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Constructing High-Performance PVDF-Based Piezoelectric Composites via Hydrogen Bond Anchoring Strategy for Flexible Sensing Applications

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ABSTRACT

Fluoropolymers are crucial for next-generation lightweight, portable, and human–computer interactive devices. Nevertheless, it remains a major challenge to realize the regulation of abundant polar phases in PVDF-based composites, which is critical to enhancing piezoelectric coefficient and sensitivity. To address this, we propose incorporating bis(isoquinoline)dibromidocopper (II) (abbreviated as (IQ)₂CuBr₂, IQ = isoquinoline) into PVDF via a full-surface hydrogen-bond anchoring strategy. DFT calculation reveals that the -CF₂ groups in PVDF can form stable hydrogen-bonding interactions with all -CH groups of isoquinoline. Interfacial hydrogen-bonding interactions promote the electroactive β phase, with $F(\beta)$ reaching 92%. The piezoelectric coefficient is up to 52 ± 1.65 pC N⁻¹, and the net spontaneous polarization raises from 0.48 to 11.39 Debye. Owing to these advantages, the optimized composite film exhibits a more than twofold enhancement in piezoelectric response. It also achieves a sensitivity of 1.20 V kPa⁻¹ in the low-pressure range and demonstrates excellent cycling stability over 10,000 cycles. Furthermore, a 3 × 3 sensor array was designed for accurate wrist motion monitoring. By integrating it into smart steering wheels, this system forms a closed-loop system for real-time multilevel driver fatigue detection assisted by machine learning. This work offers new insights into interfacial regulation of piezoelectric composites and promotes the development of next-generation intelligent sensing systems.

1 | Introduction

The rapid proliferation of the Internet of Things (IoT) and artificial intelligence has greatly accelerated the development of flexible human–machine interfaces. Advanced wearable sensors

capable of seamlessly conforming to human skin or curved surfaces have become indispensable components in numerous applications, ranging from precise kinematic monitoring [1] to virtual reality gesture control [2]. To meet these multifaceted

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demands, flexible tactile sensors must not only possess high sensitivity for detecting minute stimuli but also exhibit reliable spatial recognition capabilities. Among various sensing mechanisms, piezoelectric sensors have garnered significant attention due to their inherent self-powered operation, high dynamic responsivity, and low power consumption [3, 4], positioning them as ideal candidates for next-generation multifunctional intelligent systems. Piezoelectric materials play a crucial role in flexible tactile sensing and actuation. Owing to their excellent flexibility, biocompatibility, and lightweight characteristics, poly(vinylidene fluoride) (PVDF) has been widely utilized in wearable sensors, medical actuators, and various flexible electronic devices [5]. Despite its reliable piezoelectric performance, PVDF still suffers from a substantial gap in piezoelectric coefficient compared to ceramic piezoelectric materials, which hinders its practical applications.

At present, numerous studies worldwide have been dedicated to improving the piezoelectric performance of PVDF-based materials, and it is widely recognized that increasing the content of the polar β -phase within the material serves as the core strategy for enhancing its piezoelectric properties. Generally, the mainstream modification approaches can be categorized into three main types. First, external field-assisted fabrication techniques, such as electrospinning, hot pressing, and electrohydrodynamic printing [6, 7], are employed to optimize the electrical and mechanical properties of the material. Second, from a molecular perspective, methods, including chemical modification, compositional regulation, and functional filler, are adopted to refine the crystalline structure [8–16]. Third, incorporating functional fillers with high piezoelectric activity or high dielectric constants into the PVDF matrix has been proven to be an effective strategy for efficiently promoting β -phase formation. For example, although the incorporation of common rigid inorganic fillers, such as lead zirconate titanate (PZT) [17], barium titanate (BTO) [18], zinc oxide (ZnO) [19], and potassium sodium niobate (KNN) [20], can effectively increase the content of the β -phase and thereby enhance the piezoelectric coefficient, piezoelectric response, and sensing sensitivity, such inorganic fillers typically require a high filling ratio to efficiently induce polar phase nucleation. Consequently, they are prone to disordered agglomeration within the polymer matrix, which not only suppresses the full manifestation of interfacial polarization effects but also disrupts the continuous network structure of the polymer. This inevitably leads to deteriorated mechanical properties and increased susceptibility to brittle fracture. Hence, although the modification system of PVDF filled with conventional inorganic materials has achieved certain progress, the interfacial mismatch between the inorganic fillers and the organic matrix remains a significant challenge in this field. Moreover, this issue severely limits further breakthroughs in the overall performance of PVDF-based piezoelectric composites and hinders their practical application and development.

Organic–inorganic hybrids effectively integrate the rigidity of inorganic frameworks with the chemical diversity of organic ligands at the molecular scale [21, 22], making them highly promising alternative materials. Notably, these hybrids are not only solution-processable but also exhibit piezoelectric performance that outperforms conventional commercial ceramics.

More importantly, the bulky organic ligands exposed on their surfaces can serve as high-density proton acceptors or polar interaction sites, thereby laying a structural foundation for constructing large-area and robust interfacial hydrogen-bonding networks within the polymer matrix [23, 24]. Considering that fillers with abundant surface hydrogen bond donors are ideal candidates for constructing large-area polar interfaces, in this work, we propose a structural engineering strategy based on full-surface molecular-level interfacial anchoring. Specifically, a high-performance self-powered flexible piezoelectric composite film is fabricated by incorporating a novel lead-free hybrid metal halide, $(\text{IQ})_2\text{CuBr}_2$, into a PVDF matrix. Since the isoquinoline (IQ) component in $(\text{IQ})_2\text{CuBr}_2$ plays a crucial role in constructing the polar interface, its bulky conjugated structure can induce the PVDF molecular chains to align in a specific manner, thereby promoting the transformation of the nonpolar α -phase into the polar β -phase. To elucidate the interaction between the crystals and PVDF molecules, we combined density functional theory (DFT) calculations with experimental validation. The results demonstrate that the extremely high proportion of hydrogen bond donor exposed on the crystal surface anchors the PVDF chains through a dense network of C–H...F–C hydrogen bonds, leading to a dramatic increase in the net spontaneous polarization of the system from 0.48 to 11.39 Debye. This interfacial anchoring effect promotes the formation of the electroactive β phase, resulting in approximately 92% β -phase fraction. By optimizing the concentration of $(\text{IQ})_2\text{CuBr}_2$, the piezoelectric response of the composite film is enhanced by more than twofold, achieving a high open-circuit voltage of approximately 10.5 V, a piezoelectric constant (d_{33}) of $52 \pm 1.65 \text{ pC N}^{-1}$. The sensitivity is ultrahigh at 1.20 V kPa^{-1} in the low-pressure region. Moreover, the film shows excellent stability over more than 10,000 cycles. To facilitate its practical application, we fabricated a 3×3 flexible sensor array for accurate wrist motion monitoring. Furthermore, assisted by machine learning algorithms, this sensor array was seamlessly integrated into an intelligent steering wheel. By deeply decoupling the voltage signal features of different hand gestures and grips, we successfully established a real-time closed-loop monitoring and early warning system for driver fatigue at multiple levels (Figure 1). This study provides an efficient and scalable route for designing piezoelectric composites, and offers new perspectives for the structural design of next-generation wearable electronics and advanced driver-assistance systems.

2 | Results and Discussion

2.1 | Structural Characterization of $(\text{IQ})_2\text{CuBr}_2$ Crystals

First, we unambiguously determined the crystallographic structure and molecular configuration of the synthesized lead-free hybrid metal halide $(\text{IQ})_2\text{CuBr}_2$ by single-crystal X-ray diffraction (SC-XRD). The results indicate that the crystal belongs to the monoclinic system with the space group $\text{P}2_1/\text{n}$. The unit cell parameters are $a = 12.5220 (3) \text{ \AA}$, $b = 4.0746 (1) \text{ \AA}$, $c = 16.7791 (4) \text{ \AA}$, and $\beta = 100.308 (1)^\circ$ (Supporting Information S1: Table S1). As illustrated by the ball-and-stick model (Figure 2a), the compound features a typical zero-dimensional (0D) molecular architecture. At the atomic level, the central inorganic $[\text{CuBr}_2]$ core is fully coordinated and

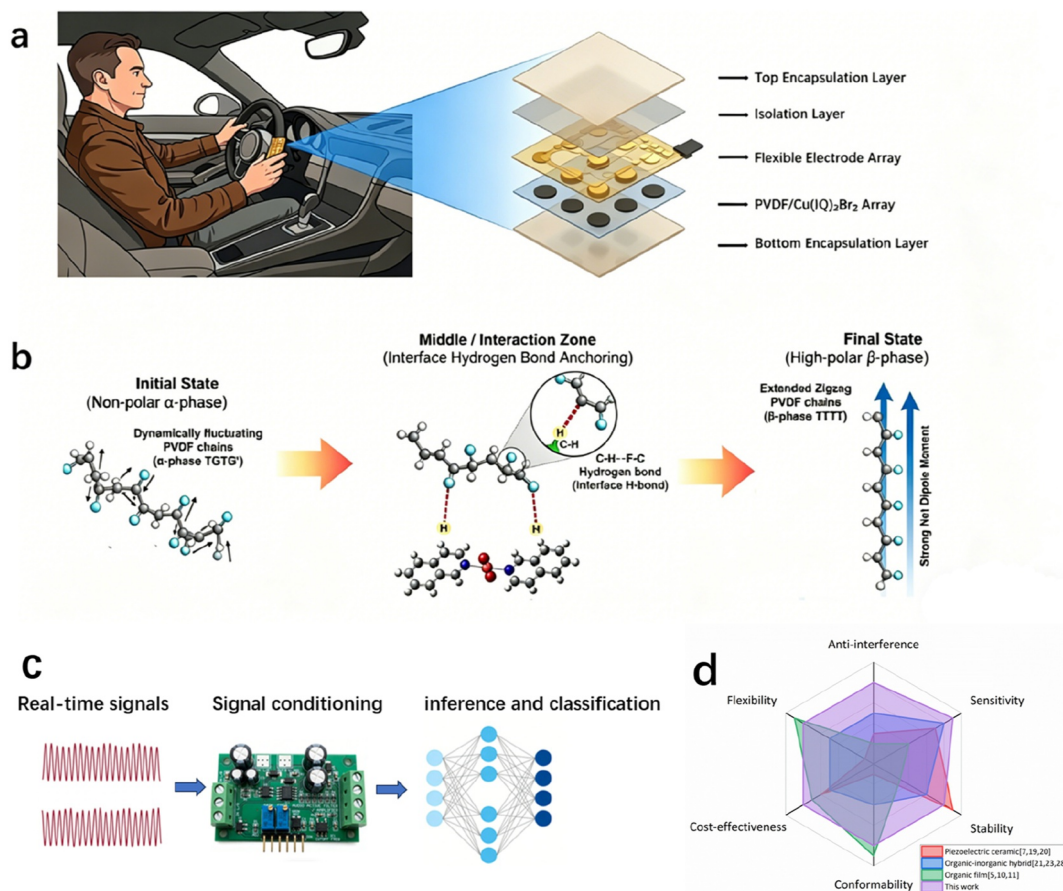


FIGURE 1 | (a) Schematic diagram of the application scenario of the sensor array in an intelligent steering wheel and its multilayer device structure. (b) Microscopic molecular mechanism of the spontaneous transformation of PVDF chains from the nonpolar α -phase to the polar β -phase, driven by the anchoring effect of (IQ)₂CuBr₂ via interfacial hydrogen bonding. (c) Workflow diagram illustrating piezoelectric signal acquisition, hardware-based filtering and amplification, and machine learning pattern recognition. (d) Radar chart comparing the comprehensive performance of the developed composite sensor in terms of flexibility, sensitivity, stability, and anti-interference capability.

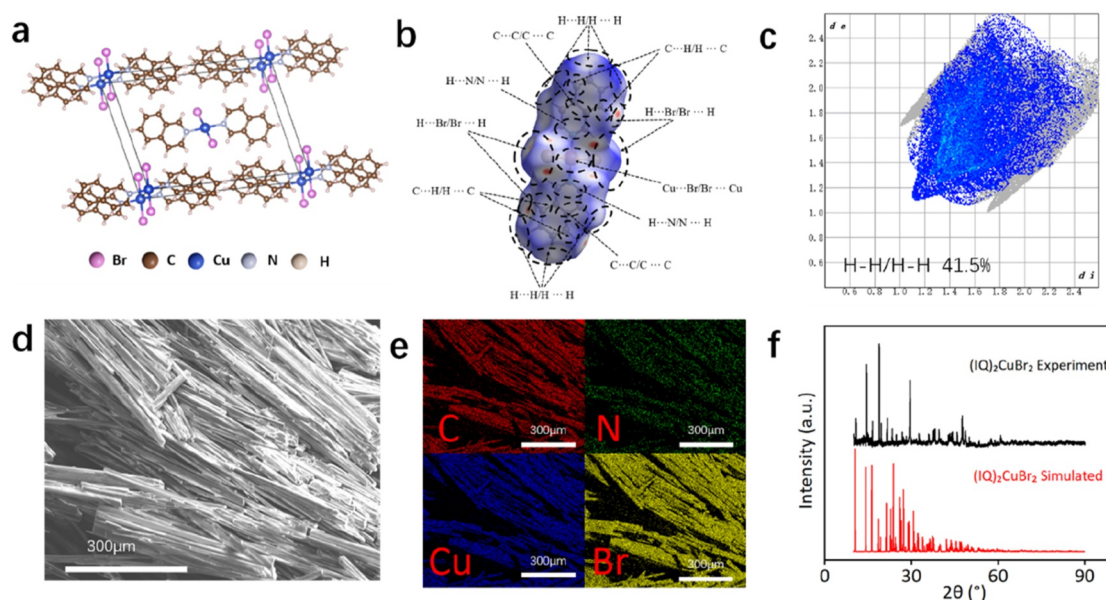


FIGURE 2 | (a) Crystal structure of (IQ)₂CuBr₂. (b) Hirshfeld surface plot and (c) two-dimensional fingerprint plot of interactions in (IQ)₂CuBr₂. (d) SEM image of (IQ)₂CuBr₂ crystals. (e) EDS elemental mapping of (IQ)₂CuBr₂ crystals. (f) Experimental and simulated PXRD patterns of (IQ)₂CuBr₂ crystals.

spatially encapsulated by bulky isoquinoline (IQ) organic ligands. The significant steric hindrance generated by these bulky IQ ligands effectively prevents the inorganic polyhedra from forming extended continuous networks via sharing halogen atoms, thereby resulting in typical isolated molecular clusters. To analyze the intensity of interatomic interactions within the crystal, the dnorm-mapped Hirshfeld surface was employed to examine the interactions in $(\text{IQ})_2\text{CuBr}_2$ (Figure 2b). The corresponding two-dimensional fingerprint plots were displayed using the CrystalExplorer 3.1 program [25] (Figure 2c). The red spots on the dnorm-mapped Hirshfeld surface correspond to regions of strong interactions in the figure. Evidently, these strong interactions are hydrogen bonds between hydrogen atoms and halogens. Quantitative analysis of the two-dimensional fingerprint plots reveals that H...H contacts account for 41.5% of the total Hirshfeld surface area, H...Br/Br...H contacts account for 24.4%, and H...C/C...H contacts account for 16.7% (C...C contacts, representing π - π stacking, account for 10.5%). This means that up to 82.6% of the entire crystal surface is covered by hydrogen atoms. Such a high proportion of hydrogen atoms quantitatively confirms that the bulky isoquinoline ligands construct a high-density three-dimensionally isotropic hydrogen-bond donor shell around the inorganic core. Therefore, isoquinoline plays the role of a crystallization template and a dipole stator in this system, essentially laying a solid molecular foundation for establishing a continuous and uniform full-interface hydrogen-bonding network with the polymer matrix subsequently.

Although $(\text{IQ})_2\text{CuBr}_2$ single crystals possess a zero-dimensional feature structurally, these isolated molecular clusters tend to undergo anisotropic aggregation primarily through strong noncovalent intermolecular forces, especially π - π stacking interactions between the aromatic IQ rings. This growth behavior results in a macroscopically highly ordered morphology with a high aspect ratio, appearing as needle-like or rod-like shapes, as shown in Figure 2d. Such a microstructure is highly advantageous for functional fillers as it provides a large specific surface area for subsequent interactions with the polymer matrix. To further elucidate the surface chemical composition and the chemical bonding states of the elements, X-ray photoelectron spectroscopy (XPS) measurements were conducted (Supporting Information S1: Figure S2). The survey spectrum first confirmed the presence of C, N, Cu, and Br elements, consistent with the EDS mapping results. Specifically, the high-resolution C 1s spectrum exhibits a symmetric peak centered at 284.8 eV, which is mainly attributed to the carbon backbone (C-C/C=C) from the isoquinoline rings as well as overlapping C-N bonds. The high-resolution N 1s spectrum displays a single strong peak at 399.6 eV, and this characteristic binding energy corresponds to the pyridine-type nitrogen atoms (N-Cu) coordinated to the copper center within the IQ ligands. In the high-resolution Cu 2p spectrum, a pair of spin-orbit splitting peaks are clearly observed at 932.5 and 952.5 eV, corresponding to Cu 2p_{3/2} and Cu 2p_{1/2}, respectively. Meanwhile, distinct and broad shake-up satellites appear on the higher binding energy side of the main peaks (around 942.5 eV), which serve as a characteristic fingerprint of the Cu²⁺ electronic configuration. Combined with the Cu LMM Auger electron kinetic energy peak at 915.9 eV, the coordination microenvironment of the divalent copper center is accurately established. Furthermore, in the binding energy

range of 60–85 eV, the strong peak at 68.8 eV corresponds to the Br 3d main peak, confirming the typical metal-halogen (Cu-Br) bonding characteristics, whereas the secondary peak observed around 75.5 eV is assigned to the Cu 3p orbital. The precise confirmation of these surface chemical states not only corroborates the molecular framework of $(\text{IQ})_2\text{CuBr}_2$ but also provides solid support for understanding the complex interfacial charge and hydrogen-bonding interactions with the PVDF matrix.

To verify the phase purity and crystallinity of the synthesized product, powder X-ray diffraction (PXRD) measurements were performed. As shown in Figure 2f, the experimental diffraction peaks of $(\text{IQ})_2\text{CuBr}_2$ are consistent with the calculated reflections of the monoclinic *P*21/*n* structure, and the main crystallographic-plane assignments are summarized in Supporting Information S1: Table S2. The sharp and well-defined diffraction peaks indicate the high crystallinity of the as-synthesized crystals. No additional diffraction peaks are observed, confirming the phase purity of the product. Furthermore, Raman spectroscopy (Supporting Information S1: Figure S3) revealed strong characteristic vibrational modes of the inorganic metal-halogen framework in the low-frequency region below 500 cm⁻¹, whereas retaining the characteristic Raman scattering of the IQ ligands at higher frequencies, confirming the structural integrity of the $(\text{IQ})_2\text{CuBr}_2$ crystals prior to composite fabrication. To investigate the optical absorption properties of these crystals, UV-Vis absorption spectroscopy was performed (Supporting Information S1: Figure S4). Based on the UV-Vis absorption spectrum, the optical absorption of the $(\text{IQ})_2\text{CuBr}_2$ extends to the near-infrared region (Supporting Information S1: Figure S4). This indicates that these molecular clusters possess excellent potential for low-energy intrinsic carrier excitation. To further verify their macroscopic semiconducting transport characteristics, temperature-dependent electrical measurements were carried out (Supporting Information S1: Figure S5). As expected, as the ambient temperature gradually increased from 293 to 373 K, the electrical resistance of the $(\text{IQ})_2\text{CuBr}_2$ crystals exhibited a clear and continuous decreasing trend, confirming that the crystals exhibit excellent semiconducting behavior. Moreover, thermogravimetric and differential thermal analysis (TGA/DTA) revealed the excellent stability of the crystals (Supporting Information S1: Figure S6). The TGA curve indicated that the material begins to undergo mass loss at temperatures as high as 380 K. This outstanding thermal stability fully meets the operational requirements for conventional devices and for applications in complex high-temperature environments.

2.2 | Microstructural Characterization and Polar Phases of Piezoelectric Films

To achieve high piezoelectric performance while maintaining excellent flexibility of the piezoelectric device, we selected the semiconductor $(\text{IQ})_2\text{CuBr}_2$ as a filler for the organic polymer PVDF and subsequently investigated its potential nature. Flexible films were successfully fabricated by dispersing the $(\text{IQ})_2\text{CuBr}_2$ into the PVDF matrix, and the schematic diagram of the fabrication process is shown in Supporting Information S1: Figure S7. To optimize the performance ratio of the films, mass fraction of 2 wt%, 4 wt%, 6 wt%, 8 wt%, 10 wt%, and 12 wt% of $(\text{IQ})_2\text{CuBr}_2$ were filled in PVDF. These films, with a thickness of

approximately 40 μm , exhibited excellent uniformity, integrity, and flexibility as revealed by SEM images and EDS mapping (Supporting Information S1: Figure S8). The composite films displayed a highly dense, uniform, and continuous cross-sectional morphology, free from any severe structural defects, microvoids, or macroscopic phase separation. Such structural compactness is highly beneficial for ensuring superior mechanical durability and efficient stress transfer during dynamic mechanical deformation. EDS mapping revealed an extremely uniform and dense distribution of Cu, Br, and N elements derived exclusively from the $(\text{IQ})_2\text{CuBr}_2$ crystals throughout the PVDF polymer.

The intrinsic piezoelectricity of PVDF primarily depends on the electroactive β -phase with an all-trans (TTTT) conformation, which serves as the inherent origin of its piezoelectric properties. To intrinsically trigger the α -to- β phase transition, we introduced $(\text{IQ})_2\text{CuBr}_2$ crystals as functional nucleating agents. In order to deeply elucidate the mechanism by which $(\text{IQ})_2\text{CuBr}_2$ influences the phase transition behavior of PVDF from the nonpolar α -phase to the polar β -phase, we performed theoretical simulations using density functional theory (DFT). Considering the zero-dimensional discrete molecular structure of $(\text{IQ})_2\text{CuBr}_2$, a molecular cluster model was adopted to construct the interfacial system. Specifically, a short PVDF chain was introduced in the vicinity of the $(\text{IQ})_2\text{CuBr}_2$ molecule to simulate the local interaction between them, thereby building a polymer/complex interfacial interaction model. In the initial configuration, the nonpolar α -phase conformation of PVDF (characterized by carbon backbone dihedral angles of approximately $\pm 60^\circ$) was deliberately selected, with its highly electronegative $-\text{CF}_2$ groups oriented toward the ligand region of the complex. Unlike conventional surface models that partially fix atoms, this model imposed no geometric constraints during the simulation. Instead, Grimme's dispersion correction D3(BJ) [26] was incorporated, and full geometric relaxation was performed to precisely capture the conformational evolution and structural optimization of the polymer chains induced by interfacial polarization forces. The computational results are presented in Figure 3a. In the initial α -phase interfacial model, the highly electronegative fluorine atoms of the $-\text{CF}_2$ groups on the PVDF chain are strongly attracted by the polar surface of the $(\text{IQ})_2\text{CuBr}_2$ molecule, forming multiple short-range non-covalent interactions ($\text{C-H}\cdots\text{F-C}$ bonds) with the hydrogen atoms of the ligands. This strong interfacial anchoring force effectively overcomes the internal rotational energy barrier of the polymer, directly driving a spontaneous torsion of the PVDF backbone. As a result, the conformation completely transforms from the nonpolar helical α -phase (with dihedral angles of approximately $\pm 60^\circ$) to the extended zigzag polar β -phase (with dihedral angles of approximately $\pm 180^\circ$). Quantitative calculations further reveal that under the strong anchoring effect of the $(\text{IQ})_2\text{CuBr}_2$ molecular cluster, the net spontaneous polarization of the PVDF system dramatically increases from an initial value of 0.48 Debye to 11.39 Debye. This remarkable enhancement of the dipole moment quantitatively confirms the strong locking effect of the interfacial hydrogen-bonding network on the polymer dipoles [27–29], fundamentally explaining the physical mechanism underlying the enhancement of the intrinsic interfacial polarization under the zero-field theoretical conditions.

To further elucidate the nature of the interfacial interactions, charge density difference analysis was performed to reveal the electronic interactions between the PVDF segment and the $(\text{IQ})_2\text{CuBr}_2$ (Figure 3b). The electron-withdrawing effect of the fluorine atoms (F_p) in PVDF induces a partial positive charge density on the adjacent hydrogen atoms (H_p), enabling the PVDF chain segment to effectively interact with the surface of $(\text{IQ})_2\text{CuBr}_2$. The detailed local structure derived from the charge density difference calculation (Figure 3c) shows that $\text{C-H}_c\cdots F_p$ interactions (where H_c represents the hydrogen atoms on the $(\text{IQ})_2\text{CuBr}_2$ ligands) coexist with weak interfacial polarization effects. The average interatomic distance of $H_c\cdots F_p$ is approximately 2.4–2.6 Å, indicating stable interfacial interactions between PVDF and $(\text{IQ})_2\text{CuBr}_2$.

In order to analyze the effect of different $(\text{IQ})_2\text{CuBr}_2$ loadings on the β -phase content in PVDF, PXRD patterns of the composite films were measured (Figure 3d). With increasing $(\text{IQ})_2\text{CuBr}_2$ filling content, the diffraction peak corresponding to the (110)/(200) planes of the β -phase gradually intensified. Raman spectroscopy of the composites further confirmed the crystalline phase evolution (Supporting Information S1: Figure S9), the characteristic peak associated with the $-\text{CF}_2$ stretching vibration in the β -phase was significantly enhanced in the composites and reached its maximum intensity at around 840 cm^{-1} , providing additional evidence for the stable interaction between the $-\text{CF}_2$ groups in PVDF and the $-\text{CH}$ groups on the $(\text{IQ})_2\text{CuBr}_2$ surface. Quantitative analysis of the β -phase content was performed using FT-IR spectroscopy (Figure 3e). The results show that the characteristic peaks of the β -phase are mainly located at around 837 cm^{-1} , 1071 cm^{-1} , 1275 cm^{-1} , and 1410 cm^{-1} [30], whereas the α -phase appear at 975 cm^{-1} and 763 cm^{-1} . Notably, the $-\text{CF}_2$ stretching vibration band (around 1182 cm^{-1}) exhibits a slight redshift of approximately 2 cm^{-1} upon incorporation of $(\text{IQ})_2\text{CuBr}_2$, which we attribute to the $\text{C-H}_c\cdots F_p$ interactions formed between the $-\text{CF}_2$ groups in PVDF and the $(\text{IQ})_2\text{CuBr}_2$ ligands. As the $(\text{IQ})_2\text{CuBr}_2$ content increases, the characteristic absorption bands of the β phase become more pronounced, indicating an increase in the relative β -phase fraction within the films. To determine the β -phase content, calculations were performed according to the equation derived from the Beer–Lambert absorbance law:

$$F(\beta) = \frac{A_{837}}{\left(\frac{k_{837}}{k_{763}}\right)A_{763} + A_{837}} \times 100\%$$

where $F(\beta)$ is the β -phase fraction and A_{763} and A_{837} are the characteristic peak intensities of the α -phase and β -phase, respectively [31]. The parameters k_{763} and k_{837} represent the corresponding absorption coefficients. The calculated results (Figure 3f) reveal that as the $(\text{IQ})_2\text{CuBr}_2$ concentration increases, the β -phase content exhibits a typical volcano-shaped trend. Initially, the β -phase fraction reaches its maximum at a filler loading of PC-8 wt%. Compared with the pure PVDF film ($F(\beta) = 69\%$), PC-8 wt% shows a significantly enhanced $F(\beta)$ value of 92%. This remarkable enhancement originates from the abundant nucleation sites provided by the dispersed $(\text{IQ})_2\text{CuBr}_2$ crystals and the rich hydrogen-bonding interactions of the contact surface. However, upon further increasing the filling content, the β -phase fraction gradually declines. This decrease is

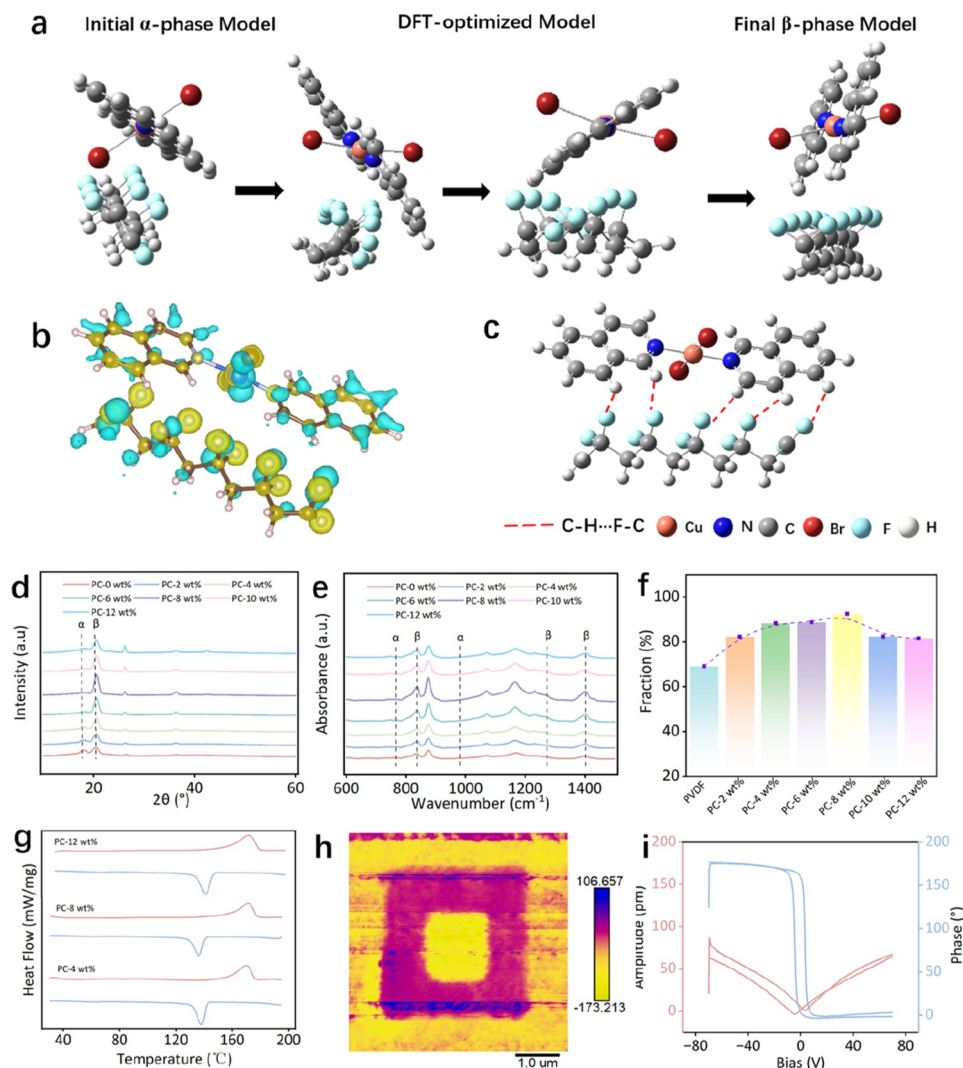


FIGURE 3 | (a) Geometric relaxation evolution of PVDF chains spontaneously transforming from the α phase to the β phase under the influence of (IQ)₂CuBr₂. (b) Distribution map of the charge density difference in the interfacial region of the composite system. (c) Schematic illustration of the local fine structure of C-H...F-C interfacial hydrogen bonding interactions between (IQ)₂CuBr₂ ligands and PVDF chains. (d) XRD patterns of composite films with different content of (IQ)₂CuBr₂. (e) Fourier transform infrared (FT-IR) absorption spectra of the corresponding films. (f) Calculated β content in the films. (g) DSC curves for PC-4 wt%, PC-8 wt%, and PC-12 wt%. (h) Local piezoelectric force microscopy (PFM) amplitude maps after DC bias erasure. (i) Local PFM polarization reversal spectra of the composite films.

mainly due to unavoidable agglomeration of the excess functional fillers, which dramatically reduces the specific interfacial area and consequently weakens the overall hydrogen-bonding effect.

To thoroughly evaluate the thermal behavior and microstructural evolution of the composite films, differential scanning calorimetry (DSC) analysis was performed. As shown in Figure 3g, all samples exhibit distinct melting endothermic peaks (T_m) and crystallization exothermic peaks (T_c) in both the heating and cooling curves. The overall crystallinity (X_c) of the polymer was calculated using the equation $X_c = \Delta H_m / [(1 - \omega)\Delta H_0] \times 100\%$, where ω is the mass fraction of (IQ)₂CuBr₂ crystals and ΔH_0 is taken as 104.5 J·g⁻¹. The calculated results reveal that the variation trend of X_c is highly consistent with that of the β -phase fraction derived from FT-IR analysis. Upon the addition of (IQ)₂CuBr₂, X_c reaches a maximum value of 35.77% for PC-8 wt%, accompanied by the

highest T_m of 171.3°C. The elevation of phase transition temperatures and the maximization of X_c indicate that an appropriate number of microcrystals effectively exerts a heterogeneous nucleation effect, thereby promoting the long-range ordered arrangement of polymer chains.

In addition, piezoresponse force microscopy (PFM) was employed to investigate the local polarization switching characteristics of the composite films [32]. For the PC-8 wt% film, clear spontaneous polarization regions and domain walls were observed even before applying any external bias (Supporting Information S1: Figure S10). To further verify its intrinsic polarization, a direct PFM domain writing and erasing test was conducted over a $5 \times 5 \mu\text{m}$ area. By applying positive and negative DC biases to specific regions, box-in-box polarization domain tests were obtained on the film. The resulting phase image (Figure 3h) reveals a clear phase contrast between the

opposite polarized regions. This distinct and stable phase reversal indicates reversible polarization switching, strongly demonstrating that the response originates from the intrinsic polarization of the material and excluding artifacts caused by charge injection or electrostatic effects. Concurrently, local PFM switching measurements were carried out to quantitatively analyze the dynamic behavior of the polarization domains [33]. As shown in Figure 3i, the phase-voltage curve exhibits a characteristic square-shaped hysteresis loop, with the phase signal undergoing an approximately 180° reversal. Meanwhile, the amplitude-voltage curve displays a classic butterfly shape. These typical characteristics further confirm the excellent intrinsic polarization behavior of the composite film. Notably, along the bias voltage axis, both the phase and amplitude curves exhibit pronounced asymmetry. The amplitude response under negative bias is significantly higher than that under positive bias. Such asymmetry in the local piezoelectric response is generally attributed to the presence of a built-in electric field within the film, which in turn contributes to further enhancing the piezoelectric performance of the material [34].

2.3 | Piezoelectric Response of the Piezoelectric Sensor

For the purpose of exploring its practical piezoelectric response and potential in flexible sensing applications, a flexible piezoelectric sensor based on the composite film was fabricated with an effective size of 1.2 cm × 0.8 cm × 120 μm. The device integrates top and bottom Au/Ag electrodes deposited by ion sputtering and is encapsulated with a polyethylene terephthalate (PET) film to ensure mechanical reliability under dynamic mechanical environments. The measurement system is illustrated in Supporting Information S1: Figure S11. By systematically adjusting the magnitude and frequency of the applied force, the voltage output of the films containing different amounts of (IQ)₂CuBr₂ was found to gradually increase under a periodic pressure of 10 Hz and 30 kPa. Notably, the PC-8 wt% film exhibited the highest open-circuit voltage (V_{oc}) of approximately 10.5 V (Figure 4a) and a short-circuit current of approximately 100 nA (Figure 4b), with a voltage output more than twice that of the pure PVDF film device. The highest piezoelectric response observed for PC-8 wt% can be attributed to several factors. First, the PC-8 wt% sample exhibits the highest mean piezoelectric coefficient of 52.0 ± 1.65 pC N⁻¹ and it possesses the highest β -phase fraction (Figure 4c). As shown in Figure 4c, the composition-dependent variation in d_{33} is consistent with the trend observed in the piezoelectric output. Second, the incorporation of the semiconducting (IQ)₂CuBr₂ leads to an increase in the electrical conductivity of the composite film. Third, the high polarization value of PC-8 wt% generates a stronger internal polarization electric field during mechanical deformation, which captures more free charges [35]. Thus, these should be the reasons for the excellent piezoelectric response. However, when the filling concentration exceeds 8 wt% (at 10 wt% and 12 wt%), a significant decrease in the output voltage is observed. This degradation is likely due to severe agglomeration of excess (IQ)₂CuBr₂ particles, which increases the defect density and grain boundary resistance within the PVDF matrix [36], thereby hindering efficient polarization and charge transfer [37].

To systematically evaluate the broadband sensing performance of the composite films under dynamic mechanical stimulation, the real-time open-circuit voltage outputs of sensors based on PVDF filled with different mass fractions (0–12 wt%) of (IQ)₂CuBr₂ were thoroughly characterized under varying frequencies (2–9 Hz) and corresponding dynamic pressures (0.96–19.17 kPa) (Supporting Information S1: Figure S12). The results indicate that the piezoelectric signals of all composite films exhibit a steady and monotonic increasing trend with increasing external mechanical driving frequency and applied pressure. Notably, across the entire tested frequency range and pressure interval, the PC-8 wt% film consistently demonstrates the optimal electromechanical conversion output. For instance, under high-frequency and high-pressure conditions of 9 Hz and 19.17 kPa, the peak voltage of PC-8 wt% rapidly rises to approximately 10.5 V, significantly outperforming the pure PVDF matrix and other low-filling compositions. When the filler concentration further increases to 10 wt% and 12 wt%, the output signal exhibits significant hysteresis and attenuation due to the inevitable agglomeration of excess molecular clusters, which leads to increased internal defects. Furthermore, based on the quantitative dependence curves of the extracted output voltage as a function of applied pressure (Supporting Information S1: Figure S12i), the response dynamics of the composite films to mechanical stresses of different magnitudes can be clearly observed. As the pressure gradually increases, the voltage signal of PC-8 wt% exhibits an excellent stepwise linear growth from several hundred millivolts under extremely low pressure, reaching a high potential output of over 10 V at nearly 20 kPa. In addition to the outstanding open-circuit voltage, the short-circuit current (I_{sc}) of the composite films also shows a strong dependence on the filling concentration (Supporting Information S1: Figure S13a). Upon the addition of (IQ)₂CuBr₂, the output current increases significantly, reaching a peak value (nearly 100 nA) for PC-8 wt%, far exceeding the output level of pure PVDF. This further confirms that PC-8 wt% effectively forms an optimal polarization network. To comprehensively evaluate its dynamic output capability, the current responses of the sensor under various mechanical stimulation conditions were systematically tested. The results demonstrate that under both stepwise pressure loading (2.13–15.14 kPa, Supporting Information S1: Figure S13b,c) and variable-frequency driving (4–7 Hz, Supporting Information S1: Figure S13d,e), the device outputs highly stable, hysteresis-free, and stepwise increasing current signals, exhibiting excellent electromechanical conversion reliability and a wide operating range. In addition, we compared the dynamic voltage responses of pure PVDF and PC-8 wt% composite films under varying pressures (0.96–19.17 kPa) (Supporting Information S1: Figure S14a,b). Under the same applied pressure, the PC-8 wt% composite film consistently exhibited a higher output voltage than pure PVDF. When the pressure reached 19.17 kPa, the output voltage of pure PVDF was approximately 4 V, whereas that of the PC-8 wt% composite film reached 10.5 V. This significant improvement confirms that the (IQ)₂CuBr₂-induced interfacial hydrogen-bonding network effectively enhances the piezoelectric activity of PVDF. The electrical resistance of the composite films was also measured (Supporting Information S1: Figure S15). The resistance decreased markedly after the incorporation of (IQ)₂CuBr₂, indicating improved electrical transport. However, the resistance continued to decrease at higher filler

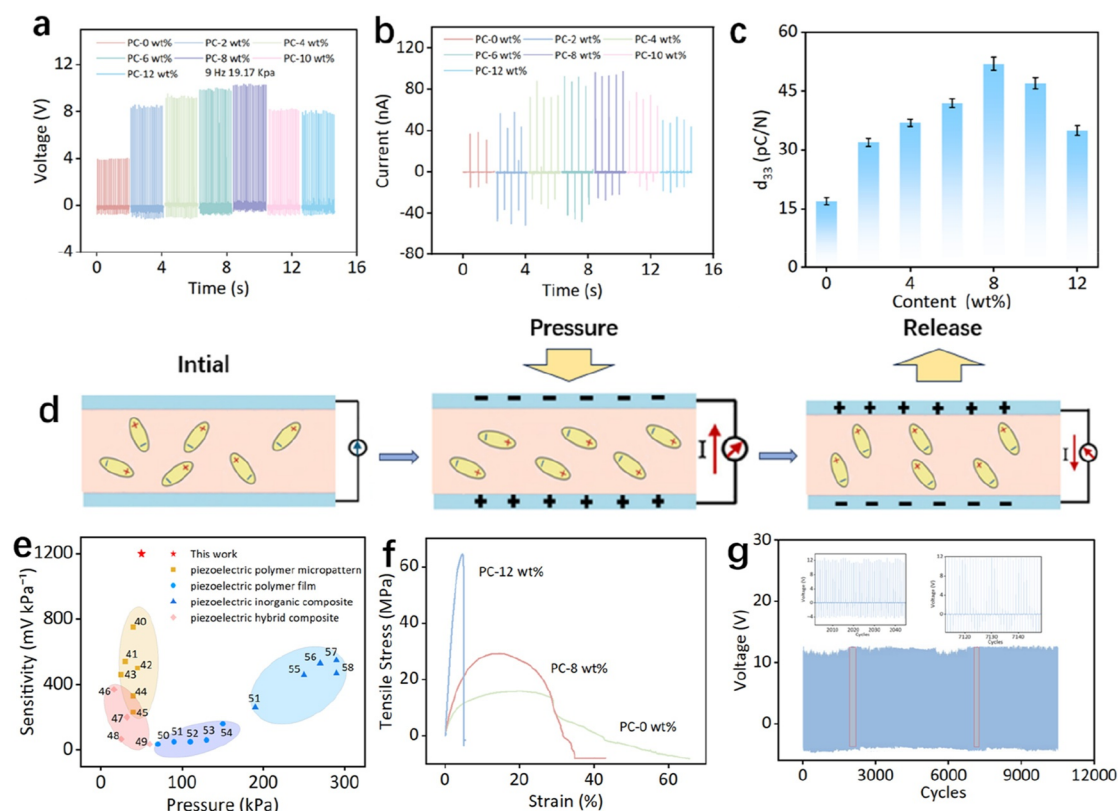


FIGURE 4 | (a) Open-circuit voltage of the films with different filling concentrations. (b) Short-circuit current of the films with different filling concentrations. (c) Piezoelectric constant d_{33} of the composite films. (d) Schematic diagram of the piezoelectric working mechanism of the sensor. (e) Comparison of the sensing sensitivity. (f) Stress–strain curves of the films. (g) Long-term operational stability test of PC-8 wt%.

contents, whereas the piezoelectric output reached its maximum at 8 wt% and subsequently declined. This different trend suggests that the enhanced piezoelectric performance cannot be attributed solely to the reduction in electrical resistance and further supports the important role of interfacial polarization regulation. Moreover, it is evident that alternating positive and negative electrical signals are generated upon pressing and releasing as shown in Figure 4d. This phenomenon can be explained as follows: when pressure is applied to the PC-8 wt% film, the dipoles align in response to mechanical stress, generating a positive voltage output. Upon removal of the force, the dipoles return to their original state due to the elastic recovery of the piezoelectric material. The release of accumulated charges produces a reverse current, resulting in a negative voltage output [38, 39].

With the aim of evaluating its sensing performance, the pressure response capability of the device was quantitatively analyzed. The voltage–pressure curve (Supporting Information S1: Figure S16) exhibits a clear two-stage linear response. In the low-pressure region (< 6 kPa), the device achieves an ultrahigh sensitivity of 1.20 V kPa⁻¹, enabling precise detection of subtle mechanical stimuli. Such high sensitivity surpasses that of many piezoelectric composite materials [40–58] as shown in the comparison in Figure 4e. In the high-pressure region (> 6 kPa), the sensitivity transitions to a stable value of 0.19 V kPa⁻¹, thereby ensuring a wide operating range. This excellent low-pressure sensitivity, combined with stable linear response and robust voltage output, makes the PC-8 wt% composite film

highly suitable for advanced wearable electronic devices. Such a dual-sensitivity profile over a broad range is particularly advantageous: the high sensitivity in the low-pressure region allows accurate detection of gentle touches, whereas the sustained linear response under heavy pressure prevents signal saturation upon excessive force, rendering the sensor ideally suited for complex human–machine interaction applications.

The stress–strain curves and Young's moduli (Figure 4f and Supporting Information S1: Figure S17) reveal a strong correlation between filler concentration and mechanical behavior. The pure PVDF film exhibits typical flexibility with a high elongation at break (> 60%) but a low tensile strength (approximately 15 MPa). Notably, the PC-8 wt% composite film achieves an ideal balance between strength and flexibility. Its tensile strength significantly increases to approximately 30 MPa, while maintaining a considerable strain of about 35%, resulting in the highest toughness of approximately 6 MJ m⁻³. In stark contrast, the PC-12 wt% sample exhibits a marked increase in Young's modulus (nearly 1400 MPa) accompanied by a sharp decline in elongation at break (< 10%), rendering the material extremely stiff and brittle. This mechanical evolution is highly consistent with the trend observed in piezoelectric performance. For the PC-8 wt% sample, its appropriate toughness and moderate flexibility enable sufficient and effective local deformation under external mechanical stimulation. This structural compliance ensures efficient stress transfer [59], generating a substantial voltage output of 10 V. Conversely, for the PC-12 wt% sample, its excessive rigidity and ultrahigh Young's modulus act

as a mechanical barrier. Under the same applied force, the stiff matrix severely restricts structural deformation, effectively constraining the reorientation of internal polarized dipoles and thereby limiting the enhancement of piezoelectricity [60]. Moreover, for the cyclic stability tests, PC-8 wt% device maintains a stable output voltage after 10,000 cycles, demonstrating highly stable performance and excellent device durability (Figure 4g). To further evaluate the overall performance of the PC-8 wt% composite film, a systematic comparison with representative PVDF-based piezoelectric composites is provided in Supporting Information S1: Table S3.

2.4 | Multidimensional Human–Machine Interaction and Intelligent System Applications

To achieve high-spatial-resolution tactile sensing and multidimensional human–machine interaction, a flexible piezoelectric sensor array fabricated using PC-8 wt% in a 3×3 pixel matrix configuration (with an effective area of $3 \times 4 \text{ cm}^2$) was investigated. Specifically, precise electrode patterning and circuit routing for the device were first designed using electronic design automation (EDA) tools (Supporting Information S1: Figure S18). This layout ensured stable signal extraction from the nine independent sensing pixels while minimizing electrical crosstalk between adjacent data channels. Based on this design, a flexible device prototype was successfully fabricated. Benefiting from the excellent mechanical toughness of the PC-8 wt% composite film and the ultrathin packaging process, the array device exhibited outstanding macroscopic flexibility and surface conformability, laying a crucial physical foundation for its seamless conformal attachment to complex three-dimensional curved surfaces. To evaluate its capability for real-time kinematic monitoring, the sensor was seamlessly attached to the human wrist (Supporting Information S1: Figure S19a). The device successfully distinguished wrist-bending motions from 10° to 90° . The values compared at different angles correspond to the peak voltages generated during the bending process rather than sustained voltages under a static bending state. A larger bending angle produces a greater transient deformation rate and strain variation, resulting in a higher piezoelectric voltage peak. Furthermore, under repetitive bending at different frequencies (0.5–2.0 Hz), the sensor output highly stable and reproducible waveforms without significant signal attenuation or phase delay, confirming its excellent dynamic reliability. The study also demonstrated its capability for dynamic pressure trajectory recognition. When a finger dynamically traced the number “3” across the array surface (Figure 5a), sequential transient voltage responses were generated by the activated pixels and reconstructed into the corresponding trajectory map (Figure 5b). The sensor array exhibits low crosstalk. These results indicate that the piezoelectric sensor array can accurately identify the contact trajectory of a press, highlighting its promising application prospects in real-time tactile sensing systems. Moreover, the sensor array was capable of clearly distinguishing simultaneous multipoint pressures at different positions, with voltage variations confined exclusively to the pressed pixels. When L-shaped and C-shaped objects were dynamically loaded onto the array (Figure 5c), the peak responses generated during the loading process were extracted from the corresponding sensing pixels and used to reconstruct the geometric patterns shown in Figure 5d. Therefore, these

maps represent transient piezoelectric responses during loading rather than continuous static-pressure outputs. These compelling results confirm the versatility of our self-powered sensor for multidimensional human motion capture and high-resolution tactile mapping.

We further developed a system-level human–machine interface by integrating the piezoelectric sensor array with an analog-to-digital converter (ADC) module, a signal conditioning module, and a Bluetooth module (Supporting Information S1: Figure S20), thereby realizing promising functionalities. The custom-designed 3×3 flexible piezoelectric sensor array was seamlessly attached to an automotive steering wheel. This intelligent steering wheel was designed to dynamically map the spatial distribution of hand-induced piezoelectric responses and monitor physiological states in real time. By continuously tracking the spatiotemporal voltage signals (Figure 5e) and the corresponding spatial thermal maps (Figure 5f) generated by the multichannel tactile array, the system could accurately identify four typical states along the driver's physiological degradation trajectory.

At the physical sensing level, the piezoelectric sensor array responds to time-varying mechanical deformation rather than ideal static pressure. During the awake state, a firm grip accompanied by natural hand adjustments, physiological micromotions, and vehicle-induced vibrations generated repeated, relatively high-amplitude piezoelectric signals of approximately 800–1000 mV after amplification, filtering, and sampling. These dynamic signals produced large red regions in the spatial response map and exhibited relatively regular temporal characteristics. During mild fatigue, intermittent changes in grip force and hand posture produced irregular dynamic responses of approximately 400–600 mV, corresponding to yellow–orange regions in the spatial map. In the tremor state, rapid and low-amplitude hand motions generated dense high-frequency voltage fluctuations, whereas the overall signal amplitude decreased to below approximately 300 mV, resulting in light blue or green regions. When the driver's hand was removed from the steering wheel, the dynamic mechanical excitation disappeared, and the signal returned to the baseline. The displayed waveforms and spatial maps were reconstructed from the amplitude, frequency, temporal, and spatial features of the piezoelectric signals within defined sampling windows and should not be interpreted as sustained DC outputs under static pressure. For the microsleep hand-off state, the system identified the absence of valid dynamic signals over a predefined time window. When this condition occurred although the vehicle was in motion, the controller activated the Bluetooth module and transmitted an emergency-warning command to the connected mobile terminal. Therefore, the system distinguishes the different driving states through the dynamic characteristics of the piezoelectric responses rather than through direct measurement of static grip pressure.

In order to unleash the application potential of this piezoelectric sensor array in advanced driver-assistance systems (ADAS), the high-quality time-series signals rich in amplitude, frequency, and spatial features were deeply integrated with machine learning (ML) algorithms (Figure 5g,h). Benefiting from the excellent piezoelectric output characteristics and high sensitivity of PC-8

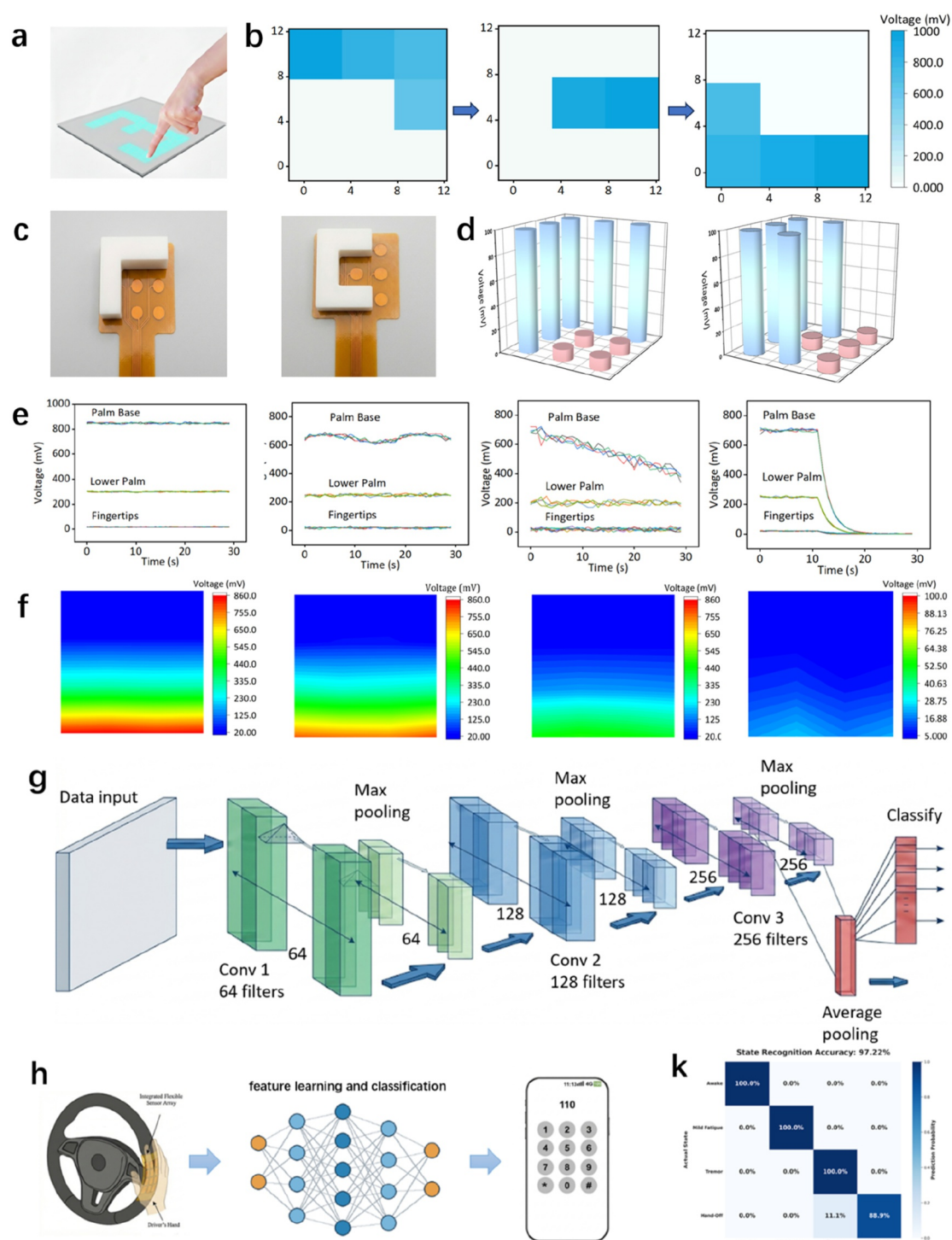


FIGURE 5 | (a) Schematic diagram of a finger tracing a digital trajectory on the surface of the flexible sensor array. (b) The voltage spatial distribution map of the finger sliding trajectory recorded by the sensor array. (c) Photographs of objects with specific geometries (L-shaped and C-shaped blocks) placed on the sensor array. (d) Spatial voltage histogram of specific geometric shapes mapped by the sensor array. (e) Real-time voltage waveforms of multichannel outputs from the sensor array under four typical driving states. (f) Spatial pressure distribution thermal maps of the steering wheel corresponding to the four typical driving states. (g) Detailed structural diagram of the constructed one-dimensional convolutional neural network (1D-CNN) model. (h) Schematic flowchart of the closed-loop system for driver fatigue monitoring and emergency warning integrating the sensor array with machine learning. (k) Confusion matrix of the machine learning algorithm for classifying the four driving states (awake, mild fatigue, tremor, and microsleep hand-off).

wt%, the sensor exhibited outstanding signal-to-noise ratio and extremely low spatial crosstalk, providing highly reliable raw feature inputs for the algorithm. The signal features of the four

typical driving states were highly decoupled, forming extremely clear clustering boundaries. In terms of classification performance, the confusion matrix revealed that the system achieved an

exceptionally high overall prediction accuracy of 97.22% (Figure 5k). Notably, the recognition accuracy for the three easily confusable early fatigue states, such as “Awake,” “Mild Fatigue,” and “Tremor,” reached 100%. Meanwhile, the recognition rate for the highly accident-prone “microsleep hand-off” state remained at a high level of nearly 90% (88.9%). Furthermore, the real-time probability output curves further demonstrated the capability of this closed-loop system to dynamically track the trajectory of the driver's physiological state degradation. These compelling demonstrations not only confirm the substantial commercial translation potential of our self-powered flexible sensor array for active safety warning in ADAS.

3 | Conclusion

In summary, we have designed a flexible piezoelectric composite film based on molecular-level precise interfacial anchoring to achieve a significant enhancement in piezoelectric performance. Through DFT calculations and experimental validation, this study clearly reveals the detailed microscopic mechanism underlying the dramatic increase in polymer polarization and the enhanced piezoelectric properties of the composite, which is attributed to the strong interfacial hydrogen-bonding network (C-H...F-C). The substantial steric hindrance arising from the bulky organic ligands in (IQ)₂CuBr₂ not only prevents filler agglomeration defects but also maximizes the polarizable interface. This robust interfacial anchoring effect spontaneously triggers a remarkably high content of the electroactive β -phase in PVDF, endowing the composite film with excellent mechanical flexibility, an ultra-high sensitivity in the low-pressure region (1.20 V kPa⁻¹), and an outstanding piezoelectric coefficient (52 ± 1.65 pC N⁻¹). Leveraging these superior properties, we integrated a 3×3 flexible sensor array for precise wrist motion monitoring and seamlessly incorporated it into an intelligent steering wheel assisted by machine learning algorithms, successfully achieving accurate feature recognition of the driver's multistage fatigue signals and closed-loop warning. This study provides an efficient and scalable route for polarization enhancement in interfacial piezoelectric composites and offers a new perspective for the design of next-generation advanced driver-assistance systems.

Author Contributions

Yuying Wu: methodology, investigation, funding acquisition, writing – original draft, writing – review and editing. **Si Chen:** investigation, software. **Zijie Luo:** software, investigation. **Gang Zhou:** methodology, data curation. **Lei Zhu:** writing – review and editing. **Xinyuan Zhu:** investigation, methodology, resources. **Youfu Wang:** conceptualization, investigation, writing – review and editing, resources. **Xin Jin:** methodology, writing – review and editing.

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Conflicts of Interest

The authors declare no conflicts of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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Supporting Information

Additional supporting information can be found online in the Supporting Information section.

Supporting Information S1: tch270020-sup-0001-suppl-data.pdf.