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Interface-induced high piezoelectric γ -glycine-based flexible biodegradable films

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ABSTRACT

Flexible biodegradable piezoelectric composite films prepared by combining water-soluble rigid piezoelectric crystals with flexible polymers have immense potential in the fields of wearable and implantable bioelectronics due to their self-powered, biocompatible, and biodegradable properties. However, comprehensive research on maintaining a high piezoelectric coefficient during fabrication of a flexible film is still lacking. In this work, based on γ -glycine, a simplest natural biodegradable piezoelectric crystal, we investigated the effects of different watersoluble biodegradable polymers and film-forming interfaces on the crystal type, arrangement, structure, and piezoelectric properties. The glycine-PEO composite film prepared using the co-dissolution-evaporation method on the more hydrophobic PTFE interface exhibits a higher out-of-plane piezoelectric coefficient (d_{33}) of ~8.2 pC/ N, which is very close to the theoretical d_{33} (10.4 pC/N) of the γ -glycine crystal. This study establishes that interface-induced effects have significant impacts on the crystal arrangement and piezoelectricity of composite films. This study provides important guidance for future research on flexible preparation of other flexible piezoelectric materials.

1. Introduction

Piezoelectric materials and devices [1] can convert mechanical energy to electrical energy based on the piezoelectric effect, which exhibit great potential in the fields of implantable or wearable biomedicine [2], such as for self-powered energy harvesting, active sensing and electrical stimulation therapy. To meet the application requirements, demands are put forward in terms of flexibility and biodegradability. First, piezoelectric materials or devices need to be adequately attached to tissue or skin, and their mechanical properties should satisfy the biocompatibility requirement of the implantation site [3,4]. In addition, improving the biodegradability of implantable or wearable devices in the human body or in the environment can avoid the problem of secondary removal surgery or environmental pollution [5-8]. Piezoelectric materials

mainly include rigid or brittle ceramics and crystals, and relatively flexible polymers. Unfortunately, ceramics [9] are not biodegradable, and some piezoelectric ceramics contain toxic metal elements. On the other hand, piezoelectric polymers [10] have lower piezoelectric coefficients and fewer available types, especially biodegradable piezoelectric polymers. In contrast, the number of types of piezoelectric crystals have continuously increased [11,12], and many of them are biodegradable and biocompatible [13]. Methods such as co-crystallization can further improve the piezoelectricity or enrich the variety [14]. Therefore, combining rigid piezoelectric crystals with flexible polymers to prepare biodegradable piezoelectric composite films is also a promising method for fabrication of flexible materials [15].

We first focus on the flexible fabrication of piezoelectric amino acids,

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because amino acids are one of the simplest and cheapest naturally degradable piezoelectric materials.[10,16] Among the 20 common types of amino acids, γ -glycine has been predicted to have a higher longitudinal piezoelectric coefficient (d₃₃ of up to 10.4 pC/N) [17]. Therefore, flexible biodegradable piezoelectric composite films based on γ -glycine are expected to have good piezoelectricity and potential for biomedical applications. However, glycine is a polymorphic amino acid, mainly including α , β , and γ crystal structures. The crystal unit of α -glycine is centrosymmetric without piezoelectricity. β -glycine is predicted to show a strong shear piezoelectric coefficient (d₁₆ ~ 178 pC/N), but its longitudinal piezoelectric performance is not good as γ -glycine. In addition, β -glycine is prone to crystal transformation in the atmosphere [18]. Therefore, during the flexible fabrication, biodegradable polymers and preparation methods must induce glycine to form γ crystals to obtain

piezoelectric films with application potential. In recent years, Wang et al. prepared a flexible biodegradable piezoelectric glycine-polyvinyl alcohol (PVA) composite film with a sandwich structure through the co-dissolution-evaporation method [19] and then further induced crystal alignment through interface and film edge regulation, resulting in an enhanced d₃₃ (approximately 6.13 pC/N) for the composite film [20]. However, there is still a gap compared to the theoretical d₃₃ (10.4 pC/N) of γ -glycine. Therefore, further study of flexible polymers, interface properties and induction mechanisms on crystal growth and alignment is still of great significance, as is research on maintaining a high piezoelectric coefficient during flexible fabrication. Furthermore, the advantage of the co-dissolution-evaporation method is its simple and low-cost process without using elaborate machines. Comparatively, other methods (such as direct blending) of preparing γ -glycine-based



Fig. 1. Characterization of flexible piezoelectric glycine composite films prepared with different polymers. The mass ratio of glycine to the polymer is 3:1. (a) Chemical structures of the polymers in glycine-polymer composite films. (b) Glycine-polymer composite films and their SEM images of the top and bottom surfaces; the order is glycine-HA, glycine-pullulan, glycine-gelatin, glycine-PVA and glycine-PEO films. (c) d_{33} piezoelectric coefficients of different glycine-polymer composite films. (n = 10 independent spot d_{33} measurements on a film. Data are presented as mean $\pm \max/\min$.) (d) XRD patterns of different glycine-polymer composite films, and standard XRD patterns of α -, β -, and γ -glycine crystals from Jade software as references.

films with good piezoelectricity are more complicated, because the crystallization of γ -glycine requires additional additives or expensive equipment [21,22], and it is also required that the size of γ -glycine crystals should be uniform and small enough before blending, which needs special grinding machine or process [23,24].

In this work, we studied the effects of different water-soluble biodegradable polymers and film-forming interfaces with different wettabilities on the crystal type, arrangement, film structure and piezoelectricity. We found that the γ -glycine-polyethylene oxide (PEO) composite film with a sandwich structure prepared on the more hydrophobic polytetrafluoroethylene (PTFE) interface exhibits a higher out-of-plane d_{33} of ~8.2 pC/N, which is very close to the theoretical d_{33} (10.4 pC/N) of the γ -glycine crystal. We further fabricated flexible biodegradable piezoelectric nanogenerators (PENGs) based on the γ -glycine-PEO film and verified their efficient mechanical-to-electrical energy conversion and sensing performance in wearable and implantable applications. This work proves that the interface-induced effect has an important influence on the crystal arrangement and the piezoelectricity of composite films, and has key guiding significance for research on maintaining high piezoelectric performance flexible preparation of other flexible piezoelectric materials.

2. Results and discussion

2.1. Interface-Induced high-piezoelectric flexible γ -glycine-polymer films

The glycine-Polymer composite films were prepared using the codissolution-evaporation method on PTFE interfaces (see the Supporting Information). To obtain high-piezoelectric-coefficient flexible glycine-polymer composite films, we first investigated the effects of polymers containing different chemical groups on the glycine crystal type, film structure and piezoelectricity and further analyzed the interface-induced mechanisms of polymers and related chemical groups for the arrangement or orientation of glycine crystals. These six polymers have the following characteristics and differences in structure (Fig. 1a). Sodium hyaluronic acid [25] (sodium HA), the sodium salt of HA, is a glycosaminoglycan composed of sodium D-glucuronic acid and N-acetylglucosamine repeating units. The main chain of sodium HA contains alkane chains of five-carbon sugars and glycosidic bonds, and the side chain of each repeating unit contains four hydroxyl groups, a carboxylate group and an N-acetyl amide group. Pullulan [26] consists of maltotriose repeating units linked by α -1,6 glycosidic bonds. The chemical structure of the backbone of pullulan is similar to that of sodium HA, but the side chain only contains many hydroxyl groups. The main chain of PAM [27] is composed of [-CH2-CH2-] repeating units, and each repeating unit contains an amide side group. Gelatin [28] is a linear protein composed of amino acids connected by peptide bonds, and the proportions of glycine-proline-X (X: other amino acid) and glycine-X-hydroxyproline are relatively large. The main chain of PVA [19] is composed of [-CH₂-CH₂-] repeating units, with an average of \sim 0.9 hydroxyl side groups per repeating unit. The main chain of PEO [29] is composed of [-CH₂-CH₂-O-] repeating units, containing many alternating ether bonds and two-carbon alkane chains. After co-dissolution of these linear water-soluble polymers with glycine in water and then evaporation and co-precipitation, the composite films obtained all have sandwich structures (Fig. 1b). And the top and bottom layers are continuous polymer surface, and the interlayers are mainly glycine crystals. The functional groups of polymers play an important role in the crystal types and arrangement of glycine. By comparing the out-of-plane piezoelectric coefficient (d₃₃) (Fig. 1c) of different glycine-polymer composite films, we found that the glycine-PEO film has the highest average d_{33} (~8.2 pC/N), and the highest value of d_{33} reaches 13 pC/N, even exceeding the theoretical d_{33} (10.4 pC/N) of the γ -glycine crystal (Fig. S1). By analyzing and comparing the XRD patterns (Fig. 1d), the glycine-PEO film is found to show the most obvious (101), (110) and (102) peaks, which is consistent with the standard XRD

pattern of γ -glycine. This shows that the chemical structure of PEO composed of alternating ether bonds and short alkane chains has a very good induction effect on the formation and arrangement or orientation of γ-glycine crystals. Glycine-PVA and glycine-gelatin have an obvious (110) peak, indicating that PVA and gelatin are also conducive to the formation of γ -glycine crystals, but there is no obvious (102) peak, indicating that PVA and gelatin are not beneficial to the growth of the (001) facets of glycine crystals parallel to the plane of the film because the (102) and (001) facets of γ -glycine are only 24.2° from each other. When the (001) facets are parallel to the film plane, the film will exhibit the largest out-of-plane d_{33} [20]. As a result, the d_{33} values of glycine-PVA and glycine-gelatin are lower than that of glycine-PEO (Fig. 1c). The XRD patterns of glycine-PAM, glycine-pullulan, and glycine-sodium HA show fewer characteristic peaks of γ -glycine, and the out-of-plane d₃₃ values of these three films are far less than that of glycine-PEO. Therefore, we infer that the amide side group is not helpful for the formation of γ -glycine crystals because the difference between PAM and PVA is mainly in the side groups. In addition, the main chain of the polysaccharide chain has fewer advantages for the formation of the y-phase because polysaccharides and PVA both have abundant hydroxyl side groups. Therefore, the glycine-PEO composite film has the best piezoelectric performance.

Additionally, we investigated the effect of the film-forming interface on the piezoelectricity of the glycine-PEO composite films. The glycine-PEO composite film (mass ratio of glycine to PEO is 3:1) prepared on the more hydrophobic PTFE interface has the largest out-of-plane d_{33} (~8.2 pC/N) (Fig. 2c). In contrast, the maximum d_{33} of the composite films induced by the glass interface and PS interface is only 5 pC/N (Fig. 2a) and 4 pC/N (Fig. 2b), respectively. The d₃₃ values of the top and bottom surfaces are very close. The XRD patterns (Fig. 2d) of the glycine-PEO films prepared on the three interfaces all show obvious (101), (110) and (102) peaks, which are consistent with the standard pattern of γ -glycine. Meanwhile, there are no obvious peaks at the positions corresponding to α -glycine and β -glycine. In addition, we used the three interfaces to induce crystallization of glycine from glycine aqueous solution, obtaining only α -crystals (Figs. 2e and S2). This demonstrates that none of the three interfaces can directly induce glycine to form the γ phase but can affect the orientation or arrangement of PEO or γ-glycine during the film formation process, resulting in the difference in d_{33} . Additionally, we found that the mass ratio of glycine to PEO has a significant effect on the out-of-plane d_{33} of the film. As the ratio of γ -glycine increases, d₃₃ gradually increases. When the mass ratio of glycine to PEO is 3:1, the composite film has the largest out-of-plane d_{33} . The characteristic peak (such as the (110) peak) corresponding to γ -glycine is enhanced (Fig. 2 f). However, when the proportion of glycine is further increased to over 3:1, d₃₃ tends to decrease. As shown in the XRD patterns, the (110) peak of the composite film gradually increases, but the (102) peak decreases (Fig. 2 f), indicating that a further increase in γ -glycine leads to disorder of the overall γ -glycine crystal arrangement or orientation in the films or causes the angle between the (001) facet of γ -glycine and the plane of the film to increase because the (102) and (001) facets are only 24.2° from each other and a larger (102) peak reflects a smaller angle between the (001) facets and the film plane. When the angle between the (001) facets of more γ -glycine crystals and the film plane is smaller, the out-of-plane d₃₃ of the film will increase accordingly [20].

We deduce that the hydrophobic interface-induced effect of PTFE on the molecular orientation regulation of bottom layer PEO and γ -glycine crystals is the reason for the increase in the out-of-plane d₃₃. Through the combination of contact angle, SEM, EDS and other characterization methods, the mechanism is becoming clear. The contact angles of glycine-PEO aqueous solution on glass, PS and PTFE interfaces are 37°, 87° and 109°, respectively (Fig. 3a), and the hydrophobicity of the three interfaces increased sequentially. During the evaporation and drying process of the composite solution on different interfaces, especially in the later stage of the process, the hydrophilic part of the PEO (rich in -O-

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Fig. 2. d_{33} piezoelectric coefficients and XRD patterns of glycine-PEO composite films prepared on different interfaces. (a, b, and c) d_{33} piezoelectric coefficients of glycine-PEO films prepared on glass, PS and PTFE interfaces, respectively. (n = 10 independent spot d_{33} measurements on a film. Data are presented as mean \pm standard deviation.) (d) XRD patterns of glycine-PEO films prepared on different interfaces. (e) XRD patterns of glycine-PEO films with different glycine/PEO mass ratios prepared on the PTFE interface.



Fig. 4. Mechanical and piezoelectric properties of glycine-PEO films. (a) Stress-strain curves of glycine-PEO films with different mass ratios. (b) Dynamic mechanical analysis of glycine-PEO films in frequency sweep mode from 0.1 to 100 Hz at a constant strain of 0.1%. (c) Dynamic mechanical analysis of glycine-PEO films in strain sweep mode at a constant frequency of 2 Hz. (d) Piezoelectric output (V_{oc}) of glycine-PEO-based PENGs measured under a constant impulse force. (e) Schematic diagram of the apparatus for testing the piezoelectric output using the periodic pressing method. The piezoelectric output was characterized by the digital oscilloscope and electrometer.

bonds) of the bottom layer is more concentrated on and faces the glass interface because of the good hydrophilicity of the glass interface, which leads to the hydrophobic part of the PEO (rich in -CH₂-CH₂- bonds) of the bottom layer to face the opposite direction. Due to its

hydrophobicity, the upper surface of the bottom layer of PEO plays a certain role in inducing orientation of glycine, which results in a moderate d_{33} for the composite film. In comparison, the PS interface has moderate hydrophobic properties. At the end of evaporation, the PEO in



Fig. 3. Characterization and analysis of the interface-induced mechanism. (a) Contact angles of glycine-PEO aqueous solutions on glass, PS and PTFE interfaces. (b) Schematic illustration of different interface-induced orientations of the bottom PEO layer and γ -glycine crystals. (c) Schematic illustration of the evaporation and drying process of glycine-PEO aqueous solutions on PTFE interfaces. (d) SEM images of bottom surfaces of glycine-PEO composite films prepared on glass, PS and PTFE interfaces. (e) SEM image of the bottom layer (especially near a hollow site) of the composite film prepared on the PTFE interface, and corresponding EDS maps of H, O, N and C. (f) Cross-sectional SEM image and EDS maps confirming the PEO-glycine-PEO sandwich structure.

contact with the PS interface has both hydrophilic and hydrophobic parts due to some amphiphilic properties of the PEO molecule, which causes the upper surface of the bottom PEO layer to also contain mixed hydrophilic and hydrophobic parts, which is not conducive to guiding the growth of glycine crystals in the same direction, resulting in a lower out-of-plane d₃₃. In contrast, the PTFE interface has the strongest hydrophobic properties. After evaporation, the hydrophobic parts of the bottom PEO layer are more enriched at the PTFE interface, which leads to the more hydrophilic part of the bottom PEO layer orienting toward glycine. The hydrophilic part (-O- bond) of PEO can interact with the amino group or carboxyl group of glycine via hydrogen bonds, which play a beneficial role in arrangement or orientation of γ -glycine crystals, resulting in the highest d₃₃ of glycine-PEO prepared on the PTFE interface. In addition, the upper PEO layer of the composite film is far away from the interface of the dish and is less affected, but its orientation is mainly affected by the interface between air and water, with the hydrophilic part facing downward and the hydrophobic part facing the air upward (Fig. 3b). However, due to the alternating arrangement of hydrophilic and hydrophobic groups in the PEO main chain [30], it is difficult to form a real Janus bilayer structure [31] for PEO, only the enrichment of hydrophilic or hydrophobic groups at different interfaces, so we attempt to elaborate on the interface induction mechanism from more aspects (Fig. 3c).

Furthermore, we found that the increase in interface hydrophobicity (from glass to PS to PTFE) resulted in increased porosity of bottom PEO layers (Fig. 3d). By analysis, during a certain period of the late stage of evaporation and drying process, both PEO and water in the bottom accounted for a large proportion, resulting in poor fluidity of bottom solution due to the large PEO content, but its interfacial properties are still hydrophilic and oleophobic because water also accounted for a considerable proportion. Due to the analogous amphiphilic properties of PEO, and the glass interface has a good affinity for PEO aqueous solution and PEO polymers, so the high-concentration PEO aqueous solution and PEO molecules can spread well on the glass interface, resulting in rare porosity of bottom PEO layer after drying. However, because the moderate hydrophobicity of the PS interface, the spreading performance of the high-concentration PEO aqueous solution is weakened on PS interface, leading to some holes appearing in the bottom PEO layer after drying. In comparison, PTFE interface is most hydrophobic, so the spreading performance of the high-concentration PEO aqueous solution is further weakened and a serious porous phenomenon occurs in the bottom PEO layer. Through EDS analysis from the bottom surface perspective, it is found that the middle layer regions, which exposed by the holes of bottom layer, are rich in nitrogen (N) element, mainly glycine crystals, while the nonporous parts nearby of the bottom layer has almost none N element, which is only PEO (Fig. 3e), because N element only exists in glycine, not PEO. We also found that the bottom PEO is prone to form striped crystalline morphology after drying on hydrophobic PTFE interface (Fig. 3d). We speculate that the flat interface caused by the crystallization of the bottom PEO layer also contributes to better alignment of the glycine, which can boost the out-ofplane d₃₃. On the other hand, compared to other interfaces, PTFE interface exhibits the strongest negative polarity due to its electronwithdrawing ability, while PEO, glycine and their aqueous solutions have positive polarity [32,33]. During the evaporation and film formation, the electric field created between negative PTFE and positive solution may also contribute to the arrangement of crystals in the film [34] (Fig. 3c). Moreover, through a cross-sectional SEM and EDS analysis (Fig. 3f), we confirm that the glycine-PEO composite film has a sandwich structure with clearly defined three layers [19]. The middle layer (~40 μm in thickness) is mainly $\gamma\text{-glycine,}$ and the top (~25 μm in thickness) and bottom layers (~10 µm in thickness) are PEO layers, due to the N element (only from glycine) is mainly concentrated in the middle layer, while there is little in the top and bottom layers. Comparatively, the bottom PEO layer is thinner, which is also beneficial for assembly and orientation of the hydrophilic and hydrophobic parts

of the bottom PEO molecules. However, compared with the ideal sandwich structure of γ -glycine-PVA, the structure of γ -glycine-PEO film prepared on PTFE is not a perfect sandwich, because that some PEO of top layer tend to collapse and fill in the stripe-like gaps among the glycine crystals of the middle layer due to the greater molecule flexibility of PEO in the end stage of the co-dissolution-evaporation process (Fig. S5), and that the bottom PEO layer is porous (Fig. 3d).

In addition, we also found some other phenomena that may also be the reasons for the higher out-of-plane d₃₃ of the glycine-PEO composite film prepared on the PTFE interface. During the evaporation process, glycine crystals begin to appear in the middle of the PTFE culture dish and then gradually grow (Fig. S3). Glycine crystals emerging from the middle position were previously reported to contribute to a larger d₃₃ than those emerging from the edge [20]. In addition, in composite films with a higher mass ratio of glycine to PEO, glycine crystals appear at multiple positions and then gradually grow (Fig. S4). Moreover, we found that the interlayer mainly composed of glycine crystals still has some PEO (Fig. S5), so the top and bottom PEO layers can be linked by the interlayer PEO, which contributes to the integrity and stability of the multilayered structure. In contrast, the glycine-PVA composite film (especially when the mass ratio of glycine to PEO exceeds 3:1) is prone to producing separation or cavities between the top and bottom layers due to the lack of a PVA linker in the interlayer [19] (Fig. S6), resulting in a decrease in piezoelectricity and a reduction in the working life. Regarding the appearance of PEO in the interlayer, we found possible reasons in the literature. When the droplets of PEO aqueous solution spread and dry on different interfaces, pinning or pillar-shaped protrusions easily appear, especially for PEO with a molecular weight of 100,000 and on the PTFE interface [35,36]. Furthermore, the greater molecule flexibility of PEO may contribute to some PEO of top layer collapsing into the stripe-like gaps among the glycine crystals of the middle layer in the end stage of the co-dissolution-evaporation process.

In this work, there are two types of interfaces mentioned, including the interfaces between the composite film (or glycine-polymer solution) and the petri dishes, and the interfaces between glycine crystals and the polymer, so the "interface-induced effect" mainly refers to two aspects. On the one hand, the dish surfaces have "interface-induced effect" on the glycine-polymer composite films, mainly referring to that the degree of hydrophilicity of the dish material has effect on the molecular arrangement of the solution, especially on orientation of the hydrophilic and hydrophobic part of the PEO molecules of the bottom layer during the end of evaporation process, and on the spreading performance of the high-concentration bottom PEO aqueous solution on the dish surface. The different orientations and the spreading performances of the bottom PEO will affect the arrangement and orientation of γ -glycine crystals located in the middle layer, ultimately affecting the out-of-plane d₃₃ of the composite film. In this work, the most hydrophobic PTFE interface is more conducive to the high out-of-plane d_{33} . It is speculated that other material interfaces with high hydrophobicity, such as fluorinated ethylene propylene, polyvinylidene fluoride, etc., may also contribute to the good out-of-plane d₃₃ of the film. On the other hand, water-soluble polymers have "interface-induced effect" on the glycine crystals, mainly referring to that the polymers with different chemical groups affect the crystal types and orientation of the glycine. After the co-dissolutionevaporation process, y-glycine crystals can only be generated in the presence of some special polymers. Among the three special polymers (PEO, PVA, and gelatin), PEO is more conducive to the (001) facets of the γ -glycine crystals being aligned or oriented nearly parallel to the plane of the film, resulting in a higher out-of-plane d₃₃. The research on the relationship between crystal types and polymers is being conducted in depth, and important regular discoveries are expected in our future work.

2.2. Performances of glycine-PEO films and PENGs

For better application of the piezoelectric composite film, we

analyzed its mechanical properties. As shown by the stress-strain curves (Fig. 4a), as the ratio of glycine increases, the tensile strength of the film weakens, showing better stretchability. Meanwhile, all the tested composite films do not fracture when the strain reaches 0.2%, which benefits from the linking effect of PEO among different layers and the good viscoelasticity of PEO. This mechanical performance is better than that of glycine-PVA films. In addition, the dynamic mechanical responses were studied at a constant strain of 0.1% with different strain frequencies (from 0.1 to 100 Hz) (Fig. 4b), and at different strains with a constant biomechanical strain frequency (1 Hz) (Fig. 4c). The glycine-PEO strips with different proportions have stable E without fracture under increasing stretch frequency (up to 100 Hz) (Fig. 4b) or under increasing stretch length (up to 0.2%) (Fig. 4c). The mechanical tests showed that the glycine-PEO composite films have good flexibility and durability. Considering the good piezoelectric performance, we prefer to use the glycine-PEO film (mass ratio of 3:1) for the preparation and research of PENGs.

We fabricated flexible PENGs based on different glycine-PEO composite films with Mg electrodes and PLA encapsulation (see Supporting Information). First, under a light pulse force with constant frequency (2 Hz), we investigated the piezoelectric output (open-circuit voltage) of the PENGs measured by the digital oscilloscope and electrometer (Fig. 4d and e). Consistent with the law of the out-of-plane d_{33} , the piezoelectric output of the PENGs gradually increases with increasing mass ratio of glycine to PEO (from 1:1 to 3:1) in the films, and the maximum values (V_{oc}) reach 5 V (Fig. 4d). Subsequently, we verified the efficient mechanical-to-electrical energy conversion and sensing performance in wearable and implantable applications (see the Supporting Information). As shown in Fig. 5a and b, the PENG can be applied as a wearable sensor for joint movement. When it was attached to the back of the finger or hand, movement signals for different bending angles or different fingers could be monitored and recognized, which exhibits the application potential in gesture recognition. To explore its potential application in vivo, the PENG (1.2 cm \times 1.5 cm in size) was implanted under the thigh skin of an SD rat (Fig. 5c). Assisted movement of the thigh at 1 Hz can drive the PENG to generate a V_{oc} of approximately 150 mV (Fig. 5d).

The application of implantable and wearable medical devices in the human body puts forward the need for high biosafety of materials. To ensure that the glycine-PEO-based PENG has no toxic side effects on cells, the effects of glycine-PEO, glycine-PEO with a Mg electrode, and the PENG on the activity of mouse fibroblasts (L929) were evaluated by cell CCK-8 assay and immunofluorescence staining (see the Supporting Information). The results of the CCK-8 assay show that neither glycine-PEO nor the encapsulated PENG has any significant effect on cell viability, and immunofluorescence staining results confirm that all



Fig. 5. Applications and biosafety evaluation of glycine-PEO-based PENGs. (a, b) V_{oc} of the PENG attached on the back of the finger or hand to detect finger bending and movements of different fingers. (c) Digital photographs and micro-CT images of the implanted PENGs at the thigh positions of SD rats. (d) Piezoelectric voltage outputs of the PENGs driven by gentle stretching. (e) Calcein-AM staining photographs of L929 cells in coculture with glycine-PEO, glycine-PEO with Mg electrodes, and a glycine-PEO-based PENG for 1, 2 and 3 days (green: live cells). (f) Effect of glycine-PEO, glycine-PEO with a Mg electrode, and a glycine-PEO-based PENG on the viability of L929 cells cocultured for 1, 2, and 3 days. (n = 3 independent samples. **p < 0.01. All statistical analyses were performed by one-way ANOVA. Data are presented as mean \pm standard deviation.)

materials constituting the PENG have good biological safety (Fig. 5e and f). However, the Mg electrode produces a slight effect on cell activity, which may be caused by the ion concentration of the enclosed cell culture environment being altered by free Mg ions. Furthermore, the glycine-PEO film exhibits good solubility and degradability and can be basically dissolved in phosphate-buffered saline within 10 min (Fig. S7).

3. Conclusion

In conclusion, we found that the glycine-PEO composite film prepared using the co-dissolution-evaporation method on the more hydrophobic PTFE interface exhibits a higher out-of-plane d_{33} of ~8.2 pC/ N, which is very close to the theoretical d_{33} (10.4 pC/N) of the γ -glycine crystal. We analyzed and deduced the interface-induced mechanisms and the effects of different water-soluble biodegradable polymers and film-forming interfaces with different wettabilities on the crystal type, arrangement or orientation, film structure and piezoelectricity. This work has key guiding significance for research on maintaining high piezoelectric performance during flexible preparation of more piezoelectric materials.

4. Experimental section

4.1. Materials

PEO ($M_v \sim 100000$), sodium hyaluronate (sodium HA), pullulan, gelatin (gel strength ~ 240 g Bloom), polyacrylamide (PAM, $M_n \sim 150000$) and PVA (1799) were purchased from Aladdin. Glycine (99.5–100.5%) was purchased from Macklin. Phosphate buffered saline (PBS, 1X), high glucose Dulbecco's modified Eagle medium (DMEM), sodium pentobarbital, and cell viability/cytotoxicity detection and cell counting kit-8 (CCK-8) assays were purchased from Solarbio. Petri dishes (with the same diameter of ~ 66 mm) of different materials, including glass, polystyrene (PS) and PTFE, were purchased from Innochem.

4.2. Flexible preparation of γ -glycine crystals

A certain amount of glycine and different water-soluble polymers were dissolved in deionized water separately. Then, the two aqueous solutions were evenly mixed, and the glycine-polymer aqueous solution was poured into petri dishes of different interfaces (glass, PS or PTFE). After drying the solution in an air oven at 40 °C for 48 h, dried glycinepolymer composite films were obtained.

4.3. Characterization of flexible piezoelectric glycine-PEO films

4.3.1. Characterization of the structure and composition

The morphology of the top surface, bottom surface and cross-section of glycine-polymer composite films and related elemental information were characterized by scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) (SU8020). X-ray diffraction (XRD) patterns of glycine-polymer composite films and pure glycine were acquired using an X'Pert3 Powder with Cu Kα radiation.

4.3.2. Measurement of the piezoelectric coefficient

The piezoelectric coefficient was measured by a quasistatic d_{33} piezometer (ZJ-4AN, IACAS).

4.3.3. Characterization of mechanical properties

The mechanical properties of glycine-PEO composite films were tested by dynamic mechanical analysis (DMA, Q800). All tested films were cut into strips of the same size ($20 \times 5 \times 0.2 \text{ mm}^3$). The test temperature was 25 °C, the vibration frequency was 1 Hz, and the tensile range was from 0.005% to 0.2%.

4.4. Preparation of PENGs based on glycine-PEO films

Magnesium (Mg) was deposited on both sides of a glycine-PEO film as electrodes by using a magneton sputter (635, Denton Discovery), followed by cutting the sample into rectangular pieces of 1 cm \times 1 cm. Two lead copper (Cu) wires were connected to the magnesium electrodes. Using heat-sealing technology, the Mg-deposited film was packaged by polylactic acid (PLA). A digital oscilloscope (Teledyne LeCroy, HDO6104) and an electrometer (Keithley, 6517B) were employed to characterize the open-circuit voltage (V_{oc}) of the glycine-PEO-based PENG.

4.5. Characterization of PENGs based on glycine-PEO films

4.5.1. Wearable PENGs for movement monitoring

Glycine-PEO-based PENGs were fixed on the finger by Kapton tape to measure different bending angles. In addition, the devices were placed on the back of the hand to recognize the signals of different fingers tapped on a desktop. The corresponding electric signals were collected by a digital oscilloscope (Teledyne LeCroy, HDO6104) and an electrometer (Keithley, 6517B).

4.5.2. Electrical properties of PENGs in rats

All animal experiments were conducted under a protocol approved by the Committee on Ethics of the Beijing Institute of Nanoenergy and Nanosystems. The PENG was sterilized by ultraviolet light before operation. The PENG was implanted into the subcutaneous tissue of the thoracic cavity or legs of a Sprague Dawley (SD) rat (male, 150 g - 200 g) and was monitored by micro-computed tomography (CT). The efficient working properties of glycine-PEO-based PENGs were studied, and the corresponding electric signals were collected by a digital oscilloscope (Teledyne LeCroy, HDO6104) and an electrometer (Keithley, 6517B).

4.5.3. Cell viability

Glycine-PEO, glycine-PEO with Mg electrodes, and a glycine-PEObased PENG were soaked in DMEM culture medium for 3 days, which was filtered to obtain the supernatant culture media. L929 cells (5×10^3 cells per well, 100 µL per well) were cultured with the above media and incubated in a humid atmosphere containing 5% CO₂ at 37 °C for 1, 2, and 3 days. Cell viability/cytotoxicity detection and CCK-8 assays were carried out to evaluate the biocompatibility of these materials. The optical density value at a wavelength of 450 nm was measured with a multimode microplate reader (Thermo Fisher Multiskan FC, Milton Freewater, OR, USA). Immunofluorescence images were acquired with a Leica confocal fluorescence microscope (LECIA TCS SP8).

CRediT authorship contribution statement

Qiao Yu: Conceptualization, Data curation, Investigation, Methodology, Writing – original draft. Yuan Bai: Data curation, Investigation, Methodology, Writing – original draft. Zhe Li: Investigation. Fengying Jiang: Investigation. Ruizeng Luo: Visualization. Yansong Gai: Software. Zhuo Liu: Methodology. Lili Zhou: Formal analysis. Yiqian Wang: Visualization. Cong Li: Software. Kailiang Ren: Resources. Dan Luo: Formal analysis. Hongyu Meng: Conceptualization, Investigation, Found acquisition, Validation, Project administration, Writing – original draft. Zhou Li: Supervision, Found acquisition, Methodology, Project administration, Writing – review & editing.

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.

Data availability

Data will be made available on request.

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Data availability

Data will be made available on request.

Appendix A. Supporting information

Supplementary data associated with this article can be found in the online version at doi:10.1016/j.nanoen.2023.109196.

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