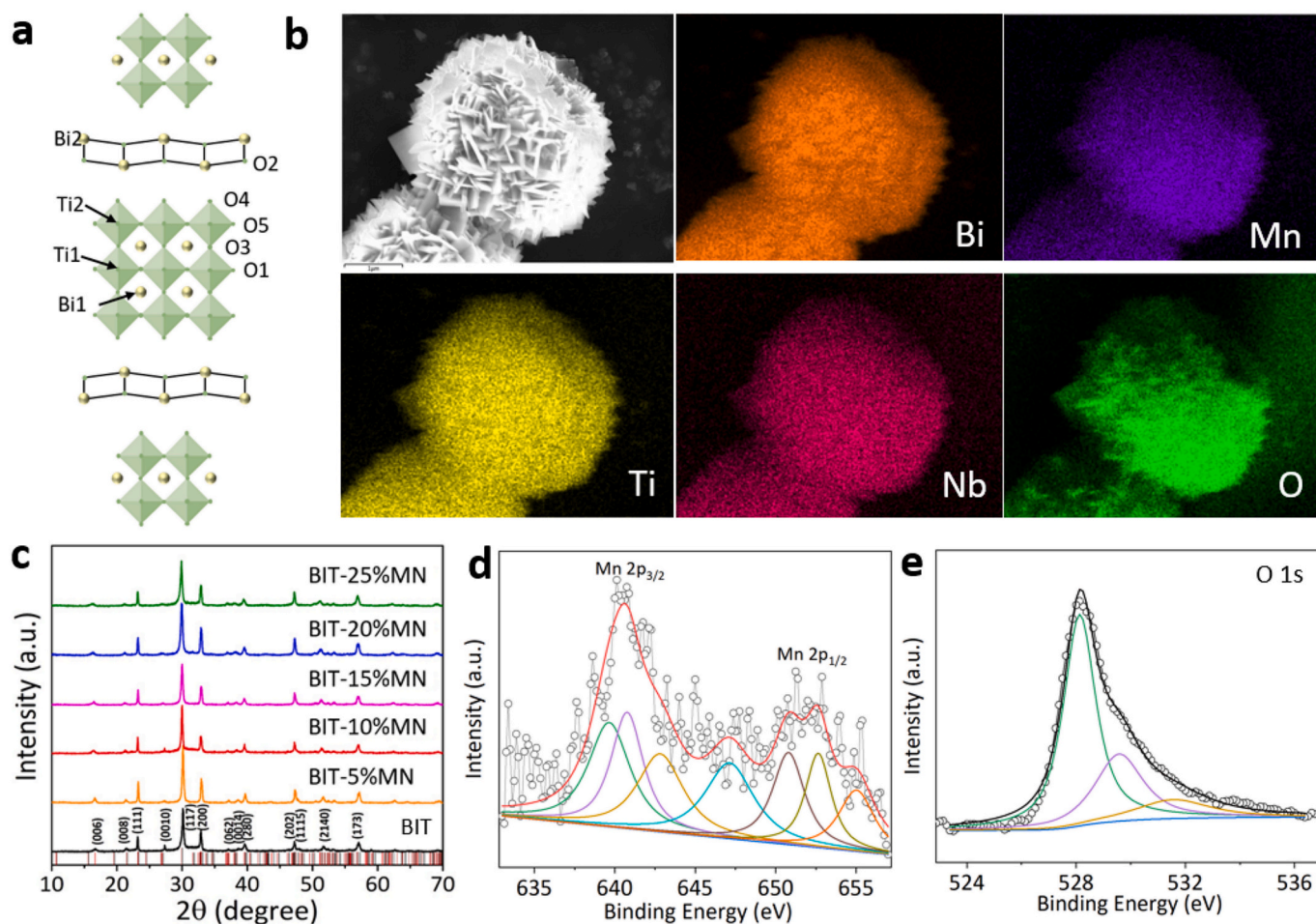


Fig. 2. Structural characterization of BIT-*x*%Mn powders. (a) Crystal structure of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$. (b) Scanning electron microscopy (SEM) images of BIT-20%Mn, and corresponding energy dispersive X-ray spectroscopy (EDS) elemental mapping of Bi, Mn, Ti, Nb, and O. (c) The powder X-ray diffraction (PXRD) patterns of BIT and BIT-*x*%Mn with different Mn/Nb doping ratios. (d) Mn 2p X-ray photoelectron spectroscopy (XPS) spectrum of BIT-25%Mn. (e) O 1s XPS spectrum of BIT-25%Mn.

integrity. In contrast, Fig. 3c depicts the composite film, in which a substantial number of nanoflower-like particles are uniformly dispersed across the surface of the PVDF matrix. These particles correspond to the filler components of the composite system and are mechanically interlocked within the matrix. Their well-defined crystalline morphology and excellent dispersion confirm that the BIT-25%Mn nanoflowers achieve sufficient interfacial contact with the PVDF matrix, which is essential for effective interface interaction.

To evaluate the water stability of the composite films, water contact angle measurements were performed. As shown in Fig. 3d, the pure PVDF film exhibits an angle of 80.5° , falling within the weakly hydrophobic regime ($70^\circ < \text{contact angle} < 90^\circ$). This characteristic is attributed to the low surface energy dominated by the C—F bonds in the PVDF molecular chains. In contrast, the PVDF/BIT-25%Mn composite film (Fig. 3e) displays a reduced water contact angle of 63.8° , representing a decrease of approximately 16.7° compared to pure PVDF and indicating a transition to the weakly hydrophilic regime (contact angle $< 70^\circ$). This significant transition originates from the incorporation of BIT-25%Mn. BIT itself is a hydrophilic perovskite featuring polar hydrophilic sites on its surface. When the BIT-25%Mn particles are dispersed within the PVDF matrix, they expose a high density of hydrophilic sites on the film surface. The strong interaction between these sites and water molecules significantly enhances the surface wettability, partially counteracting the hydrophobic effect of PVDF. Consequently, the composite film undergoes a transition from weak hydrophobicity to weak hydrophilicity. Due to the insulation nature of PVDF, its electrical output signals are inherently weak. However, the resistance of the

PVDF/BIT-*x*%Mn films decrease with increasing mass fraction of Mn and Nb (Fig. 3f). The PVDF/BIT-25%Mn sample exhibits the lowest resistance value. The reason can be attributed to the valence fluctuations of the metal dopants, which induce ionic ionization, providing additional charge carriers and thereby tuning the conductivity.

Owing to the unique morphology and modified surface electrical properties of the BIT-*x*%Mn fillers, the interfacial interactions between the fillers and the PVDF matrix promote the phase transition of PVDF molecular chains from the α -phase to the β -phase. Consequently, FT-IR spectroscopy was employed to evaluate the β -phase fraction. In the PVDF/BIT-*x*%Mn composite system, prominent characteristic peaks of the β -phase are clearly observed, including the $-\text{CH}_2$ rocking vibration at 840 cm^{-1} , the C—F stretching vibration at 1176 cm^{-1} , and the C—F out-of-plane deformation vibration at 1275 cm^{-1} [33]. Based on the FTIR data, the β -phase fraction can be calculated using the following formula:

$$F(\beta) = \frac{A_\beta}{\frac{K_\beta}{K_\alpha} A_\alpha + A_\beta}$$

where A_α and A_β represent the absorbance areas at 763 cm^{-1} and 840 cm^{-1} , respectively [34,35]. The calculated β -phase fractions are presented in Fig. 3h. The results indicate that the highest β -phase fraction, observed for the PVDF/BIT-25%Mn sample, reaches as high as 82.5%. The increase in the polar phase can be attributed to two primary factors. On one hand, the non-uniform surface metal valence states induce interfacial electrostatic interactions with PVDF chains. Furthermore, Mn^{3+} ions possess unpaired e_g electrons, which impart strong Lewis

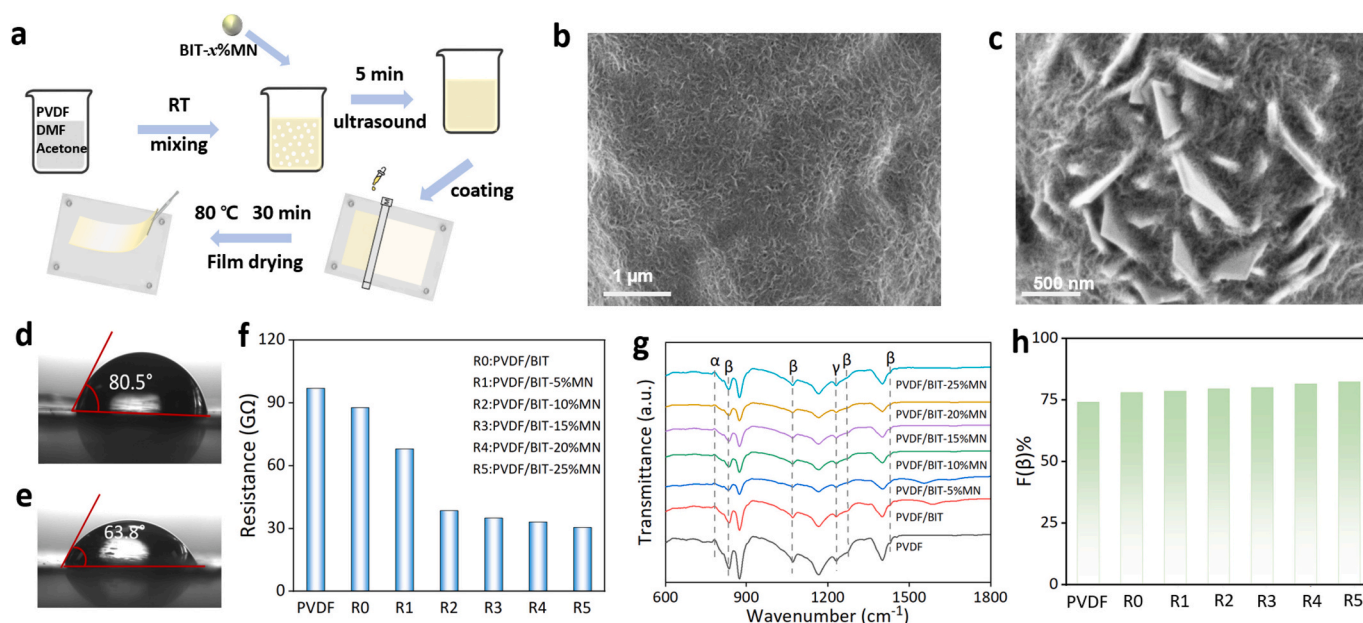


Fig. 3. Fabrication process, microstructure, and structural characterization of PVDF/BIT-x%Mn composite films. (a) Schematic illustration of the film fabrication process. (b, c) SEM images of pure PVDF film (b) and PVDF/BIT-25%Mn composite film (c). (d, e) Water contact angles of pure PVDF film (d) and PVDF/BIT-25%Mn composite film (e). (f) Electrical resistance of PVDF/BIT-x%Mn composite films. (g) FT-IR spectra of PVDF/BIT-x%Mn composite films. (h) The β -phase fraction ($F(\beta)$) of PVDF/BIT-x%Mn composite films.

acidity to its surface [36]. These Lewis acidic Mn sites exert a powerful attraction on the lone pair electrons of the F atoms. This interaction is significantly stronger than typical van der Waals forces, leading to the stretching of C—F bonds. The F 1s spectra in the XPS analysis exhibit a slight shift in binding energy after compositing (Fig. S8 and S9), providing direct evidence of Lewis acid-base interactions. This shift

confirms a significant change in the electron cloud density surrounding the F atoms. On the other hand, oxygen vacancies act as high-energy surface defects. According to heterogeneous nucleation theory, these defect sites can substantially reduce the nucleation energy [37]. Thus, these vacancies serve as active nucleation sites, promoting the preferential crystallization of PVDF into the β -phase fraction at the interface,

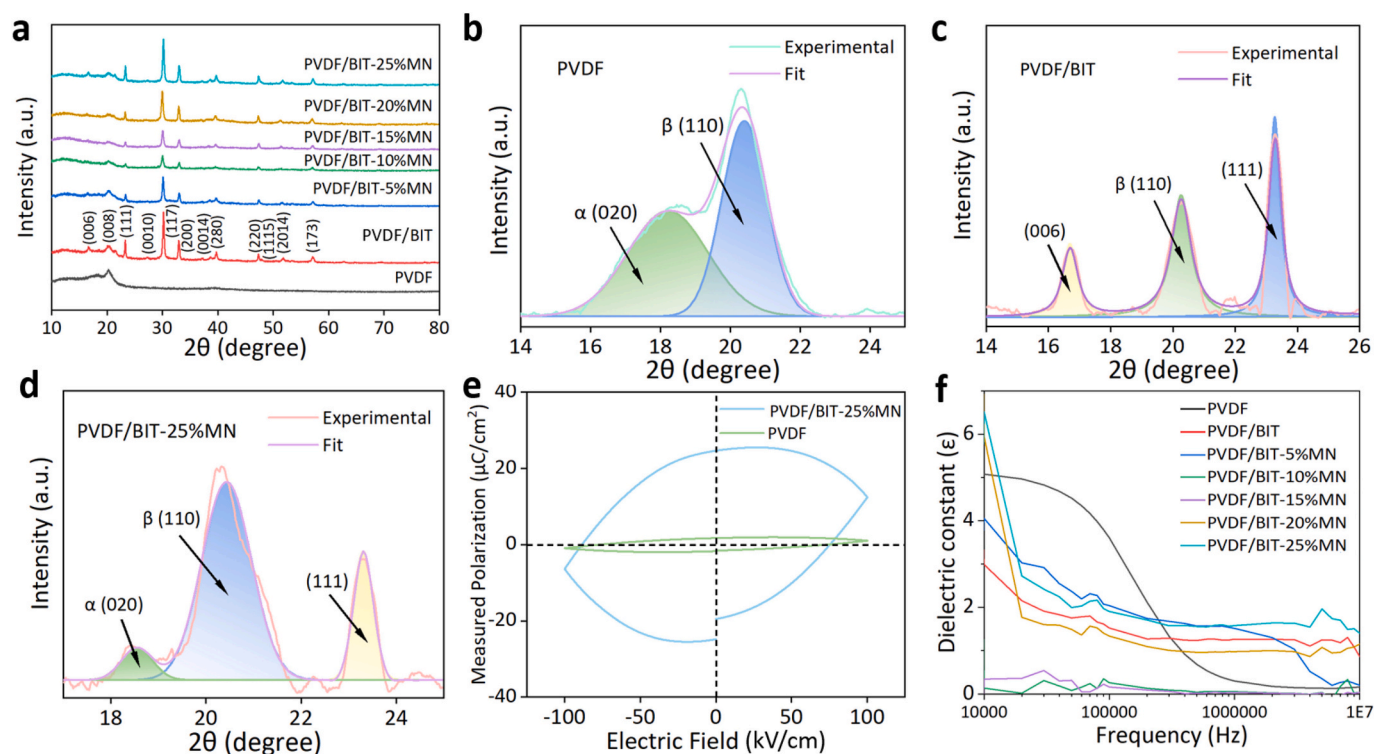


Fig. 4. (a) X-ray diffraction (XRD) patterns of BIT-x%Mn. (b–d) Variations in specific lattice planes intensities and the β -phase fraction as a function of Mn and Nb doping concentration, quantitatively determined via Gaussian peak fitting of the XRD patterns. (e) P-E hysteresis loops of pure PVDF and PVDF/BIT-25%Mn samples. (f) Dielectric constant of BIT-x%Mn.

which subsequently extends into the bulk phase.

To further investigate the enhancement of the β -phase fraction by BIT- $x\%$ MN fillers, XRD patterns of the PVDF/BIT- $x\%$ MN composites and pure PVDF films were recorded (Fig. 4a). The coexistence of the PVDF matrix and BIT components, along with the absence of new impurity peaks, indicates that no significant chemical reactions occurred during the composite preparation. Notably, the prominent diffraction peak at $2\theta = 20.5^\circ$ corresponds to the β (110) crystal plane, while the relatively weak peaks at 18.4° and 36° are assigned to the α (020) and α (200) planes, respectively [38]. To precisely resolve the crystalline composition, peak deconvolution was performed. As shown in Fig. 4b, the fitted XRD peaks for pure PVDF reveal the contributions of the α (020) and β (110) phases. Similarly, Fig. 4c and Fig. S10 display the deconvolution results for PVDF/BIT- $x\%$ MN, identifying the (006) and (111) peaks of BIT alongside the PVDF (110) peak. Furthermore, Fig. 4d shows the PVDF/BIT-25%Mn composite, confirming the coexistence of PVDF α (020) and β (110) peaks with the BIT (111) peak. These results confirm that the incorporation of BIT- $x\%$ MN fillers does not disrupt the fundamental phase structures of either component. Moreover, as illustrated in Fig. S3, the diffraction intensities of the PVDF phases vary systematically with increasing nanoflower content, while the BIT peaks remain stable. This disparity clearly indicates that the filler primarily modulates the crystalline phase transition of the PVDF matrix rather than altering the lattice of the filler itself. Therefore, the XRD and deconvolution analyses provide robust evidence that BIT- $x\%$ MN significantly promotes β -phase fraction.

The macroscopic impact of this phase transition is evidenced in Fig. 4e, which presents the electric hysteresis loops (P-E curves) for pure

PVDF and the PVDF/BIT-25%Mn composite. Pure PVDF, dominated by the non-ferroelectric α -phase (TGTT' conformation), exhibits a nearly linear P-E curve with negligible polarization. In contrast, the PVDF/BIT-25%Mn composite displays a well-defined ferroelectric hysteresis loop with significantly enhanced polarization. As a typical perovskite ferroelectric, BIT possesses intrinsic polarization. Combining the intrinsic ferroelectricity of BIT with the increased β -phase fraction in PVDF gives rise to the observed macroscopic ferroelectricity behavior. As a typical perovskite ferroelectric ceramic, BIT possesses intrinsic polarization. Combining the intrinsic ferroelectricity of BIT with the increased β -phase fraction in PVDF gives rise to the observed macroscopic ferroelectricity behavior. Furthermore, the dielectric constant plot (Fig. 4f) reveals that the dielectric constant increases with BIT- $x\%$ MN loading, this phenomenon primarily attributed to the enhanced interfacial polarization between the fillers and the polymer matrix.

The higher β -phase fraction in PVDF/BIT- $x\%$ MN endows these composites with superior piezoelectric performance, making them ideal candidates for mechanical energy harvesting and pressure sensing. As illustrated in Fig. 5a, the PVDF/BIT- $x\%$ MN composite films were integrated into a piezoelectric sensor featuring a typical sandwich structure. The operating principle of the fabricated sensor is illustrated in Fig. 5b. In its initial state, the composite film remains electrically neutral. When a vertical external force is applied, the piezoelectric film undergoes deformation, thereby generating an internal electric field. This field drives the positive and negative charges generated on the surfaces toward opposite sides of the film, creating a potential difference across the thickness. Therefore, the electrodes on both surfaces accumulate charges of opposite polarity via electrostatic induction, inducing a current that

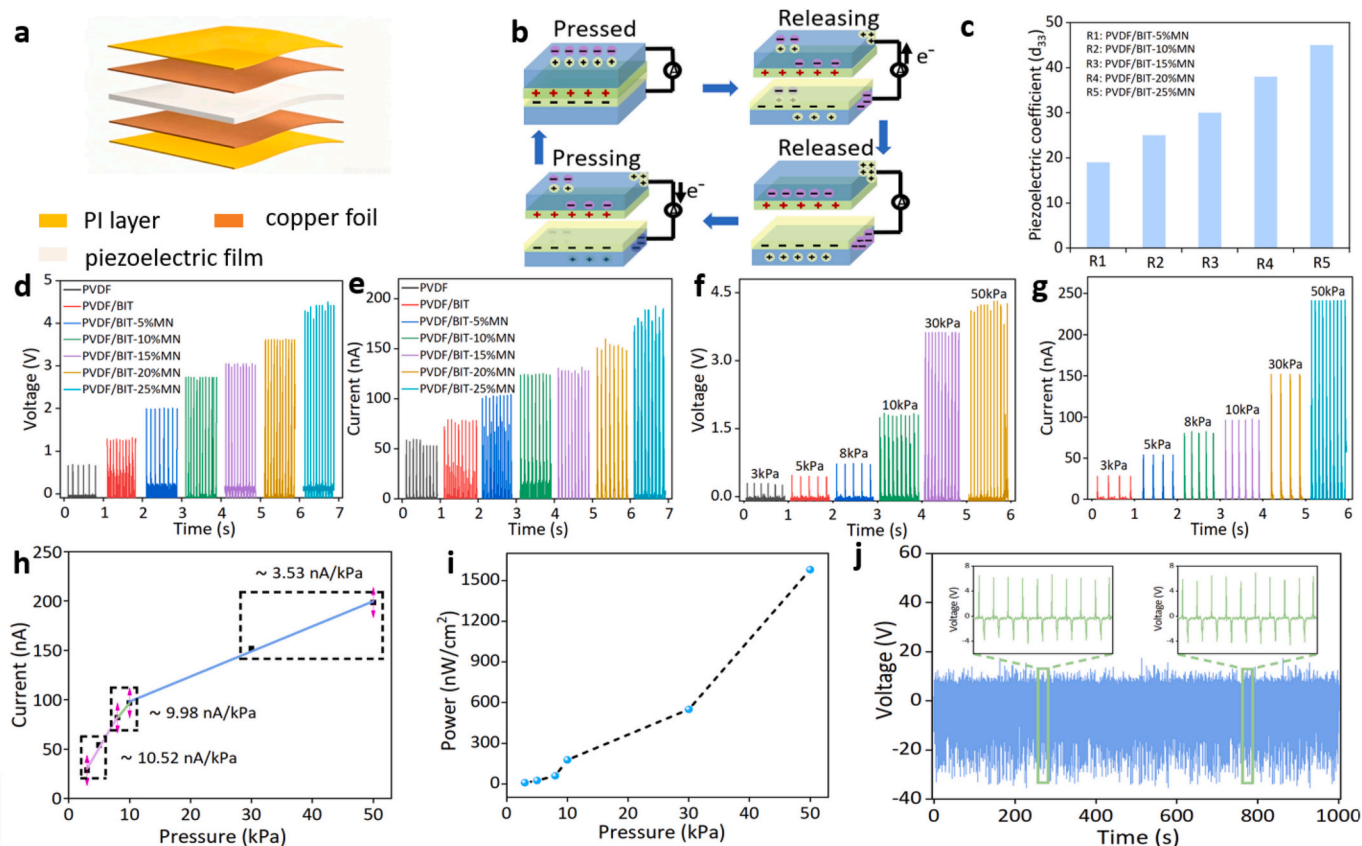


Fig. 5. Output performance of piezoelectric sensors based on PVDF/BIT- $x\%$ MN composite films. (a) Schematic diagram of the piezoelectric sensor structure based on PVDF/BIT- $x\%$ MN composite films. (b) Schematic illustration of the working mechanism of the PVDF/BIT- $x\%$ MN piezoelectric sensor during pressing and releasing cycles. (c) Piezoelectric coefficient (d_{33}) of PVDF/BIT- $x\%$ MN composite films. (d) Output voltage signals of PVDF/BIT- $x\%$ MN composite films. (e) Output current signals of PVDF/BIT- $x\%$ MN composite film under various pressures. (f) Output voltage signals of PVDF/BIT-25%Mn composite film under various pressures. (g) Output current signals of PVDF/BIT-25%Mn composite film under various pressures. (h) Calculation current sensitivity of PVDF/BIT-25%Mn. (i) Power performance of PVDF/BIT-25%Mn under various pressures. (j) Long-term stability and durability tests of PVDF/BIT-25%Mn composite film at 20 Hz.

flows from the top electrode to the bottom electrode. It is observed that a greater applied stress results in a higher density of polarization charges, leading to a larger induced potential difference and a stronger current in the external circuit. Once the pressure is released, the piezoelectric film returns to its original state. The internal electric field subsequently vanishes, and the charges flow back to their original positions, generating a reverse output voltage.

Prior to evaluating the piezoelectric response, the piezoelectric coefficient d_{33} of the polarized films was measured (Fig. 5c). The data reveals that the d_{33} values are significantly modulated by the BIT- $x\%$ MN. Specifically, as x increases from 5 to 25, the d_{33} value rises progressively from $19 \text{ pC}\cdot\text{N}^{-1}$ to $47 \text{ pC}\cdot\text{N}^{-1}$. This enhancement is highly consistent with the increasing trend of the β -phase fraction determined by FT-IR. Notably, the PVDF/BIT-25%MN composite film exhibits the highest piezoelectric coefficient of $47 \text{ pC}\cdot\text{N}^{-1}$, which surpasses that of TMCM-CdBrCl₂/P(VDF-TrFE) ($45 \text{ pC}\cdot\text{N}^{-1}$) and poled PVDF-pBT-4Ag composite ($9 \text{ pC}\cdot\text{N}^{-1}$) [39,40]. These results demonstrate the substantial potential of PVDF/BIT- $x\%$ MN composites for high-performance flexible piezoelectric devices. Hence, the electrical output of the piezoelectric composite PVDF/BIT- $x\%$ MN was evaluated, as depicted in Fig. 5d, e. With the increasing of x , the composite films exhibit progressively higher output voltage and current. It is evident that the PVDF/BIT-25%MN sensor delivers the superior performance. At an operating frequency of 10 Hz, the peak output voltage and current of the pure PVDF are recorded at 0.65 V and 53 nA, respectively. In sharp contrast, the PVDF/BIT-25%MN sensor reaches a maximum output of 4.5 V and 193 nA. This implies that the voltage output of the PVDF/BIT-25%MN sensor is approximately 6.9 times that of pure PVDF, and a current output approximately 3.65 times that of pure PVDF. These findings are highly consistent with the previous conclusion that the PVDF/BIT-25%MN composite film possesses the highest β -phase fraction. The enhancement in piezoelectric performance can be attributed to the following factors: (i) The increased β -phase fraction directly improves the intrinsic piezoelectric coefficient d_{33} of the material. (ii) The mechanical interlocking between the PVDF matrix and the BIT- $x\%$ MN nanoflowers improves the interfacial contact, thereby enabling more efficient transfer of external mechanical stress to the active phases when the device is subjected to force. (iii) The smaller and thinner morphology of the BIT-25%MN nanoflowers leads to an increased specific surface area, which provides more contact sites and further strengthens interfacial interactions. In addition, to benchmark the performance of our PVDF/BIT-25%MN composite sensor, we compare it with several representative PVDF-based piezoelectric systems reported in recent literature (Table S1). From the perspective of piezoelectric characteristics, the superiority of BIT-25%MN is demonstrated.

To further evaluate the effect of BIT- $x\%$ MN on the piezoelectric response performance, Fig. 5f-g and Fig. S11 show the output current and voltage signals under varying pressures, respectively. These data illustrate the incremental changes in output across a pressure range from 3 kPa to 50 kPa. Specifically, in the low-pressure regime (3–10 kPa), the PVDF/BIT-25%MN sensor achieves a peak voltage sensitivity of $1.83 \text{ V}\cdot\text{kPa}^{-1}$. However, as the detection range expands, the voltage sensitivity decreases, particularly within the 10–50 kPa range (dropping to $0.121 \text{ V}\cdot\text{kPa}^{-1}$ for 10–30 kPa and $0.105 \text{ V}\cdot\text{kPa}^{-1}$ for 30–50 kPa). In contrast, the current sensitivity remains significantly higher and more stable, reaching $10.52 \text{ nA}\cdot\text{kPa}^{-1}$ in the low-pressure range, $9.98 \text{ nA}\cdot\text{kPa}^{-1}$ in the mid-range, and $3.53 \text{ nA}\cdot\text{kPa}^{-1}$ at high pressures, as shown in Fig. 5h. Furthermore, the output power was calculated, reaching a maximum of $1580 \text{ nW}\cdot\text{cm}^{-2}$. As shown in Fig. 5i, the power sensitivity of the PVDF/BIT-25%MN sensor is approximately $20 \text{ nW}/\text{cm}^2\cdot\text{kPa}$ in the low-pressure range (0–10 kPa). As the pressure increases to the 10–30 kPa range, the power sensitivity decreases slightly to approximately $15 \text{ nW}/\text{cm}^2\cdot\text{kPa}$. Interestingly, once the pressure enters the 30–50 kPa regime, the power sensitivity exhibits a significant increase, reaching approximately $30 \text{ nW}/\text{cm}^2\cdot\text{kPa}$. This distinctive evolution in power sensitivity is closely related to the coupled output of

voltage and current. Although the voltage sensitivity continues to decline after the initial low-pressure stage, the current sensitivity maintains a substantial level in the mid-to-high pressure intervals. This phenomenon can be attributed to nonlinear contact mechanics, enhanced stress transfer, and optimized electrical output coupling, which ultimately manifest as a leap in power sensitivity [41]. Finally, to assess the long-term reliability of the device, a cyclic force test was performed on the PVDF/BIT-25%MN sensor at a frequency of 20 Hz. As shown in Fig. 5j, the sensor maintained a stable voltage output throughout the prolonged cycling, thereby confirming the excellent structural and electrical stability of the device.

Wearable sensors must possess exceptional mechanical stability and flexibility, as they are intended for direct application onto human skin [42]. The as-prepared PVDF/BIT-25%MN piezoelectric film demonstrates remarkable structural integrity when subjected to complex mechanical deformations, such as folding, twisting, and curling. As shown in Fig. 6a-c, the output current of the film remains detectable and stable during repeated bending, confirming its ability to maintain consistent functionality under rigorous mechanical stress. Owing to its inherent flexibility and lightweight nature, the film is well-suited for use as a wearable sensor to monitor both macroscopic body movements and subtle physiological activities, as shown in Fig. 6d, i. Furthermore, owing to its exceptional sensitivity to weak mechanical stimuli, the PVDF/BIT-25%MN sensor is capable of accurately detecting a wide spectrum of pressure fluctuations. This capability enables the conversion of subtle pressures generated by movements of the finger, wrist, elbow, and knee movements into quantifiable electrical signals, thereby facilitating comprehensive health monitoring. Specifically, Fig. 6d, e display the output signals generated when the sensor is attached to the elbow and knee, respectively. These data capture the flexion and extension movements of the limbs. When mounted on the elbow, the sensor successfully detects bending angles from a straightened state to 45° , 90° and 135° , yielding peak currents of 4 nA, 20 nA, and 35 nA, respectively. In this context, the positive and negative current peaks correspond to the specific bending actions and the resulting angles [43]. Similarly, when applied to the knee, the sensor detects bending angles ranging from straight to 45° , 90° and 135° , with corresponding peak currents of 10 nA, 23 nA, and 40 nA. In agreement with these findings, the sensor can also monitor the movements of fingers and wrists (Fig. 6h, i). The results indicate that within the range of 30° to 90° , the output current is directly proportional to the bending angle, thereby enabling the autonomous differentiation of specific joint postures. These experimental results underscore the high sensitivity and practical applicability of the PVDF/BIT-25%MN sensor.

In order to further evaluate the micro-force sensing capability of the sensor, it was adhered to the throat of a participant, as depicted in Fig. 6f, g. The results reveal that coughing and swallowing generate distinctly different output patterns, further confirming the exceptional sensitivity to subtle human physiological responses. Subsequently, the sensor was integrated with a wireless transmission module. Under various compressive pressures, the output signals were transmitted to a computer in real-time (Fig. 6j). Collectively, these experiments demonstrate that the PVDF/BIT-25%MN sensor exhibits real-time data transmission capability and a fast response time. These features enable its application in motion capture and tactile sensing, indicating substantial potential for remote human-machine interaction and control. Ultimately, this work confirms the feasibility of the sensor for applications in the field of intelligent human health monitoring.

To facilitate high-precision identification of various joint bending angles, we implemented a machine learning workflow. This framework employs a one-dimensional convolutional neural network (1D-CNN) as the primary architecture for deep learning-based feature extraction and classification, together with a Random Forest model as a traditional ensemble learning baseline for comparative validation of classification performance [44,45]. Specifically, the 1D-CNN performs end-to-end automatic feature extraction and classification, while the Random

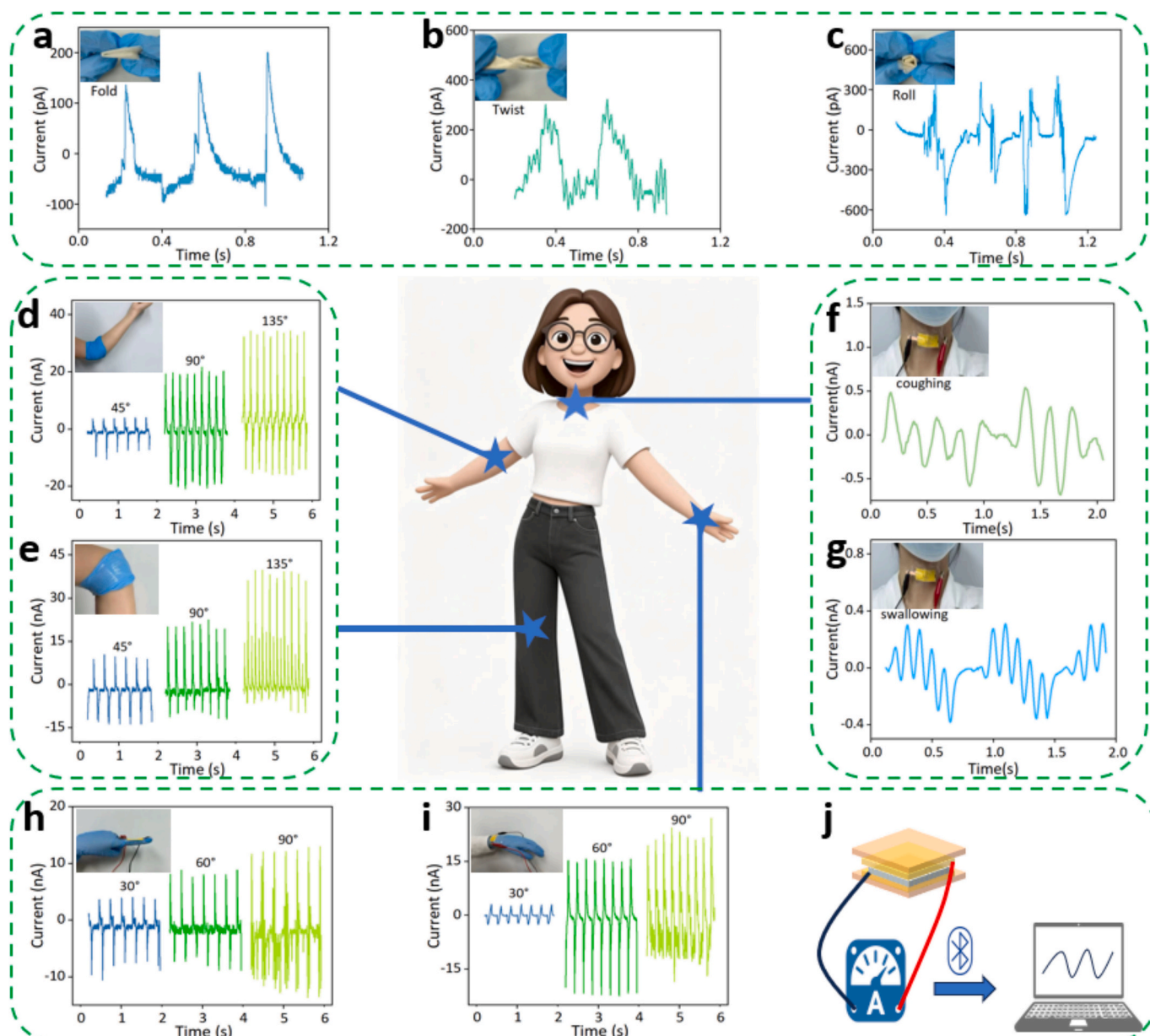


Fig. 6. Mechanical stability tests and physiological monitoring applications of the PVDF/BIT-25%Mn sensor. (a-c) Mechanical stability tests under folding, twisting, and rolling conditions. (d, e) Real-time output current signals for (d) elbow bending and (e) knee bending motions. (f, g) Real-time output current signals generated by (f) coughing and (g) swallowing. (h, i) Real-time output current signals for (h) finger flexion and (i) wrist flexion. (j) Schematic diagram of the wireless transmission system for the sensor.

Forest model provides auxiliary validation based on handcrafted time-domain statistical features. The synergy of these two models enhances both the robustness and interpretability of motion recognition, and a comparative analysis of classification accuracy and robustness between them was conducted to verify this improvement [46]. As illustrated in Fig. 7a, the proposed architecture comprises two distinct stages: feature extraction and classification. The neural network functions primarily as an efficient “feature extractor”, mapping raw input current waveforms into discrete vector points within a high-dimensional feature space (Fig. 7b). During this transformation, unwanted noise is effectively filtered out, while the critical features that characterize specific motion types are preserved and encoded. Consequently, a pronounced clustering pattern is observed in the resulting visualization space. Specifically, sample points corresponding to the “Arm,” “Leg,” and “Wrist” motions automatically converge into three distinct clusters. This spatial distribution demonstrates that the model has successfully captured the

intrinsic disparities in frequency, amplitude, and temporal patterns among the various limb movements [47]. Such a geometric organization in high-dimensional space provides a robust foundation for classification. To illustrate, when a new current signal is introduced into the system, the model projects it onto this learned feature map. As shown in Fig. 7b, the red highlighted node falls precisely within the “Arm” cluster and is well separated from the decision boundaries of the other categories, thereby allowing the system to identify the movement with high confidence. This mechanism, grounded in the Euclidean distance within the feature space, underpins the system’s robustness when encountering unknown or slightly perturbed signals [48]. In agreement with these findings, Fig. 7c presents the machine-learned response characteristics for different body parts (arm, leg, wrist, and finger), which exhibit excellent agreement with the bending angle responses obtained from practical experimental tests.

To further quantify this classification performance, Fig. 7d presents

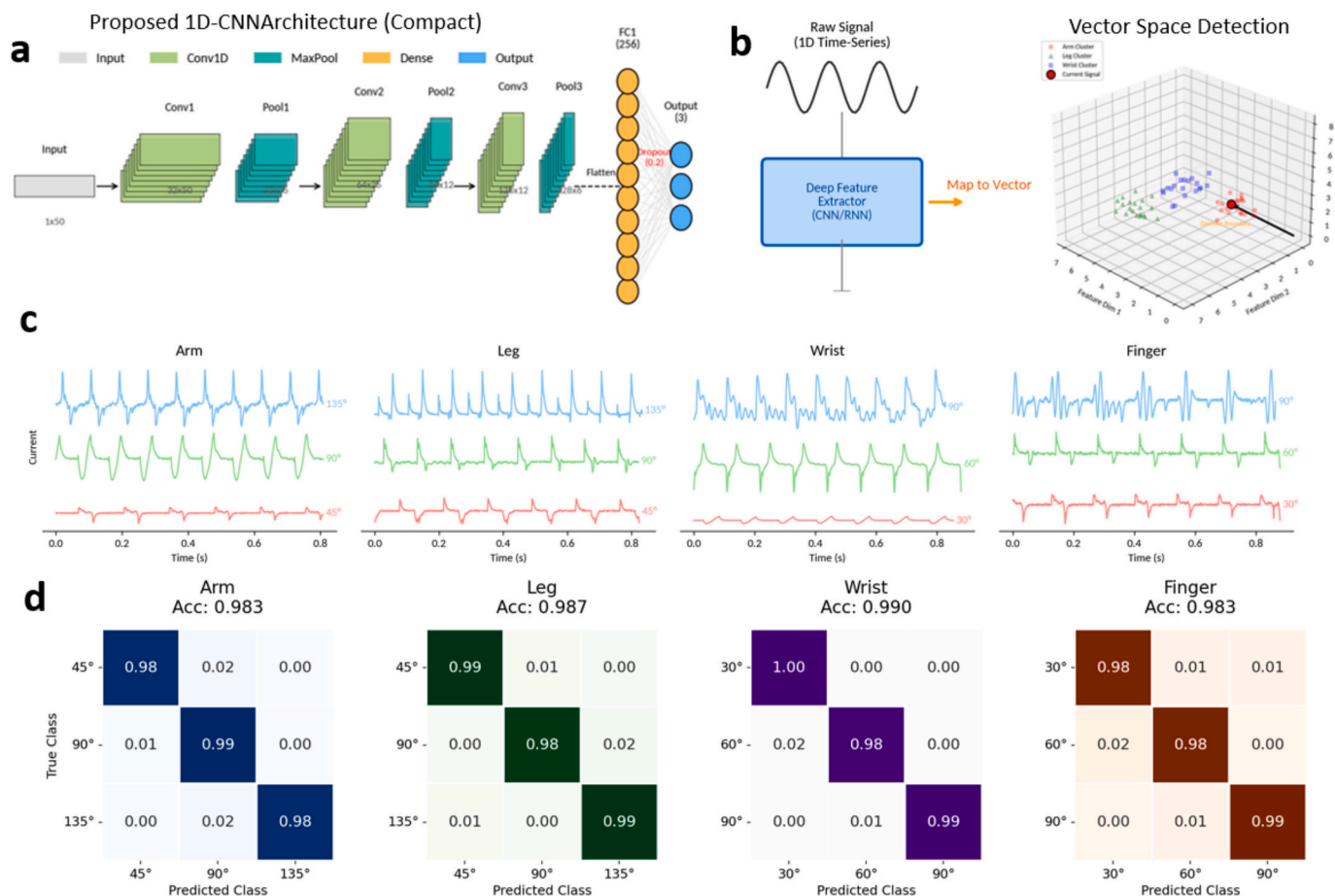


Fig. 7. Human motion recognition system integrating piezoelectric sensors and machine learning. (a) Architecture of the custom-designed 1D convolutional neural network (1D-CNN) model. (b) Visualization analysis of various body joint movements. (c) Output current signals of the prepared PVDF/BIT-25%MN composite piezoelectric sensor during human motion monitoring. (d) Confusion matrix for body joint motion recognition based on the Random Forest model.

the confusion matrix for the classification of flexion and extension angles across the four independent body sites using a Random Forest algorithm [49,50]. This method has been well applied in previous studies [51–53]. By incorporating multi-dimensional statistical features from the time domain, the model achieves high classification accuracy. Notably, wrist bend achieved the highest recognition accuracy of 99%, while the accuracies for the fingers, leg and arm reached 98.3%, 98.7% and 98.3%, respectively. The sub-matrices clearly reveal that the predicted results are highly concentrated along the main diagonal (indicated by the dark, high-frequency regions), thereby corroborating the high accuracy values reported above. In conclusion, these quantitative results provide compelling evidence that the proposed sensor array and feature engineering scheme can effectively decouple temporal signals from both large joints and fine joints with high precision, demonstrating exceptional robustness and a minimal misjudgment rate for multi-degree-of-freedom human posture monitoring.

Furthermore, we implemented the PVDF/BIT-25%MN sensor as a wearable device for human health monitoring and voice recognition applications. As the most fundamental vital sign, the pulse plays a critical role in the diagnosis of cardiovascular diseases [54,55]. To this end, the sensor was attached to the carotid artery in the neck and the radial artery at the wrist to monitor diverse pulse signals, as illustrated in Fig. 8a, b. Specifically, Fig. 8c provides an enlarged view of the radial artery signal, revealing three characteristic peaks (P1-P3) that correspond to the well-established features of human pulse waves [56]. This experimental evidence confirms the ability of the sensor to rapidly perceive and respond to external stimuli. Consequently, it serves as an effective tool for the real-time monitoring of the cardiovascular system's

physiological state.

To validate the feasibility and applicability of the PVDF/BIT-25%MN sensor in speech pattern recognition, the sensor was attached to the throat to capture vocalizations of “hello,” “nǐ hǎo,” “A,” and “B” (Fig. 8d–h). In this context, the disyllabic utterances “hello” and “nǐ hǎo” correspond to double-peak waveforms (Fig. 8e, f), whereas the monosyllabic utterances of “A” and “B” generate single-peak output currents (Fig. 8g, h). Both the “Hello” and “nǐ hǎo” signals exhibit non-stationary transient characteristics, with significant amplitude fluctuations occurring within the intervals of 0.3–1.8 s and 0.2–2.8 s, respectively. This behavior is highly consistent with the short-term acoustic signatures of human speech.

Regarding the monosyllabic utterances, signal A demonstrates typical periodic oscillation within a 0.2–2.6 s window, encompassing seven complete cycles. The overall smoothness of the waveform indicates low noise levels in the raw data, as well as a stable and regular temporal pattern. Similarly, signal B exhibits periodic oscillations with approximately five cycles within a 0.2–1.8 s window. Compared to signal A, signal B possesses richer high-frequency details, reflecting distinct acoustic excitation properties. The disparities in cycle length, peak intervals, and waveform contours constitute the primary basis for classification, thereby confirming the sensitive response of this sensor to varied acoustic signals. Taken together, these results indicate that the PVDF/BIT-25%MN sensor can accurately discern subtle phonetic variations with high reproducibility, offering a simplified alternative to traditional sound acquisition methods.

Leveraging machine learning frameworks, Fig. 8i–k present the learned signal profiles for A, B, and “Hello,” which show excellent

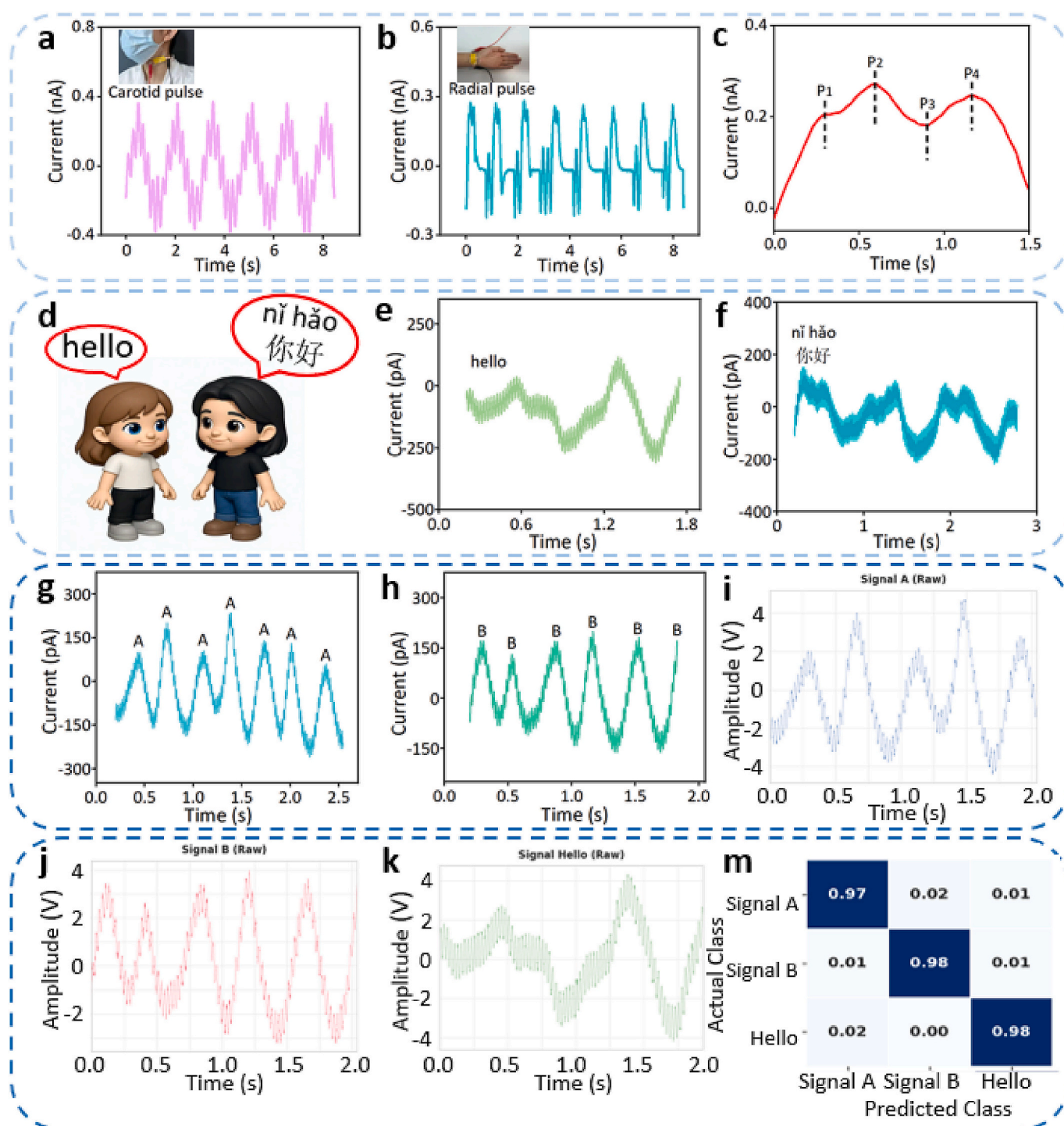


Fig. 8. Applications of the PVDF/BIT-25%Mn sensor as a wearable device for pulse detection and voice recognition. (a) Real-time output current signal of the carotid artery pulse. (b) Real-time output current signal of the radial artery pulse and (c) magnified view of the pulse signal. (d) Schematic of the PCP sensor for human voice signal acquisition and recognition. Recognition of spoken words and letters: (e) “hello”, (f) “nǐ hǎo”, (g) “A”, and (h) “B”. Time-domain characteristics of raw acoustic signals from the PVDF/BIT-25%Mn composite piezoelectric sensor for machine learning: (i) Raw time-domain waveform of Signal A. (j) Raw time-domain waveform of Signal B. (k) Raw time-domain waveform of Signal “Hello”. (m) Confusion matrix and model accuracy.

agreement with the experimentally acquired data. Furthermore, the confusion matrix in Fig. 8m visually summarizes the classification performance of these three signal types, yielding an overall model accuracy of 97.6%. The diagonal elements reveal that the classification accuracies for signal A and signal B are 97% and 98%, respectively, with some misclassification between them arising from their structural similarities. Notably, the “Hello” signal achieved the classification precision of 98%.

These findings demonstrate that the model can effectively capture subtle feature differences between signals, with the highest robustness observed in the recognition of the “Hello” speech signal. Ultimately, this validates the signal separability provided by the sensor and underscores the viability of utilizing machine learning algorithms for intelligent acoustic recognition.

3. Conclusion

In this work, we significantly enhanced the piezoelectric performance of flexible PVDF-based sensors by chemically modulating interfacial ion-dipole interactions, rather than relying on conventional hydrogen bonding or complex surface functionalization of inorganic fillers. Specifically, Mn/Nb co-doped $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ (BIT- $x\%$ MN) nanoflowers were first synthesized via a hydrothermal method. The synergistic substitution of Ti^{4+} by multivalent Mn ions ($\text{Mn}^{2+}/\text{Mn}^{3+}/\text{Mn}^{4+}$) and Nb^{5+} introduces charge imbalance and oxygen vacancies. These defects serve as high-energy nucleation sites and induce strong Lewis acid–base interactions with the fluorine atoms of PVDF, driving the conformational transition from the nonpolar α -phase to the polar β -phase. The resulting PVDF/BIT-25%MN composite achieves a β -phase fraction of 82.5%, a piezoelectric coefficient d_{33} of $47 \text{ pC}\cdot\text{N}^{-1}$, a power density of $1580 \text{ nW}\cdot\text{cm}^{-2}$, and a sensing sensitivity of $1.83 \text{ V}\cdot\text{kPa}^{-1}$. Owing to these outstanding properties, the sensor reliably monitors both large-scale human motions and weak physiological signals. Furthermore, integration with machine learning algorithms (1D-CNN and Random Forest) enables intelligent classification and precise recognition of complex motion signals. This work provides a theoretical foundation and technical support for the development of high-performance piezoelectric sensors.

Studies in human

This study was performed in compliance with relevant laws, regulatory frameworks and guidelines where the research took place.

Ethics committee approval was not required under relevant laws and institutional guidelines. There are no ethical experiments involved, and the data provided is true and reliable.

CRediT authorship contribution statement

Yuying Wu: Writing – original draft, Methodology, Investigation, Funding acquisition. **Jingfei Zhang:** Methodology, Investigation. **Zijie Luo:** Investigation. **Gang Zhou:** Investigation, Funding acquisition. **Shulin Jiao:** Investigation. **Xin Jin:** Methodology. **Xinyuan Zhu:** Resources, Investigation. **Youfu Wang:** Supervision, Resources, Investigation.

Informed consent and patient details

Written informed consent to take part in the study and to publish the article has been obtained from all participants or their legal representatives. The privacy rights of participants have been observed.

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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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.jcis.2026.141473>.

Data availability

Data will be made available on request.

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