

Hofmeister effect regulated gel iontronic sensors for wide-range pressure perception

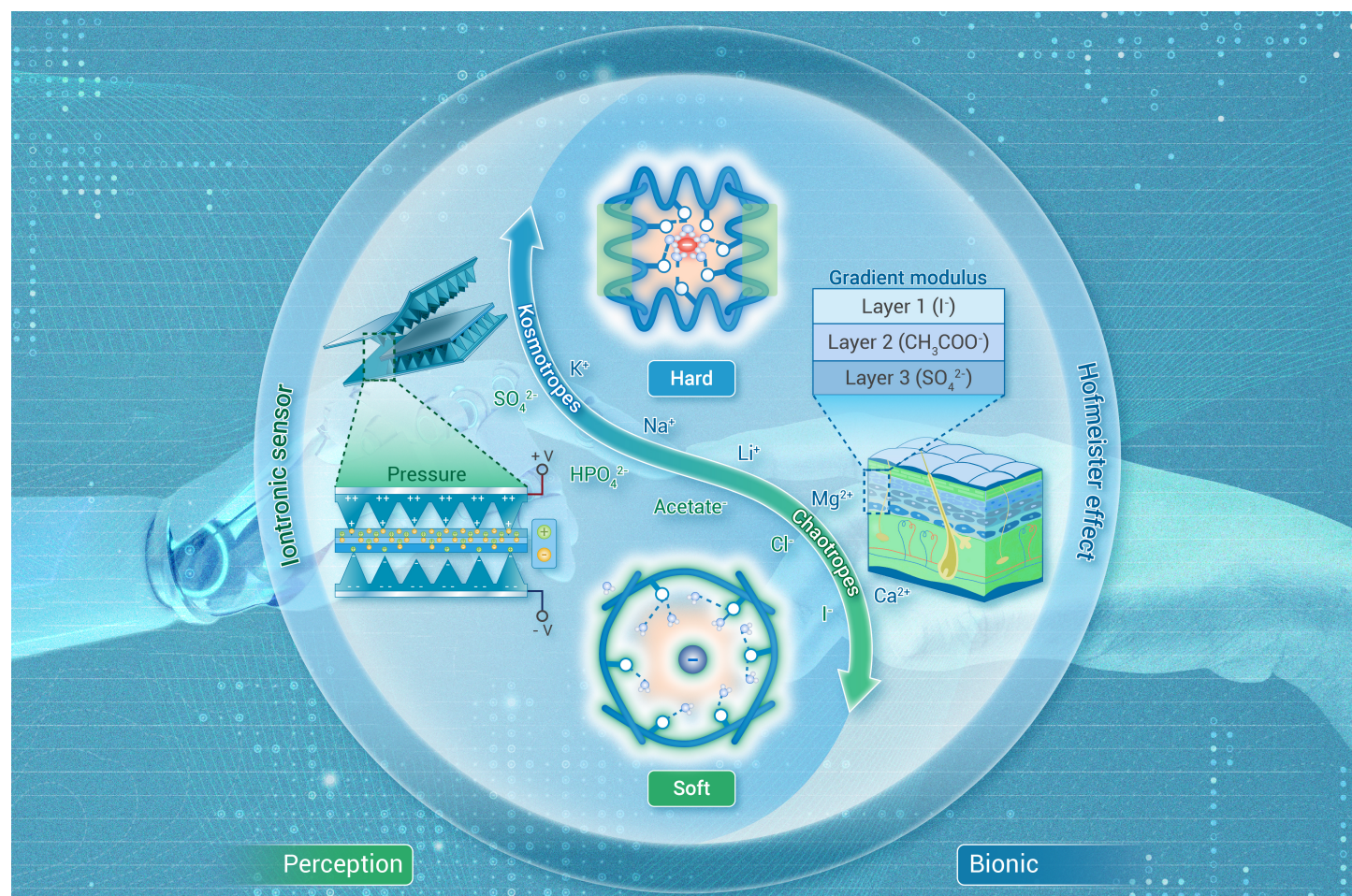
Zilong He,¹ Yonghuan Chen,¹ Jiang Li,¹ Jihan Qu,¹ Li Chen,^{2,*} and Fengyu Li^{1,3,*}

*Correspondence: chenli@301hospital.com.cn (L. C.); lifengyu@jnu.edu.cn (F. L.)

Received: March 11, 2024; Accepted: May 21, 2024; Published Online: May 28, 2024; <https://doi.org/10.59717/j.xinn-mater.2024.100078>

© 2024 The Author(s). This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

GRAPHICAL ABSTRACT



PUBLIC SUMMARY

- The gradient elastic modulus of the skin is key to achieving wide-range pressure perception.
- The modulus of hydrogels can be precisely regulated by *Hofmeister* effect.
- An iontronic sensor with a biomimetic gradient modulus (BGGITS) for ultra-sensitive, wide-range perception was proposed.

Hofmeister effect regulated gel iontronic sensors for wide-range pressure perception

Zilong He,¹ Yonghuan Chen,¹ Jiang Li,¹ Jihan Qu,¹ Li Chen,^{2,*} and Fengyu Li^{1,3,*}

¹College of Chemistry and Materials Science, Guangdong Provincial Key Laboratory of Speed Capability Research, Su Bingtian Center for Speed Research and Training, Jinan University, Guangzhou 510632, China

²Department of General Practice, First Medical Center, Chinese PLA General Hospital, Beijing 100853, China

³College of Chemistry, Zhengzhou University, Zhengzhou 450001, China

*Correspondence: chenli@301hospital.com.cn (L. C.); lifengyu@jnu.edu.cn (F. L.)

Received: March 11, 2024; Accepted: May 21, 2024; Published Online: May 28, 2024; <https://doi.org/10.59717/j.xinn-mater.2024.100078>

© 2024 The Author(s). This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Citation: He Z., Chen Y., Li J., et al., (2024). Hofmeister effect regulated gel iontronic sensors for wide-range pressure perception. The Innovation Materials 2(3): 100078.

Flexible pressure sensors, vital for medical, human-machine interaction, and intelligent recognition applications due to their high-sensitivity, excellent-linearity, and broad-pressure response, face challenges in achieving a harmonious balance among these attributes. Inspired by the gradient modulus in human skin layers, we proposed a pioneering method to adjust the gradient elastic modulus of amino trimethylene phosphonic acid (ATMP)-assisted polyvinyl alcohol (PVA) hydrogel through the Hofmeister effect, introducing micro-pyramid electrodes. This innovative approach successfully constructs a bio-gradient gel iontronic sensor (BGGITS) with an ultra-wide-range perception. The BGGITS exhibits a linear high-sensitivity of 700 kPa⁻¹ within a broad-pressure detection range of up to 800 kPa. The composite design, integrating gradient gel and microstructure electrodes, demonstrates exceptional pressure resolution and mechanical stability. This biomimetic skin pressure sensor holds promise for achieving linear high-sensitivity across a broader pressure range simultaneously and may find applications in electronic skin for health monitoring and tactile perception in the future.

INTRODUCTION

With the rapid development of intelligent robots and wearable medical technologies,^{1–5} the performance requirements for flexible pressure sensors have escalated. An ideal flexible pressure sensor should possess comprehensive characteristics such as high-sensitivity, high-linearity, and a wide-pressure perception range.^{6–8} High-sensitivity enables the detection of subtle mechanical stimuli, while a linear signal facilitates signal processing using simplified circuits and more accurate stimulus responsiveness. Compared to sensors with a narrow-pressure perception range, those with a broader range offer more extensive application scenarios. To achieve this goal, researchers have systematically developed and studied pressure sensors with different conduction principles,⁹ such as resistive,¹⁰ capacitive,¹¹ piezoelectric,¹² frictional,¹³ and optical sensors.¹⁴ Among these, capacitive flexible pressure sensors (CTS) stand out as the preferred choice for tactile sensing systems due to their advantages of simple device structure, stable signals, and low energy consumption. Typically, flexible capacitive sensors feature a three-layer structure with soft dielectric sandwiched between electrodes. The capacitance, denoted as $C \approx \epsilon A/d$, where ϵ is the dielectric constant, A is the contact area between the electrode and dielectric, and d is the distance between the two electrodes. Meanwhile, the limited capacitance change in compressible soft dielectrics results in low sensitivity. The introduction of microstructures such as micro-cones,¹⁵ micro-pyramids,¹¹ and micro-columns¹⁶ has proven effective in enhancing sensor sensitivity by increasing the compressibility of the soft dielectric. On the other hand, these microstructures are prone to signal saturation due to increased resistance against additional loads caused by structural hardening. Therefore, sensors with such microstructures exhibit poorer performance in signal linearity and perception range.^{11,17–19} Recently, Professor Guo and his team proposed an iontronic sensor, forming an electronic double layer (EDL) at the interface of the conductive hydrogel dielectric/electrode.²⁰ The superior capacitive properties of EDL significantly enhance the capacitance of iontronic devices, achieving extremely high pressure sensitivity.^{21,22} In comparison to traditional elastomers, conductive hydrogels possess a 3D cross-linked network and skin-matching elasticity, providing high biocompatibility and tunable mechanical

properties.^{23–29} However, achieving excellent-linearity and high-sensitivity simultaneously across a wide-pressure perception range remains a major challenge.

Influenced by the gradient distribution of elastic modulus from the outer to inner layers of the dermis, mechanical receptors within human skin demonstrate heightened sensitivity and an extensive range of responsiveness to mechanical stimuli.^{30,31} This is because mechanical receptors on the skin's surface, composed of Merkel cells and low elastic modulus Meissner corpuscles, are sensitive to minor pressure stimuli. In contrast, deep dermal mechanical receptors, consisting of high elastic modulus Pacinian corpuscles, demonstrate sensitivity to larger pressure stimuli. Therefore, constructing a gradient hydrogel structure simulating the skin as the dielectric layer of a sensor holds the potential to achieve both high-sensitivity and a wide-pressure perception range. However, the precise adjustment of the gradient elastic modulus still requires urgent resolution.

The Hofmeister effect, first proposed by Franz Hofmeister in 1888, elucidates the impact of different salt ions on the denaturation of proteins, revealing distinct precipitating abilities for proteins in aqueous solutions. The establishment of the Hofmeister series based on the ionic solvation capacity summarized the influence on proteins behavior. "Kosmotropes" with rich hydration capacity enhance the mechanical strength of hydrogel networks, while "Chaotropes" with limited hydration capacity weaken the mechanical strength of hydrogel networks.^{32–34} Inspired by the Hofmeister effect, we prepared an ATMP-PVA hydrogel through facile freeze-thaw treatment PVA constructs the hydrogel framework, and ATMP contributes to the hydrogen bond network for electron or ion migration. The oxygen-containing functional groups of ATMP molecule can form rich hydrogen bonds with PVA chains, or interact with various hydrated cosolvents. The "Kosmotropic" effect accelerates the aggregation of a hydrophobic solute and results in the entanglement of polymer chains. By contrast, the "Chaotropic" effect suppresses hydration and induces the polymer chain slack. Professor He and his team have extensively investigated the Hofmeister effect on PVA hydrogels, aiming to modulate mechanical properties over a wide range.³⁵ The Hofmeister effect offers a versatile and convenient methods to adjust the mechanical properties of hydrogels. This capability can be harnessed for constructing the dielectric layer in pressure sensors, providing a swift means of fine-tuning sensor performance. Modulating hydrogel mechanics through the Hofmeister effect offers an innovative approach to building and optimizing the dielectric layer of pressure sensors, providing a quick and accurate means to adjust the gradient elastic modulus of the sensors.

Inspired by the gradient elastic modulus distribution in human skin for broad-range mechanical perception, we proposed a pioneering gradient elastic modulus hydrogel layer in an iontronic sensor, with the ability to precisely adjust the hydrogel modulus using the Hofmeister effect. Using ATMP-PVA hydrogel as the dielectric layer, stacked to form a gradient elastic modulus, and employing a layered micro-pyramid structure, we successfully constructed the biomimetic gradient gel interlayered iontronic sensor (BGGITS). The gradient hydrogel forms an EDL with the electrode. Finite element analysis and experimental studies demonstrate its superior structural compressibility and gradient compressibility. These structural features significantly improve the BGGITS's sensitivity and extend the linear pressure perception range. Consequently, the BGGITS maintains ultra-high sensitivity (> 700 kPa⁻¹) within an extremely-broad linear range of up to 800 kPa,

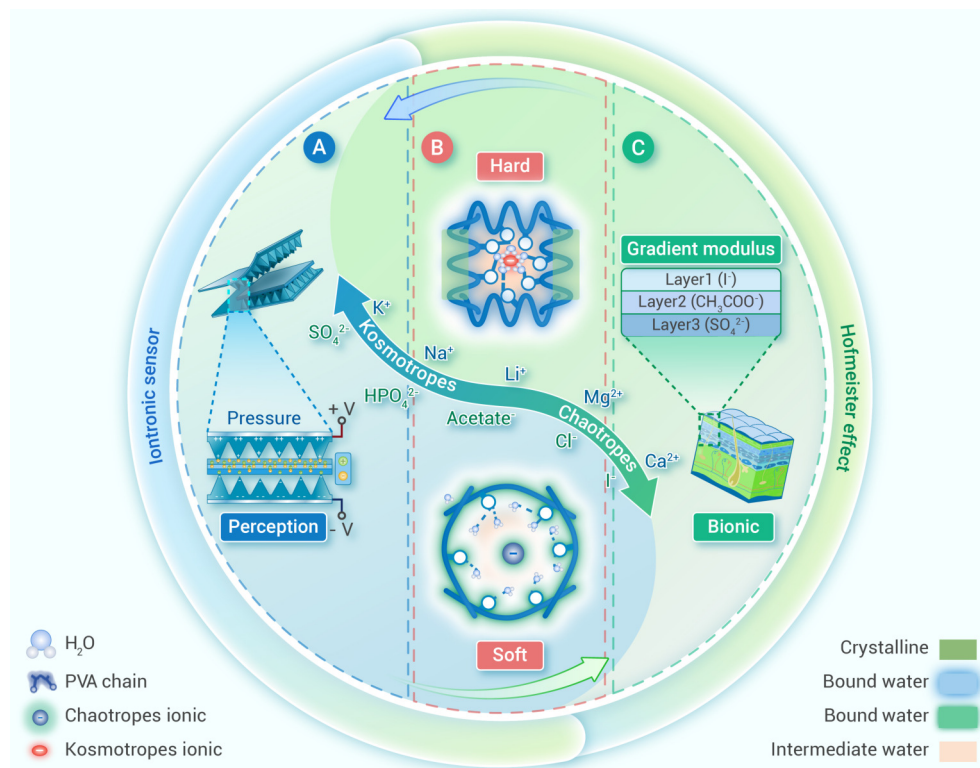


Figure 1. Schematic illustration of the biomimetic gradient gel iontronic pressure sensor (BGGITS) (A) The sandwiching capacitance with hierarchical pyramid electrodes and gradient hydrogel dielectric layer construct the iontronic sensor. (B) The *Hofmeister* effect in the hydrogel manages the gel elasticity modulus of the dielectric layer with the presence of various chemical cosolvents. (C) Schematic diagram of human skin gradient modulus structure.

with copper wire, and pressure was applied using a JK-50E single-column microcomputer-controlled universal testing machine. Capacitance was measured using an LCR meter (IM3536, HIOKI). The distribution of micro-pyramids was observed using an optical microscope.

RESULTS

Design concept and principle of BGGITS

The skin, serving as a physical barrier in mediating interactions with the surrounding environment, consists of epidermal and dermal layers distinguished by a gradient distribution of elastic moduli. Utilizing the *Hofmeister* effect, we have controlled the mechanical properties of hydrogels. Inspired by the gradient modulus

exhibiting excellent high-pressure resolution and mechanical stability. We further apply the BGGITS to recreate scenes from "Journey to the West." Utilizing the BGGITS's linear high-sensitivity and outstanding performance in wide-range perception, accurate character recognition can be achieved through changes in electrical signals. The biomimetic design based on BGGITS provides a new strategy for manufacturing tactile sensors with a wide-range pressure perception.

MATERIALS AND METHODS

Preparation of ATMP-PVA Hydrogel

Polyvinyl alcohol (PVA) powder (4 g) was dissolved in deionized water (30 mL) and aminotris (methylene phosphonic acid) (ATMP, 10 mL). The mixture was stirred magnetically and heated for 2 hours at 105°C, resulting in a homogeneous solution. Subsequently, the solution was cooled to room temperature and poured into preformed molds. The molds were then stored at -18°C for 24 hours, yielding ATMP-PVA hydrogels with diverse morphologies. The PVA Model 1799 (alcohol solubility 98%~99%, 80,000~100,000 average molecular weight (Mw), by Macklin co. was adopted in our experiment.

Preparation of BGGITS

Gold-plated PDMS electrodes were obtained by deposition of 100 nm gold on the surface of layered micro-pyramid PDMS using ultra-high vacuum resistance evaporation coating device (VZZ-400). Then the ATMP-PVA hydrogel film with different moduli is cut into a certain size of 1.5 cm × 1.5 cm and stacked into a gradient modulus structure as the dielectric layer of BGGITS. Finally, the assembled BGGITS was packaged with PI tape.

Characterization and measurements

The finite element simulation of BGGITS structure was conducted using ABAQUS software. Compression tests were performed on ATMP-PVA hydrogel transformed into specific cylinders with a diameter of 1.5 cm. Prior to compression, the thickness of each sample was measured using calipers. Compression stress-strain data were acquired using an electrical universal testing machine (AGS-X-10 KN) with a 1000 N load cell. The microstructure of the hydrogel was characterized using scanning electron microscopy (SEM) with a ZEISS Supra 40 VP. Before characterization, the hydrogel samples underwent freeze-drying, exposing them to liquid nitrogen to induce internal fractures, followed by gold sputtering. The BGGITS was electrically connected

structure of the human skin and the *Hofmeister* effect, we proposed an iontronic pressure sensor with a gradient hydrogel structure (Figures 1 & S1). The BGGITS (Figure S2) incorporates a gradient hydrogel as the sensing material, with ATMP-PVA hydrogel serving as the dielectric layer. The oxygen-containing functional groups in ATMP molecules can form abundant hydrogen bonds with the PVA chains and coordinate with various ionic solutions. Using Au-PDMS as the electrodes, the intention is to replicate and surpass the extensive sensing capabilities of human skin. In this work, we introduced hierarchical micro-pyramids onto the gradient hydrogel structure (Figures S3-4), forming an iontronic interface with high compressibility. This interface allows stress delocalization to prevent signal saturation or non-linearity effectively. Specifically, the upper and lower hierarchical micro-pyramid electrodes make contact with the perception functional layer, creating a sandwich structure.

Construction and characterization of biomimetic gradient gel mimicking skin structure

In the *Hofmeister* series, three potential interactions may exist between the hydrating solvent and ATMP-PVA hydrogel: hydrating interaction, hydrophobic interaction, or bonding interaction. Hydration enhances the hydrogen bond network, yielding higher mechanical performance; hydrophobic interaction causes the contraction of the PVA main chains, resulting in increased mechanical stiffness, while bonding interaction induces chains relaxation, weakening the mechanical properties of the hydrogel. As shown in Figures 2A-B, the mechanical properties of ATMP-PVA hydrogel can be conveniently modulated using the *Hofmeister* effect, resulting in hydrogels with different moduli. The *Hofmeister* effect's control over the mechanical strength of the hydrogel can also be observed in the microstructure of the hydrogel polymer network (Figure S6). A softer hydrogel exhibits larger cavity sizes in the polymer network, as observed in I⁻ soaking. The harder the hydrogel, the smaller the cavity size in the polymer network, with a higher pore density, as seen in SO₄²⁻ soaking. SO₄²⁻ induces salt-out reactions, causing cross-linking of polymer chains, tightening the polymer network. I⁻ and CH₃COO⁻ ions trigger salt-in reactions, leading to localized degradation of the polymer and the formation of flexible cavities. The role of anions is more pronounced in the *Hofmeister* effect within gels, primarily due to their significant influence on water structure and their specificity and charge effects when interacting with gel components. However, cations also exhibit similar trends in the *Hofmeister* effect on gels, albeit less prominently (Figure S8).

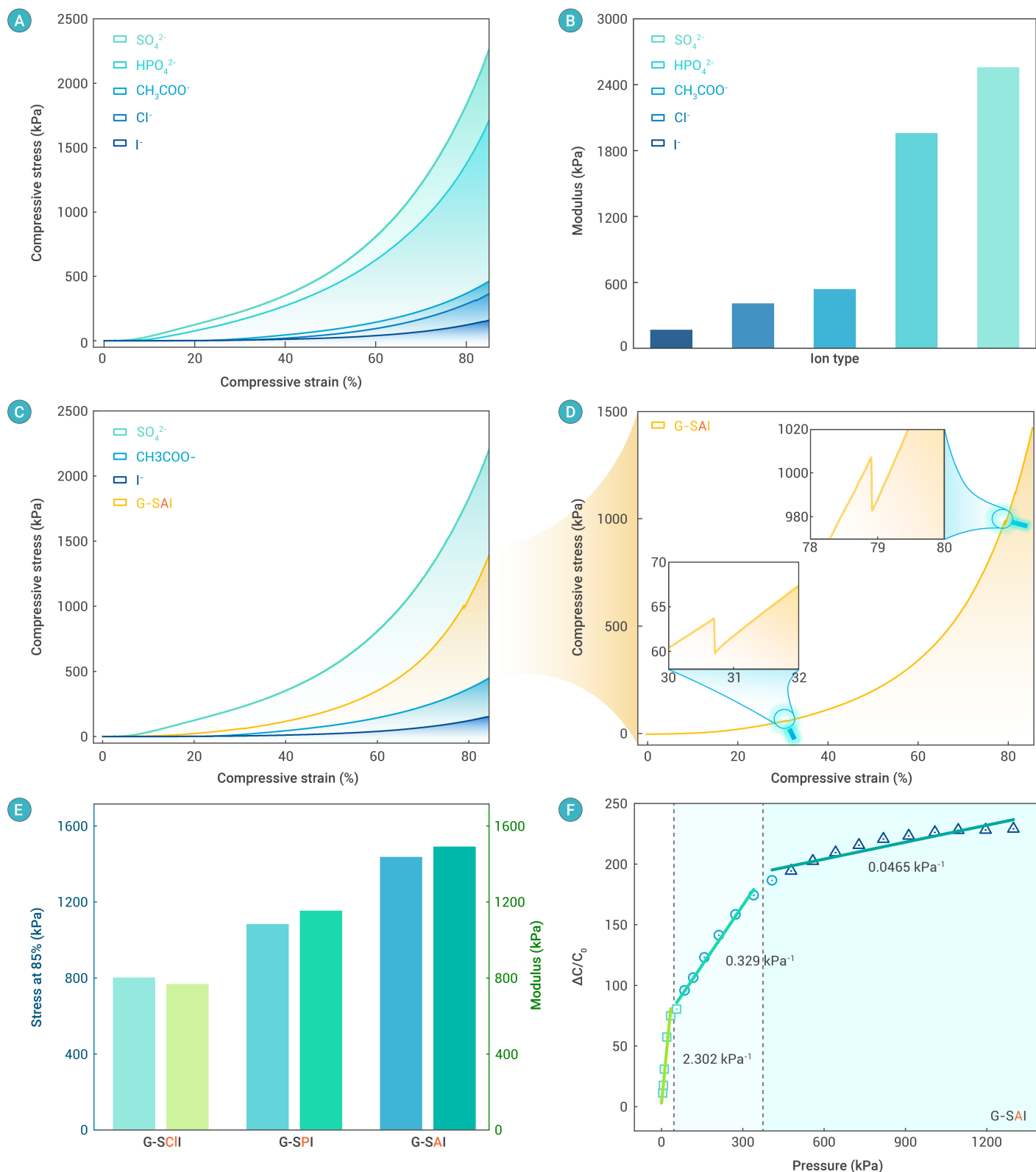


Figure 2. Characterization and Performance of Biomimetic Gradient Gel Mimicking Skin Structure (A) Stress-strain curves of the ATMP-PVA hydrogel soaked in different ionic solution. (B) Modulus of the ATMP-PVA hydrogel soaked in different ionic solution. (C-D) Stress-strain curve and its magnification in the case of CH_3COO^- in the middle layer. (E) Modulus of the different gradient gel structure combinations. Among them, G-SII is the gradient gel layer of SO_4^{2-} (S)-ATMP-PVA, Cl^- (Cl)-ATMP-PVA, I^- (I)-ATMP-PVA, from bottom to top; G-SPI is SO_4^{2-} (S)-ATMP-PVA, HPO_4^{2-} (P)-ATMP-PVA, I^- (I)-ATMP-PVA; and G-SAI is SO_4^{2-} (S)-ATMP-PVA, CH_3COO^- (A)-ATMP-PVA, I^- (I)-ATMP-PVA. (F) Normalized change in capacitance as a function of pressure up to 1200 kPa.

Following the convenient modulation of ATMP-PVA hydrogel using the Hofmeister effect, we selected the hydrogel layers with the maximum modulus (SO_4^{2-} -ATMP-PVA) and the minimum modulus (I^- -ATMP-PVA). The intermediate layer of the gradient hydrogel was chosen as Cl^- , CH_3COO^- , and

HPO_4^{2-} , and corresponding gradient hydrogel structures underwent compression testing to obtain stress-strain curves (Figure S9). As illustrated in Figure 2E, when the intermediate layer of the gradient hydrogel was CH_3COO^- , both the compressibility range and modulus reached their maximum values.

Simultaneously, the stress-strain curve and its magnified views revealed a double inflection point during the compression process (Figures 2C-D). This phenomenon can be explained as modulus adaptation, representing the key factor behind the maximum modulus and compressibility range. To showcase the advantages of this gradient structure, we subsequently evaluated the capacitance changes under pressure for hydrogels consisting of three layers of $\text{SO}_4^{2-}(\text{S})$ -ATMP-PVA, $\text{CH}_3\text{COO}^-(\text{A})$ -ATMP-PVA, $\text{I}^-(\text{I})$ -ATMP-PVA, and the gradient structure (S-A-I), as shown in Figures 2F & S10. The gradient structure (S-A-I) amalgamates the individual strengths of the three layers, exhibiting sensitivity comparable to the softest layer (I-ATMP-PVA) and a broad pressure detection range similar to SO_4^{2-} -ATMP-PVA. We believed that other gradient gel combinations may also exhibit skin-like properties, as gradient gel structures regulated by the *Hofmeister* effect are commonly present. When the range of gel properties regulated by the *Hofmeister* effect is sufficiently large, other matched gradient gel combinations have the potential to demonstrate skin-like characteristics.

Perception characteristics of BGGITS

The working schematics and equivalent circuit of BGGITS (Figure 3A). Massive positive and negative ions distribute in the ATMP-PVA hydrogel. Upon contact of the gradient hydrogel with the electrode in the iontronic sensor, an electrochemical double layer (EDL) forms at the iontronic interface, with the capacitance proportional to the interface contact area. Thus, in the iontronic sensor, the adjustment of linearity is straightforward-requiring consideration of a single parameter (A_c). In this context, the EDL interface of the gradient hydrogel possesses a variable contact area determined by the applied pressure. Notably, two microstructure interfaces (C_1 and C_2) respectively form two EDL capacitors. These two capacitors are connected in series through bulk resistance (R_s) and in parallel with the coupling capacitance (C_E) generated by the two electrodes. The measured capacitance can be defined as $C = C_E + 1/[(1/C_1) + (1/C_2)]$. Here, the value of C_2 is much larger than that of C_1 , as it contacts the hardest gel layer, primarily serving the function of capacitance supply. C_1 changes sensitively under loading, while C_E is significantly smaller than the EDL capacitance, thus can be neglected. Importantly, the microstructure deformation at the iontronic interface remains unsaturated within 800 kPa. Therefore, when the applied pressure is not high, C_1 is much smaller than C_2 , and the measured capacitance (C) is approximately equal to C_1 . However, as pressure continues to rise, the variation of C_1 decreases while C_2 continues to change, serving the function of capacitance supply, determined by the contact area at the iontronic interface. Finite Element Analysis (FEA) simulations below demonstrate a linear A_c - P relationship for the gradient hydrogel and micro-pyramids, suggesting that sensors employing this structure are expected to exhibit a linear response to applied pressure (Figure 4C). In summary, the synergistic effects of the designed structure and the signal enhancement provided by the iontronic interface confer upon the BGGITS a combination of high-sensitivity, linear-response, and broad-perceptual capabilities.

Sensitivity, signal linearity, and sensing range are critical parameters for the BGGITS in this work. Sensitivity of a pressure sensor is defined as $S = \frac{\delta(\Delta C/C_0)}{\delta p}$, where C_0 is the initial capacitance before loading, and ΔC is the change in capacitance when pressure is applied. High sensitivity is achieved when small changes in pressure result in significant capacitance variations ΔC , with the $\Delta C / C_0$ of iontronic pressure sensors reaching up to 10^6 due to the formation of the electric double layer (EDL) at the dielectric/electrode interface.^{36,37} Various configurations of iontronic pressure sensors based on the gradient hydrogel structure were studied for sensitivity changes and comparisons (Figure S11). The results revealed that when only the upper layer had micro-pyramid structures, whether they were at the same level or graded, the sensitivity was consistently low, and the response signal was nonlinear. However, the graded pyramid structure showed an advantage over the same-level pyramid structure, maintaining continuous contact between the micro-pyramid cone and the gel interface, ensuring increased contact area during pressure loading, and thus, capacitive response. When both upper and lower electrodes were structured with graded micro-pyramids, adjusting the stacking order of the gradient hydrogel resulted in three different combinations. Only when the gradient hydrogel layers were arranged

as I-ATMP-PVA, CH_3COO^- -ATMP-PVA, and SO_4^{2-} -ATMP-PVA, the BGGITS exhibited a linear response and similar sensitivity values in three repeated cases (Figure 3B) ($S_1 = 704.47 \text{ kPa}^{-1}$, $S_2 = 738.70 \text{ kPa}^{-1}$, $S_3 = 724.81 \text{ kPa}^{-1}$), with a sensing range of up to 800 kPa. Table S1 illustrates a comparison of the sensitivity and linear sensing range of our sensor with existing capacitive sensors. It is evident that most reported flexible capacitive sensors have low-sensitivity or a narrow-linear sensing range. For instance, Wang et al. reported a sensor with a linear sensing range of 0-1000 kPa,³⁸ which is impressive, but its sensitivity is only 40.12 kPa^{-1} . Iontronic pressure sensors can provide higher sensitivity. Recently, Bai et al. reported an iontronic pressure sensor with a graded built-in structure, achieving a sensitivity as high as 3302.9 kPa^{-1} , but its response signal is nonlinear.¹⁸ In contrast, the proposed biomimetic gradient gel interlayered iontronic sensor (BGGITS) achieves ultra-sensitive, linear, and wide-range pressure sensing. Its broad detection capability is attributed to the bio-gradient gel structure, which maintains ultra-high sensitivity across a wide linear range. This outstanding performance enables BGGITS to be applicable across various scenarios and presents a promising universal design concept for pressure sensors, with potential applications in fields such as electronic skin. Because the capacitance change of the iontronic sensor is related to the contact area, the observed sensitivity differences based on different combinations in the gradient hydrogel during experiments can be explained by finite element simulation of the device compression process, extracting changes in the contact area between the micro-pyramid and the gel.

Response speed is another crucial parameter for pressure sensors widely used to assess their dynamic performance.³⁹⁻⁴¹ Graded micro-pyramids are introduced to shorten the response and relaxation time, as microstructures can rapidly store and release energy for elastic recovery. In this work, the BGGITS with graded micro-pyramid electrodes on both upper and lower layers was introduced, which can effectively shorten the response relaxation time. When subjected to a pressure of $\sim 50 \text{ Pa}$, our sensor exhibited a rapid response, with a response time of 30 ms (Figure 3C), nearly matching the response time of human skin (30-50 ms). The repeatability of the BGGITS under different pressures (0-500 kPa) was investigated (Figure 3D). The output curves at various pressures showed that the capacitance gradually increased with increasing pressure, and after loading and unloading for 5 cycles, the capacitance curve remained stable, indicating excellent repeatability. Owing to the design of the layered pyramid structure (with varying pyramid heights), the BGGITS maintained a linear capacitance-pressure response under different initial pressure backgrounds. When the initial pressure ($P_0 = 0, 10 \text{ kPa}$) was first applied to the BGGITS, it exhibited a noticeable response between 50 and 200 Pa pressures (Figures 3E-F). Mechanical durability is significant for the application of flexible pressure sensors. The BGGITS underwent repetitive compression-release cycles under a pressure of 50 kPa for 250 cycles, and throughout the entire cyclic testing process, the sensor exhibited no apparent drift or fluctuation (Figure 3G). In summary, BGGITS possesses ultra-high sensitivity, a linear wide working pressure range, short response time, and high mechanical durability. These characteristics make it well-suited for practical applications in various scenarios.

Principles of BGGITS design and the perception mechanism

To further analyze the sensing performance of the sensor, finite element simulations using ABAQUS software were conducted to investigate the deformation process of different gradient gel combinations and the assembly of graded micro-pyramids under various pressures. As shown in Figures 4A & S12, with the gradual increase in pressure, the pores transformed from a large diameter to a small diameter. Specifically, at lower pressures, significant deformation occurred in the large-diameter portion, while the application of higher pressure caused substantial deformation in the middle and small-diameter regions, confirming the gradient compression characteristics of the gradient gel structure. Additionally, when a certain pressure is applied to the device, the contact interface between the hierarchical micro-pyramid electrode and the gel forms a double electric layer. The unique microstructure of the graded micro-pyramid electrode ensures that, during the pressure loading process, pyramids of different heights maintain continuous contact with the gel. This helps in maintaining a stable increase in the electrode-gel interface contact area, preventing a decrease in BGGITS sensi-

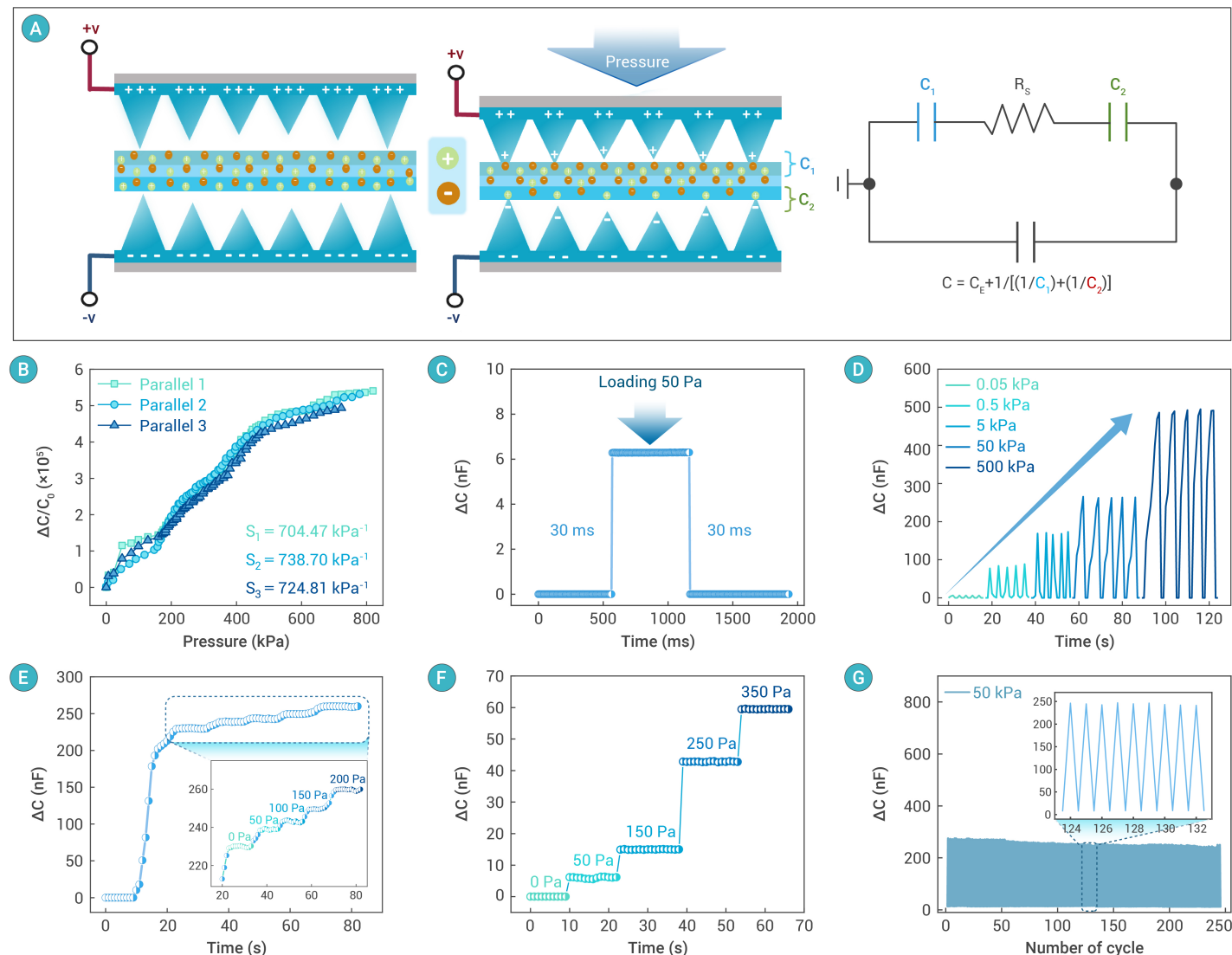


Figure 3. Perception performance of BGGITS (A) Device schematic and circuit diagram of the BGGITS. (B) Normalized change in capacitance as a function of pressure up to 800 kPa. (C) Response and relaxation time when loading a pressure of ~50 Pa and release. (D) Capacitance of the sensor under different pressures (50 Pa, 500 Pa, 5 kPa, 50 kPa and 500 kPa). (E-F) The resolution is about 50 Pa as the reference pressure of 0, 10 kPa, respectively. (G) Working stability test over 250 cycles with 50 kPa pressure loading or releasing.

tivity despite an increase in external pressure stimulus (Figure 4B). Furthermore, through the post-processing module, the calculation of the total contact area variation with pressure confirms a broader-linear response range. This indicates that within the range of 0–800 kPa, the contact area between the dual graded micro-pyramid electrode and the gradient gel exhibits a linear relationship with pressure (Figure 4C). This further validates enhanced sensitivity and an expanded linear pressure response range occur only when the three gradient gel combinations, namely I^- -ATMP-PVA, CH_3COO^- -ATMP-PVA, and SO_4^{2-} -ATMP-PVA, are assembled with the dual-graded micro-pyramid electrode.

The combined design of the gradient gel and dual micro-pyramids enables BGGITS to achieve both a broad-linear response and ultra-sensitivity. Furthermore, we conducted finite element simulation analysis on alternative combinations of gradient gels to explore the deformation process under different pressures. This further elucidated the impact of gel stacking order on the linear range (Figure S13–14). Results indicate that when stacked from top to bottom as I^- -ATMP-PVA, SO_4^{2-} -ATMP-PVA, CH_3COO^- -ATMP-PVA, and CH_3COO^- -ATMP-PVA, I^- -ATMP-PVA, SO_4^{2-} -ATMP-PVA, the compression deformation process remains the same, but the extracted interface contact area shows a nonlinear relationship with pressure. This phenomenon is primarily attributed to the placement of the hardest gel layer, SO_4^{2-} -ATMP-PVA, in the middle position, where both upper and lower micro-pyramid elec-

trodes initially contact the two softer gel layers, leading to a substantial increase in the initial contact area. However, as the pressure reaches a certain value, stress gradually shifts to the middle layer, causing a sharp reduction in the interface contact area, resulting in a nonlinear response signal (Figure S13). In contrast, when the softer gel layer is placed at the top and the softest layer is in the middle, the finite element simulation graph indicates that, during the compression process, when the pressure reaches a certain value, stress begins to transfer to the middle softest layer, causing a sudden significant decrease in modulus, leading to an increased contact area. This scenario demonstrates a nonlinear relationship between the interface contact area and pressure (Figure S14). Only when the gradient gel combination from top to bottom is I^- -ATMP-PVA, CH_3COO^- -ATMP-PVA, SO_4^{2-} -ATMP-PVA, with a gradient increase in modulus across the three layers, does the combination exhibit a linear relationship between the two interface contact areas and pressure.

Application of BGGITS with ultra-sensitivity perception resolution

The key advantages of BGGITS, based on the gradient gel structure, lie in its linear high-sensitivity and excellent pressure resolution across a wide-pressure range. Existing capacitive pressure sensors (CPS) or electronic skins with surface microstructure dielectrics typically exhibit low-sensitivity or saturated responses above 50 kPa, leading to anticipated low-pressure reso-

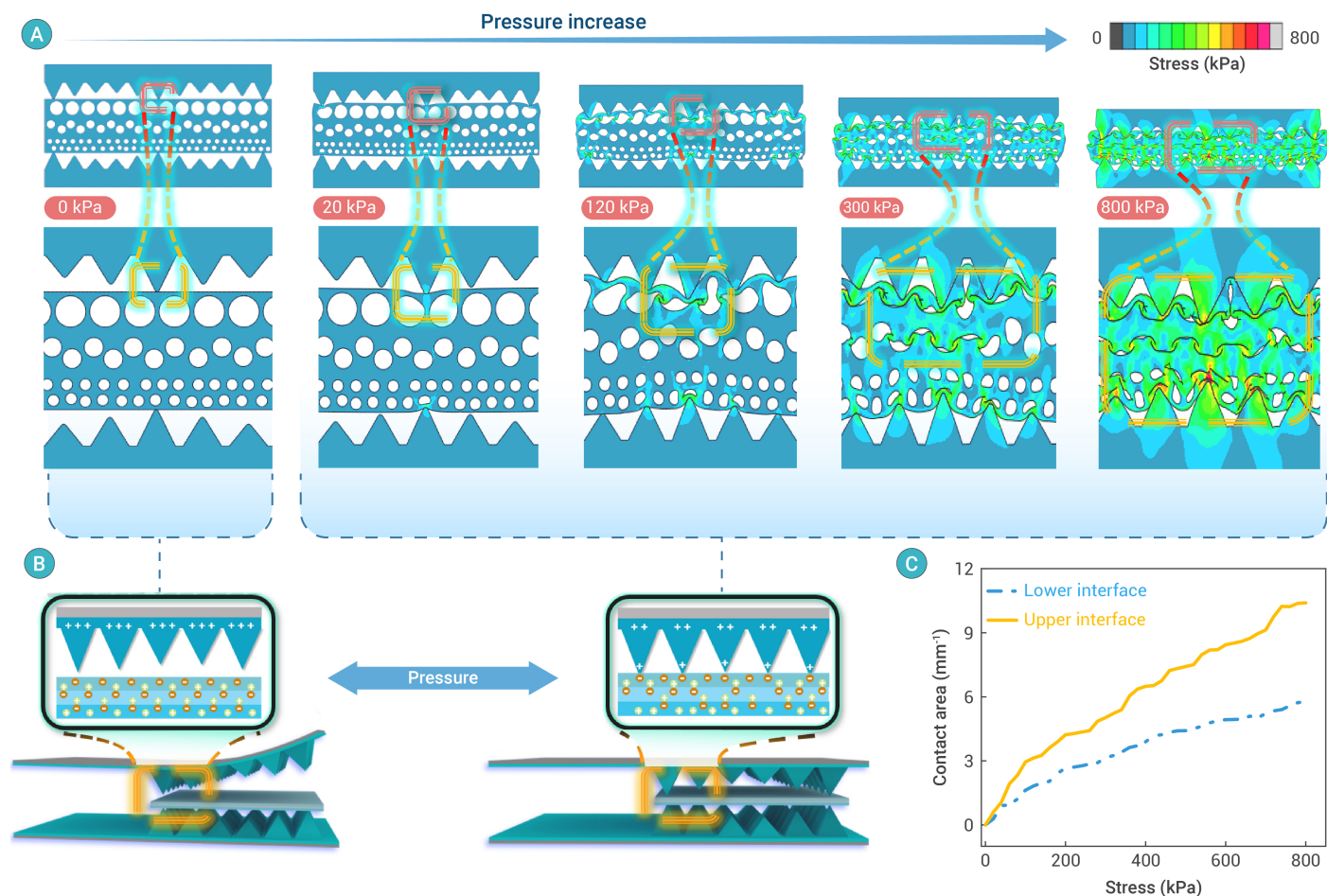


Figure 4. Working mechanism of BGGITS based pressure sensor (A) Finite element simulation of the iontronic sensor based on the gradient hydrogel structure using ABAQUS software. (B) Schematic illustration of the corresponding microscale compression process in the finite element simulation. (C) Variation curve of the contact area with stress.

lution.^{42–45} However, an ideal flexible pressure sensor should not only operate with precision under low-pressure but also accurately detect variations in pressure under high-pressure conditions. The BGGITS is applied in reenactments of two scenarios from the “Journey to the West” story: *Scenario 1* involves Tang Monk rescuing Sun Wukong trapped under the Wuzhi Mountain, and *Scenario 2* features Sun Wukong saving Tang Monk captured by the White Bone Demon (Figure 5).

To showcase the outstanding performance of BGGITS during scenario demonstrations, we aim to rely solely on changes in capacitance to identify the rescuer of Sun Wukong, confirm the success of Sun Wukong's rescue, determine who is rescuing Tang Monk, and verify the repulsion of the White Bone Demon. Initially, it is crucial to record the mass of each moving object along with its corresponding capacitance changes (Table S2).

As illustrated in Figures 5A–D, each moving object exhibits distinctive capacitance changes. In *Scenario 1*, showcasing Tang Monk rescuing Sun Wukong under the Wuzhi Mountain, Figure 5E reveals that when Tang Monk approaches Sun Wukong under the mountain, the capacitance increases by 150.38 nF, aligning with the previously recorded capacitance changes for the Tang Monk character. As the story progresses, and Sun Wukong is successfully rescued, resulting in the removal of the Wuzhi Mountain, the capacitance decreases by 172.09 nF, corresponding to the recorded capacitance change for the Wuzhi Mountain. In the *Scenario 2* demonstration, changes in capacitance indicate Sun Wukong's intervention to rescue Tang Monk. Subsequently, a decrease in capacitance corresponds to the White Bone Demon's capacitance change, signifying Sun Wukong's victory over the demon and the successful rescue. In both story scenarios, by recording the respective capacitance changes, we can identify which object is in motion. The combination of the gradient gel structure features and dielectric properties ultimately results in our device exhibiting outstanding perception behav-

ior within a sufficiently large pressure range. At the same time, we supplement the capacitive response of the sensor at different masses (Figure S15). It can be seen that the capacitance responds linearly when the mass changes from 1.5g to 2000g, and the weight of the characters in our Journey to the West story is also within the mass range of 1.5g to 2000g. we added the experiment that objects of different masses can be identified under different base weights (Figure S16). The capacitance change values corresponding to objects of different masses are measured in advance (Table S3). Then, when the base weights are 0, 1000, and 2000 g, the mass changes can be accurately identified only by the capacitance change values. This further demonstrates the sensor's recognition capabilities.

DISCUSSION

In summary, we proposed a biomimetic design based on the gradient elastic modulus of the skin, regulated by the *Hofmeister* effect, to simultaneously achieve ultra-sensitive, linear, and wide-range pressure perception. The interface between the micro-pyramid structure and the gradient gel forms an EDL, exhibiting excellent capacitive characteristics with a significant capacitance response under specific pressure conditions. The linear response is mainly attributed to the gradient micro-pyramids of different heights. As external pressure increases, pyramids of varying heights sequentially contact the gel, ensuring a stable increase in the electrode-gel interface contact area. This innovative design prevents a decrease in BGGITS sensitivity with increasing external pressure. Finally, the wide detection capability is primarily credited to the biomimetic gradient gel structure, maintaining ultra-high sensitivity of over 700 kPa⁻¹ within an exceptionally broad-linear range of up to 800 kPa. The results show a response time of 30 ms (compared to the human skin's tactile response time of 30–50 ms) and sustained high stability over 250 cycles of loading/unloading at a peak pressure of 50 kPa. Finite element

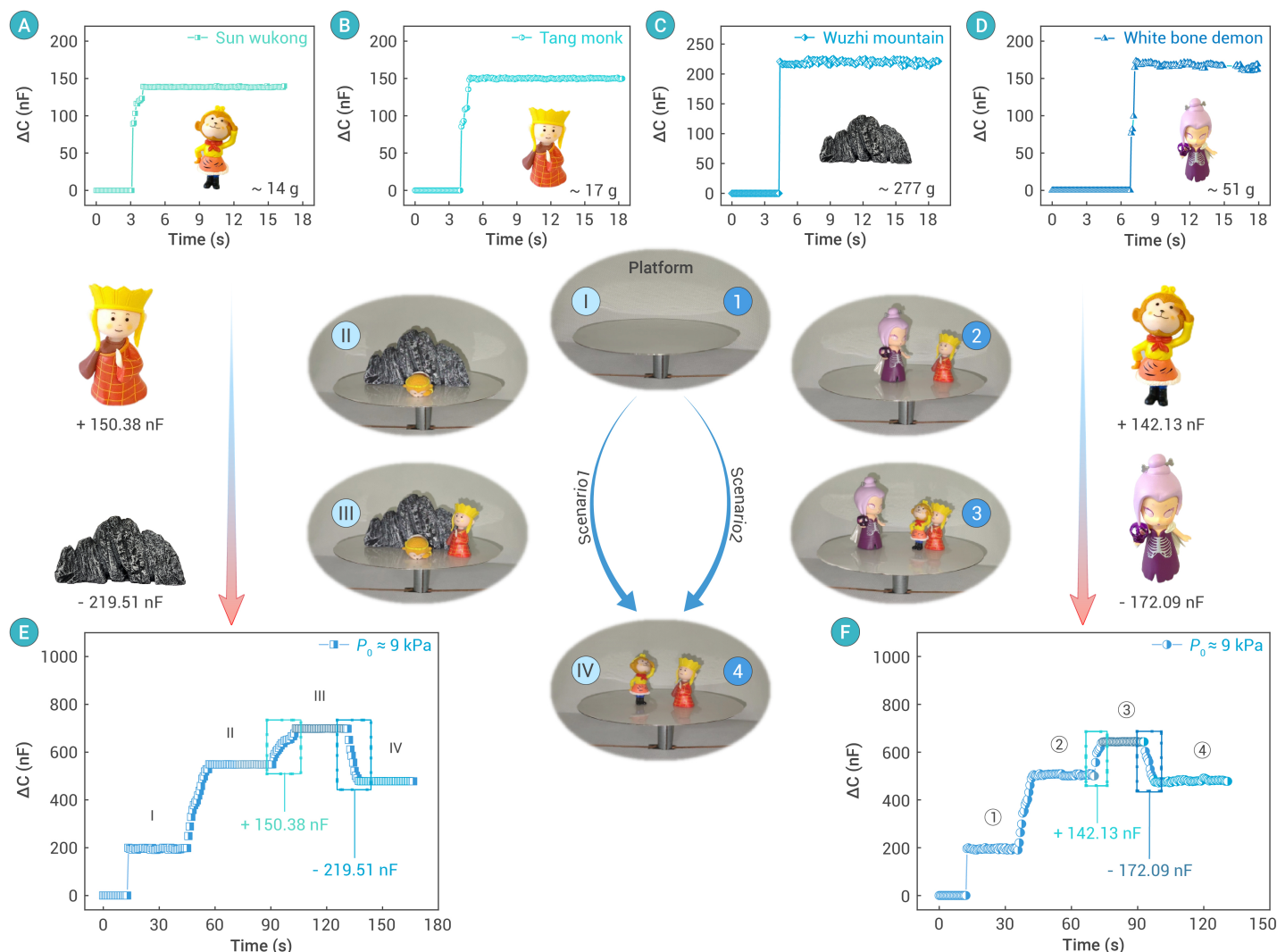


Figure 5. The Scenario reproduction from "Journey to the West" highlights the exceptional perception capability of BGGITS (A-D) The capacitance changes of Sun Wukong, Tang Monk, Wuzhi mountain, and White Bone Demon, respectively. (E) The capacitance changes diagram of Tang Monk rescued by Sun Wukong who was trapped under the Wuzhi mountain. (F) The capacitance changes diagram of Sun Wukong rescued by the White Bone Demon. (I-IV) A demonstration of the Tang Monk rescued Sun Wukong who was trapped under the Wuzhi mountain (Scenario1). (①-④) A demonstration of Sun Wukong rescued Tang Monk captured by White bone Demon (Scenario 2).

simulations verify the mechanism between the contact area of the BGGITS and interface stress. Furthermore, we demonstrated the BGGITS's ability to accurately identify scenario from the "Journey to the West" story solely through changes in capacitance values. We envision that the combination of this biomimetic gradient gel structure and iontronic sensing technology could offer a universal design approach for other pressure sensors requiring linear ultra-high sensitivity across a wide-pressure range. Additionally, we believe that BGGITS-based technology could find extensive applications in electronic skins for health monitoring and tactile perception.

REFERENCES

- Boutry, C.M., Negre, M., Jorda, M., et al. (2018). A hierarchically patterned, bioinspired e-skin able to detect the direction of applied pressure for robotics. *Sci. Robot.* **3**: eaau6914. DOI: 10.1126/scirobotics.aau6914.
- Chortos, A. and Bao, Z. (2014). Skin-inspired electronic devices. *Mater. Today* **17**: 321-331. DOI: 10.1016/j.mattod.2014.05.006.
- Li, X., Fan, Y.J., Li, H.Y., et al. (2020). Ultracomfortable hierarchical nanonetwork for highly sensitive pressure sensor. *ACS Nano* **14**: 9605-9612. DOI: 10.1021/acsnano.9b10230.
- Sundaram, S., Kellnhofer, P., Li, Y., et al. (2019). Learning the signatures of the human grasp using a scalable tactile glove. *Nature* **569**: 698-702. DOI: 10.1038/s41586-019-1234-z.
- Yang, J.C., Mun, J., Kwon, S.Y., et al. (2019). Electronic skin: Recent progress and future prospects for skin - attachable devices for health monitoring, robotics, and prosthetics. *Adv. Mater.* **31**: 1904765. DOI: 10.1002/adma.201970337.
- Huang, Y., Fan, X., Chen, S.C., et al. (2019). Emerging technologies of flexible pressure sensors: Materials, modeling, devices, and manufacturing. *Adv. Funct. Mater.* **29**: 1808509. DOI: 10.1002/adfm.201808509.
- Chen, W.P., Zhai, L.X., Zhang, S.L., et al. (2023). Cascade-heterogated biphasic gel iontronics for electronic-to-multi-ionic signal transmission. *Science* **382**: 559-565. DOI: 10.1126/science.adg0059.
- Zhao, Z.G., Cao, Z.Q., Wu, Z.X., et al. (2024). Bicontinuous vitrimer heterogels with wide-span switchable stiffness-gated iontronic coordination. *Sci. Adv.* **10**: ead12737. DOI: 10.1126/sciadv.adl2737.
- Hammock, M.L., Chortos, A., Tee, B.C.K., et al. (2013). 25th anniversary article: The evolution of electronic skin (e - skin): A brief history, design considerations, and recent progress. *Adv. Mater.* **25**: 5997-6038. DOI: 10.1002/adma.201302240.
- Tee, B.C., Wang, C., Allen, R., et al. (2012). An electrically and mechanically self-healing composite with pressure- and flexion-sensitive properties for electronic skin applications. *Nat. Nanotechnol.* **7**: 825-832. DOI: 10.1038/nnano.2012.192.
- Mannsfeld, S.C., Tee, B.C., Stoltenberg, R.M., et al. (2010). Highly sensitive flexible pressure sensors with microstructured rubber dielectric layers. *Nat. Mater.* **9**: 859-864. DOI: 10.1038/nmat2834.
- Persano, L., Dagdeviren, C., Su, Y., et al. (2013). High performance piezoelectric devices based on aligned arrays of nanofibers of poly (vinylidene fluoride-co-trifluoroethylene). *Nat. Commun.* **4**: 1633. DOI: 10.1038/ncomms2639.
- Liu, Z., Li, H., Shi, B., et al. (2019). Wearable and implantable triboelectric nanogenerators. *Adv. Funct. Mater.* **29**: 1808820. DOI: 10.1002/adfm.201808820.
- Ramuz, M., Tee, B.C.K., Tok, J.B.H., et al. (2012). Transparent, optical, pressure - sensitive artificial skin for large - area stretchable electronics. *Adv. Mater.* **24**: 3223-3227. DOI: 10.1002/adma.201200523.
- Wan, Y., Qiu, Z., Huang, J., et al. (2018). Natural plant materials as dielectric layer for

- highly sensitive flexible electronic skin. *Small* **14**: 1801657. DOI: 10.1002/sml.201801657.
16. Luo, Z., Chen, J., Zhu, Z., et al. (2021). High-resolution and high-sensitivity flexible capacitive pressure sensors enhanced by a transferable electrode array and a micropillar–PVDF film. *ACS Appl. Mater. Interfaces* **13**: 7635–7649. DOI: 10.1021/acsami.0c23042.
 17. Baek, S., Jang, H., Kim, S.Y., et al. (2017). Flexible piezocapacitive sensors based on wrinkled microstructures: Toward low-cost fabrication of pressure sensors over large areas. *RSC Adv.* **7**: 39420–39426. DOI: 10.1039/C7RA06997A.
 18. Liu, F., Han, F., Ling, L., et al. (2018). An omni - healable and highly sensitive capacitive pressure sensor with microarray structure. *Chem-Eur. J.* **24**: 16823–16832. DOI: 10.1002/chem.201803369.
 19. Luo, Y., Shao, J., Chen, S., et al. (2019). Flexible capacitive pressure sensor enhanced by tilted micropillar arrays. *ACS Appl. Mater. Interfaces* **11**: 17796–17803. DOI: 10.1021/acsami.9b03718.
 20. Bai, N., Wang, L., Wang, Q., et al. (2020). Graded intrafillable architecture-based iontronic pressure sensor with ultra-broad-range high sensitivity. *Nat. Commun.* **11**: 209. DOI: 10.1038/s41467-019-14054-9.
 21. Chang, Y., Wang, L., Li, R., et al. (2021). Interfacial iontronic sensing: First decade of interfacial iontronic sensing: From droplet sensors to artificial skins. *Adv. Mater.* **33**: 2170050. DOI: 10.1002/adma.202170050.
 22. Liu, Y., Zhao, C., Xiong, Y., et al. (2023). Versatile ion-gel fibrous membrane for energy-harvesting iontronic skin. *Adv. Funct. Mater.* **33**: 2303723. DOI: 10.1002/adfm.202303723.
 23. Chang, Y., Wang, L., Li, R., et al. (2021). First decade of interfacial iontronic sensing: From droplet sensors to artificial skins. *Adv. Mater.* **33**: 2003464. DOI: 10.1002/adma.202003464.
 24. Lu, P., Wang, L., Zhu, P., et al. (2021). Iontronic pressure sensor with high sensitivity and linear response over a wide pressure range based on soft micropillared electrodes. *Sci. Bull.* **66**: 1091–1100. DOI: 10.1016/j.scib.2021.02.019.
 25. Nie, B., Li, R., Brandt, J.D., et al. (2014). Iontronic microdroplet array for flexible ultrasensitive tactile sensing. *Lab. Chip* **14**: 1107–1116. DOI: 10.1039/C3LC50994J.
 26. Nie, B., Li, R., Cao, J., et al. (2015). Flexible transparent iontronic film for interfacial capacitive pressure sensing. *Adv. Mater.* **27**: 6055–6062. DOI: 10.1002/adma.201502556.
 27. Qiu, Z., Wan, Y., Zhou, W., et al. (2018). Ionic skin with biomimetic dielectric layer templated from calathea zebrine leaf. *Adv. Funct. Mater.* **28**: 1802343. DOI: 10.1002/adfm.201802343.
 28. Zhu, Z., Li, R., and Pan, T. (2018). Imperceptible epidermal–iontronic interface for wearable sensing. *Adv. Mater.* **30**: 1705122. DOI: 10.1002/adma.201705122.
 29. He, Q., Huang, Y., and Wang, S. (2018). Hofmeister effect - assisted one step fabrication of ductile and strong gelatin hydrogels. *Adv. Funct. Mater.* **28**: 1705069. DOI: 10.1002/adfm.201705069.
 30. Dandekar, K., Raju, B.I., and Srinivasan, M.A. (2003). 3-D finite-element models of human and monkey fingertips to investigate the mechanics of tactile sense. *J. Biomech. Eng.* **125**: 682–691. DOI: 10.1115/1.1613673.
 31. Quindlen-Hotek, J.C. and Barocas, V.H. (2018). A finite-element model of mechanosensation by a Pacinian corpuscle cluster in human skin. *Biomech. Model. Mechan.* **17**: 1053–1067. DOI: 10.1007/s10237-018-1011-1.
 32. Zhang, M., Yang, Y., Li, M., et al. (2023). Toughening double-network hydrogels by polyelectrolytes. *Adv. Mater.* **35**: 2301551. DOI: 10.1002/adma.202301551.
 33. Jaspers, M., Rowan, A.E., and Kowar, P.H. (2015). Tuning hydrogel mechanics using the hofmeister effect. *Adv. Funct. Mater.* **25**: 6503–6510. DOI: 10.1002/adfm.201502241.
 34. Shen, B., Peng, W., Su, B., et al. (2022). Elastic–electric coefficient-sensitive hydrogel sensors toward sweat detection. *Anal. Chem.* **94**: 1910–1917. DOI: 10.1021/acs.analchem.1c05363.
 35. Lai, Y.C., Deng, J., Liu, R., et al. (2018). Actively perceiving and responsive soft robots enabled by self - powered, highly extensible, and highly sensitive triboelectric proximity - and pressure - sensing skins. *Adv. Mater.* **30**: 1801114. DOI: 10.1002/adma.201801114.
 36. Yuan, Y., Liu, B., Adibeig, M. R., et al. (2024). Microstructured polyelectrolyte elastomer-based iontronic sensors with high sensitivities and excellent stability for artificial skins. *Adv. Mater.* **36**: 2310429. DOI: 10.1002/adma.202310429.
 37. Deng, S.H., Li, Y., Li, S.Z., et al. (2024). A multifunctional flexible sensor based on PI-MXene/SrTiO₃ hybrid aerogel for tactile perception. *The Innovation* **5**: 100596. DOI: 10.1016/j.xinn.2024.100596.
 38. Wang, S., Zhang, Z., Yang, B., et al. (2023). High sensitivity tactile sensors with ultrabroad linear range based on gradient hybrid structure for gesture recognition and precise grasping. *Chem. Eng. J.* **457**: 141136. DOI: 10.1016/j.cej.2022.141136.
 39. Boutry, C.M., Nguyen, A., Lawal, Q.O., et al. (2015). A sensitive and biodegradable pressure sensor array for cardiovascular monitoring. *Adv. Mater.* **27**: 6954–6961. DOI: 10.1002/adma.201502535.
 40. Liu, M., Pu, X., Jiang, C., et al. (2017). Large-area all-textile pressure sensors for monitoring human motion and physiological signals. *Adv. Mater.* **29**: 1703700. DOI: 10.1002/adma.201703700.
 41. Huang, C.-B., Witomska, S., Aliprandi, A., et al. (2019). Molecule–graphene hybrid materials with tunable mechanoresponse: Highly sensitive pressure sensors for health monitoring. *Adv. Mater.* **31**: 1804600. DOI: 10.1002/adma.201804600.
 42. Luo, S., Zhou, X., Tang, X.Y., et al. (2020). Microconformal electrode-dielectric integration for flexible ultrasensitive robotic tactile sensing. *Nano Energy* **80**: 2211–2855. DOI: 10.1016/j.nanoen.2020.105580.
 43. Shen, Z., Zhu, X., Majidi, C., et al. (2021). Cutaneous ionogel mechanoreceptors for soft machines, physiological sensing, and amputee prostheses. *Adv. Mater.* **33**: 2102069. DOI: 10.1002/adma.202102069.
 44. Lee, D., Lee, H., Jeong, Y., et al. (2016). Highly sensitive, transparent, and durable pressure sensors based on sea-urchin shaped metal nanoparticles. *Adv. Mater.* **28**: 9364–9369. DOI: 10.1002/adma.201603526.
 45. Ha, K.-H., Zhang, W., Jang, H., et al. (2021). Highly sensitive capacitive pressure sensors over a wide pressure range enabled by the hybrid responses of a highly porous nanocomposite. *Adv. Mater.* **33**: 2103320. DOI: 10.1002/adma.202103320.

FUNDING AND ACKNOWLEDGMENTS

This work is supported by the National Natural Science Foundation of China (21874056 and 52003103), the National Key R&D Program of China (2016YFC1100502), the Key research and development project of Guangdong Province (Grant No.2023A1515011031). The funders had no role in study design, data collection and analysis, decision to publish or preparation of the manuscript.

AUTHOR CONTRIBUTIONS

Z.H. and F.L. conceived and designed the experiments. Z.H., Y.C., J.L., J.Q., and F.L. performed the measurements and experiments. Z.H., Y.C., J.L., J.Q. and F.L. contributed to the data analysis. Z.H. and F.L. wrote the manuscript. All authors reviewed and commented on the manuscript.

DECLARATION OF INTERESTS

The authors declare no competing interests.

DATA AND CODE AVAILABILITY

All data and code are available from the corresponding authors upon reasonable request.

SUPPLEMENTAL INFORMATION

It can be found online at <https://doi.org/10.59717/j.xinn-mater.2024.100078>