Wet-Adhesive Multifunctional Hydrogel with Anti-swelling and a Skin-Seamless Interface for Underwater Electrophysiological Monitoring and Communication

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ABSTRACT: A stable and seamless adhesion between the human skin and the hydrogel-based electronic skin is necessary for accurate sensing and human health monitoring in aquatic environments. Despite achieving significant progress in this field, it remains a great challenge to design skin-interfaced conductive hydrogels with high electrical conductivity, stability, and seamless underwater adhesion to skin. Herein, a skin-inspired conductive multifunctional hydrogel is proposed, which has a wet-adhesive/hydrophilic and a non-adhesive/hydrophobic bilayer structure. The hydrogel shows high stretchability (∼2400%) and an ultra-low modulus (4.5 kPa), which facilitate the conformal and seamless attachment of the hydrogel to the skin with reduced motion artifacts. Owing to synergistic physical and chemical interactions, this hydrogel can achieve reliable underwater adhesion and display remarkable underwater adhesion strength (388.1 kPa) to porcine skin. In addition, MXene has been employed to obtain high electrical conductivity, create a route for stable electron transport, and reinforce mechanical properties. The hydrogel also possesses self-healing ability, a low swelling ratio (∼3.8%), biocompatibility, and specific adhesion to biological tissues in water. Facilitated with these advantages, the hydrogel-based electrodes achieve reliable electrophysiological signal detection in both air and wet conditions and demonstrate a higher signal-to-noise ratio (28.3 dB) than that of commercial Ag/AgCl gel electrodes (18.5 dB). Also, the hydrogel can be utilized as a strain sensor with high sensitivity for underwater communication. This multifunctional hydrogel improves the stability of the skin–hydrogel interface in aquatic environments and is expected to be promising for the next-generation bio-integrated electronics.

KEYWORDS: conductive hydrogel, skin-interfaced sensor, skin–sensor interface, seamless adhesion, wet adhesion

INTRODUCTION

The ability for wet/underwater adhesion is essential for skin-interfaced hydrogels owing to the inevitable exposure to aqueous environments (e.g., sweating, raining, bathing, and swimming), notably for the monitoring of swimmers’ body motions, and it is of great value to detect real-time bioelectrical signals underwater for safety of underwater operations. For instance, heart attacks have risen to the second ranking cause of death for divers, which makes aquatic electrocardiogram (ECG) monitoring crucial before a heart attack occurs. Nevertheless, conventional adhesive hydrogels that are applied in a dry environment are not suitable for adhesion in these aquatic conditions because water prevents direct contact between the sensor and the skin. Moreover, because of the instability of the polymer backbone and the unrestrained diffusion of conductive ions in aqueous environments, it ultimately leads to deterioration in the mechanical and electrical performances of hydrogels (e.g., structural collapse,
swelling, and electroconductive degradation). Despite that a number of hydrogels designed for biomedical applications (e.g., wound dressing and hemostatic agents) with wet/underwater adhesion capability have been reported, most of their electrical conductivity, especially long-term stability, has not been fully explored. To achieve reliable long-term physiological signal acquisition in aquatic conditions, it becomes a prerequisite to design and synthesize novel hydrogels with high electrical conductivity, long-term stable underwater adhesion, and conformal contact with skin.

In general, there remain lots of obstacles to achieve long-term stable sensing in aquatic conditions. First, most reported hydrogels can hardly form a seamless or conformal adhesion with the texturized skin, which will cause motion artifacts and signal deterioration. This is because these hydrogels still have a large modulus (tens of kPa to several MPa) and a compliance mismatch with the skin (<100 kPa), which are primarily attributed to their high internal crosslink density, especially with the usage of chemical cross-linkers. Second, wet adhesion mainly based on chemical interaction mechanisms is usually not suitable for long-lasting stable biosignal acquisition, especially hydrogels based on catechol groups which are susceptible to oxidation, leading to the decrease of adhesion strength to the skin with time. Consequently, the instability in the adhesion at the skin–hydrogel interface hinders reliable sensing. It is believed that physical adhesion mechanisms (e.g., mechanical interlocking and topological entanglements) are more stable than the chemical interactions owing to less susceptibility with time.

Third, most reported hydrogels may suffer from unstable conductive pathways and low electrical conductivity (<1 S m⁻¹). It may be ascribed to ions and molecules of hydrogels being exchanged with the surrounding aquatic environment (i.e., ion diffusion and leakage from hydrogels, various ions in the aquatic environment reversely penetrating the hydrogel, etc.), leading to unstable conductivity of these hydrogels. Moreover, ions in conductive hydrogels that are employed as crosslinkers may fail to be electrically sensitive. In contrast, the composite strategy that commonly involves the addition of conductive nanomaterials has controllable and superb electron conductivity and no potential cytotoxic unreactive conductive polymer monomers. Therefore, it is still a challenge to achieve a skin-interfaced conductive hydrogel with long-term stable seamless

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**Figure 1.** Design strategy for the multifunctional DLH hydrogel. (a) Schematic illustration of the construction of DLH hydrogel. (b) Multifunction of the hydrogel, including stretchability, biocompatibility, self-healing, anti-swelling, conductivity, seamless and underwater specific adhesion, and waterproof. (c) Multiple reversible non-covalent interactions within the PCAM.
Inspired by the human skin with hydrophilic dermis and hydrophobic epidermis (Janus structure), we propose a conductive hydrogel with a wet-adhesive/hydrophilic and a non-adhesive/hydrophobic bilayer structure in this work. The hydrogel shows an elastic modulus (4.5 kPa) similar to those of living tissues, due to which it can seamlessly and conformally adhere to tissues with minimum contact damage caused by mechanical mismatches between hydrogels and soft tissues. Besides, the hydrogel has a remarkable adhesion strength (388.1 kPa) through synergistic chemical and physical interactions, including hydrogen bonds, electrostatic attractions, and physical entanglements. To achieve stable and high electrical conductivity, MXene has been employed not only to create a route for stable electron transport but also to reinforce the mechanical properties of the hydrogel as a physical crosslinker. Moreover, the outer hydrophobic coating of the hydrogel presents water resistance to daily liquids and isolates the hydrogel from direct contact with the surrounding environment, avoiding possible electrical conductivity changes.

adhesion to skin in aquatic conditions for reliable and highly accurate biosignal sensing.

![Figure 2. Characterization and mechanical properties of hydrogels. (a) The tensile stress–strain curves of the PCAM with varied MXene proportions. (b) Rheological data of PCAM samples with different contents of MXene. (c) SEM image and EDS mapping of the PCAM. Initial (d) and stretching (d’) states of the M100 hydrogel. (e) SEM images of the DLH’s cross-section and hydrophobic layer’s surface (inset), showing a seamless interface and rough surface. (f) Hydrophobic surface of the DLH has the waterproof capability to various liquids, including water, tea, coffee, and milk. (g) Hydrophobic performance of the DLH under 250% tensile strain. (h) FTIR spectra of the PCAM hydrogel, hydrophobic hydrogel.](https://doi.org/10.1021/acsami.2c21595)

**RESULTS AND DISCUSSION**

**Design Strategy, Mechanical Properties, and Hydrophobic Performance of the Double-Layered Structure Hydrogel.** Inspired by the Janus structure of skin that consists of hydrophilic dermis and hydrophobic epidermis (Figure 1a), we designed a double-layered structure hydrogel (DLH) with multifunction: (i) a hydrophilic bio-adhesive layer composed of PAA−CHI−Al-MXene hydrogel (PCAM), (ii) a hydrophobic non-adhesive layer composed of stearic acid (STA) modified PCAM hydrogel. Adhesive PCAM was first synthesized by one-pot free-radical polymerization, where diphenyl(2,4,6-trimethylbenzoyl)phosphine oxide (TPO) was used as an initiator. It should be noted that no chemical crosslinker agent was added to effectively dissipate energy and enlarge the stretchability. A hydrophobic coating was employed to encapsulate PCAM by surface modification with STA, which has a hydrophobic long-chain alkyl end. By immersing PCAM into the APTES/EA, STA/EA solution and silicone oil in succession, where APTES acts as a linker between the hydroxyl groups on the surface of the PCAM and the carboxyl groups of STA.21 The hydrophobic oil layer can effectively prevent hydrogel from dehydration and contamination. As can be seen in Figure 1b, the synthesized DLH through electrophysiological recording, which shows better signal-to-noise ratios (SNRs) than commercial Ag/AgCl gel electrodes in both dry and wet adhesion.
shows multifunctionality, including wet/underwater specific adhesion, self-healing, anti-swelling, conductivity, biocompatibility, stretchability, and a seamless skin interface.

**Figure 1c** is an illustration of the crosslinking interactions inside the PCAM. Briefly, a double network is formed through PAA and CHI, which serve as the main backbone of PCAM. In addition, there are plenty of hydrogen bonds and multiple electrostatic interactions among PAA, CHI, Al$^{3+}$, and MXene. These reversible non-covalent interactions work synergistically in the hydrogel, which strengthen the cohesion strength and toughen the interpenetrating networks. Meanwhile, these interactions can also dissipate the energy under deformation, resulting in exceptional toughness and stretchability.

The amounts of AA, CHI, Al$^{3+}$, and MXene appeared critical in regulating the mechanical properties of hydrogels. Tensile tests were carried out to measure the ultimate strain and elastic
modulus. As shown in Figure S1a, with the increasing content of AA, the fracture strain of the PAA–CHI–Al hydrogel reduced from 3650 to 2000% and the elastic modulus increased notably owing to the rigidity of PAA. Similarly, as the content of CHI increases, the fracture strain of PAA–CHI–Al hydrogel dramatically declines because semirigid CHI can serve as a reinforcer to strengthen the hydrogel network (Figure S1b). Besides, although the fracture strain of PAA–CHI–Al hydrogel reduced from 3650 to 2000% and the elastic modulus of AA, the fracture strain of the PAA–CHI–Al hydrogel gradually decreased with the increase of Al3+ content, the fracture strain remains ~2500% even when the Al3+ content increased to 250 mg (Figure S1c). This may be attributed to PAA–Al3+ interactions tend to break preferentially to dissipate energy under tension, improving the stretchability of the hydrogel. Although PAA–CHI–Al hydrogels display excellent stretchability, hydrogel tearing and residue on skin are observed owing to their poor cohesion. Furthermore, MXene that was utilized not only serves as mechanical reinforcement (Figure 2a) but also enhances the conductivity of the hydrogel. MXene in PCAM can enhance the cohesion and toughness of the hydrogel, which contains many functional groups (e.g., −OH, −F) and can form hydrogen bonds and electrostatic interactions with the functional groups of PAA and CHI. Moreover, MXene and Al3+ both contribute to the high electrical conductivity of the hydrogel, enabling reliable electrical signal output underwater even in the case of a small amount of ion leakage. Therefore, PCAM was selected instead of the PAA–CHI–Al hydrogels.

The viscoelasticity of PCAM was further revealed by the storage modulus (G′) and the loss modulus (G″). The rheology tests exhibited that G′ of all the hydrogels tested was larger than the corresponding G″ in the range of 0.1–10 Hz (Figure 2b), indicating the elastic properties of the hydrogels. The G′ tended to increase monotonically when the content of MXene increased, indicating that the interactions of MXene with other components could further enhance the crosslink density of the hydrogel. The X-ray photoelectron spectroscopy elemental mapping images revealed that the uniform distribution of Ti, P, and Al elements in PCAM (Figure 2c). The morphologies of PCAM hydrogels showed interconnected porous microstructures with smaller pore size as the content of MXene is increased (Figure S2), indicating enlarged cohesion and density of the crosslinked network. However, excess of the MXene could degenerate the stretchability and mechanical compliance owing to the high cross-linking density. The elastic modules of hydrogels gradually increase from 3.7 kPa (1.5P−0.1CHI−0.15Al) to 53.3 kPa (1.5P−0.1CHI−0.15Al−0.2M). Figure 2d presents a 1.5P−0.1CHI−0.15Al−0.1M hydrogel (M100, details of the naming rules are described in the Experimental Section) that was stretched to 24 times of its initial length, which has a low elastic modulus of 4.5 kPa. Besides, a strip of PCAM can withstand a load of 200 g without rupture, showing outstanding mechanical properties (Figure S3a). The hydrogel can be expanded to a sizable balloon when blown up by air (Figure S3b and Movie S1). Additionally, the hydrogel can withstand puncturing and can further stretch without fracture, demonstrating the anti-puncturing and toughness of the hydrogel (Figure S3c).

Inspired by the Janus structure of skin,22 a hydrophobic coating layer was employed to encapsulate the PCAM, making the exposed outer surface waterproof and non-adhesion (e.g., not stick to external substances such as clothes during sensing). The hydrophobic modification was obtained by successively immersing the PCAM into water-immiscible APTES/EA, STA/EA solutions, and silicone oil, where APTES acts as the linker between the hydrogel surface and STA.21 The details of the hydrophobic modification can be found in the Methods section. This modification only occurred on the surface of the hydrogel, benefiting from the poor miscibility of EA with water, which does not change the body of the hydrogel. Figure 2e depicts the scanning electron microscopy (SEM) cross-sectional view of DLH, indicating the hydrophobic coating and the adhesive hydrogel body are seamlessly integrated. This seamless integration of the DLH is crucial for withstanding large tensile strain and resisting delamination. STA has a long-chain alkyl group at one end, which contributes to the hydrophobicity of the PCAM. Besides, the modification process created wrinkled structures on the surface (inset of Figure 2e), which also enhanced the hydrophobic property. The DLH hydrogel presented water resistance to daily liquids including water, milk, coffee, and tea (Figure 2f), preventing from unfavorable impacts on the sensing performance of the hydrogel. Moreover, it also isolates the hydrogel from matter exchange with the surrounding environment, avoiding possible electrical conductivity changes in the body. In the absence of strain, DLH showed hydrophobicity with a water contact angle of 95°. In addition, the DLH also showed similar hydrophobicity even under 150 and 250% tensile strain without delamination (Figures 2g and S3d,e), indicating superb structural and hydrophobic stability under deformation. Fourier transform infrared spectroscopy (FTIR) spectra are displayed in Figure 2h, the characteristic peaks at 2913 and 2846 cm−1 confirmed the successful grafting of the carbon long tails on the surface of the hydrogel.24

Adhesion Performance, Mechanism, and Conductivity. In air, PCAM hydrogel can adhere to not only the non-biotic substrates [e.g., polystyrene, polypropylene, glass, rubber, polyethylene terephthalate (PET), polytetrafluoroethylene (PTFE), wood, copper, steel, and rubber] but also the biological tissues (e.g., porcine skin, chicken liver, and pork heart) (Figure 3a). The adhesion mechanisms to various substrates in air are shown in Figure S4. To explore the adhesion mechanism of hydrogels in air, urea solution (0.1 mol L−1) was applied at the adhesion interface to dissociate the hydrogel bond. It was observed that PCAM hydrogel detaches from non-biotic substrates (e.g., glass, PET, and PTFE), while the hydrogel can still adhere to the biological tissues (e.g., porcine skin), indicating that the adhesion to non-biotic substrates was mainly contributed to hydrogen bonds. The synergistic physicochemical effects of electrostatic interactions, hydrogen bonding, and mechanical interlocking were considered to contribute to the good adhesion to biological tissues. As can be seen in Figure 3b, the addition of MXene enhanced the cohesion of the hydrogel, leading to enlarged adhesion strength. However, excess amount of MXene caused high crosslink density and may interact with the functional groups on the hydrogel surface, resulting in adhesion strength reduction and fluidity deterioration. Among varied PCAM, M100 hydrogel displayed the highest adhesion strength (494.2 kPa) and maximum peel-off strength (147.2 N m−1) to porcine skin in air (Figure 3b,c).

Moreover, distinguished from reported catechol-based underwater adhesion hydrogels,24−27 the PCAM exhibited specific underwater adhesion to biological tissues (e.g., porcine skin and chicken liver) but not to non-biotic substrates (e.g., glass, copper, and PTFE) (Figure 3d and Movie S2). This underwater selective adhesion could facilitate the handling of
hydrogel with rubber gloves or metal clamps. Similarly, M100 hydrogel also showed the highest adhesion strength (388.1 kPa) and peel-off strength (74.8 ± 2.5 N m⁻¹) to porcine skin among varied PCAM (Figure 3e,f). As a result, M100 hydrogel is chosen as the adhesive layer of the DLH hydrogel in the following experiments. In addition, M100 hydrogel can achieve robust adhesion to wet porcine skin even under water rinsing, vibration, bending, and twisting (Movie S3). The adhesion strengths and peel strength of M100 hydrogel in air and underwater adhesion to different non-biotic substrates were also tested. As indicated in Figure S5a,c, the adhesion in air of M100 hydrogel to wood owned the highest adhesion strength and peeling force due to the infiltration into the porous structures of the wood. In contrast, the adhesion strengths were all less than 8 kPa, and the peeling forces were also negligible for M100 hydrogel adhering to non-biotic substrates underwater (Figure S5b,d).

The strong specific wet/underwater adhesion mechanism of the hydrogel is as follows: (I) The adhesion of hydrogel to non-biotic materials mainly relies on hydrogen bonds owing to the absence of aromatic or charged groups on these surfaces. However, water molecules at the skin–hydrogel interface prevent direct interfacial interactions between the hydrogel and non-biotic substrates underwater. Therefore, it is difficult to adhere to the non-biotic substrates underwater because water molecules can interact with functional groups on the surface of the hydrogel via hydrogen bonding, blocking the formation of hydrogen bonding between non-biotic substrates and hydrogel. Thereby the adhesion is greatly eliminated. In contrast, the adhesion to biotic materials depends on not only the hydrogel bonding but also on non-hydrogel multiple interactions such as electrostatic and cation–π interactions. Take porcine skin as an example, at the hydrogel–skin interface, the –NH₃⁺ cation groups on the CHI form electrostatic and cation–π interactions with the negatively charged cell membrane and the benzene ring groups of the skin, respectively. Meanwhile, –COO⁻ groups on PAA chains also form electrostatic interactions with positively charged amino acids on the skin surface. These electrostatic interactions contribute to enhanced underwater skin adhesion, facilitating the contact between the hydrogel and skin. In addition, after the hydrogel is intimately contacted with skin, hydrogen bonds could also form with the –OH, –NH₂, and –COOH functional groups on skin. These above interactions contribute to the strong underwater adhesion to skin. (II) Owing to the low modulus of the hydrogel, short-chain polymers or chain ends of the polymers could penetrate the porous skin and form interfacial chain entanglement and mechanical interlocking networks with the skin, serving as sutures to bind the hydrogel and skin together. In contrast, the polymer chains rarely penetrate the smooth non-biotic materials (e.g., glass and copper), and the interfacial chain interlocking could hardly happen. As a result, the hydrogel exhibits strong underwater adhesion to biological tissues but no significant adhesion to non-biological materials due to the synergistic effect of interfacial interactions and mechanical interlocking.

The electrical conductivity of PCAM hydrogels was also tested, which is mainly related to the content of Al³⁺ and MXene. As the increasing content of Al³⁺ and MXene, more free ions participated in the conductivity. The electrical conductivity of M100 hydrogel in air was ∼1.12 S m⁻¹, which is higher than PAA–CHI–Al hydrogels (<0.7 S m⁻¹) that without MXene. Besides, with the employment of the hydrophobic layer, the conductivity of DLH hydrogel was almost constant even when immersed in water after 2 days. This indicated the stability of the electrical conductivity of DLH hydrogel underwater.

Figure 4. Anti-swelling, self-healing, and biocompatibility of the hydrogel. (a) Photographs of the PCAM before/after 7 d immersion in DI water. (b) Swelling ratio of the PCAM and commercial Ag/AgCl gel after immersion in DI water. (c) Self-healing capability of the PCAM. (d) Fluorescence micrographs of human cells incubated in hydrogel extracts after 3 d. (e) Relative cell viability with a conditioning time of 1, 2, 3 d.
Anti-swelling, Self-Healing, and Biocompatibility Properties. M100 hydrogel also exhibited anti-swelling ability and stable in water, which showed no obvious changes in the volume of M100 hydrogel after being immersed in water for 7 days (Figure 4a). This can be attributed to the high crosslink density inside the M100 hydrogel. In contrast to commercial gel electrode that quickly swells to 4.2 times of its initial weight within 1 day, the maximum weight increase of the M100 hydrogel was only 3.8% (at the day 1). It should be noted that the weight loss after 7 days of immersion may be caused by the leakage of AA monomer and a small amount of Al\(^{3+}\) ions. Besides, M100 hydrogel also possesses rapid self-healing capability. In addition, when being cut into two parts, the electrical conductivity of M100 hydrogel was almost completely restored and could be stretched (Figure S6) after self-healing for 2 min. And M100 hydrogel could be completely repaired with no visible cut trails after 1 h (Figure 4c). This quick self-healing ability was originated from not only the fluidity of the hydrogel but also reversible as well as fast-forming electrostatic interactions inside the hydrogel.

Biocompatibility is also crucial for the hydrogel owing to the direct contact with the skin\(^ {32,33}\). Cytotoxicity tests were assessed by culturing human fibroblasts with hydrogel extracts (5 mg mL\(^{-1}\)) for 3 days. The live/dead cell images of A2 hydrogel, M100 hydrogel, and control group are given in Figure 4d, indicating that nearly all cells were alive during the entire culture period [live cells showed green stained by calcein-AM, dead cells showed red stained by propidium iodide (PI)]. Besides, the relative cell viabilities of M100 hydrogel were >80% for all 3 days and >100% after 3 days (Figure 4e), which is comparable or higher compared to the control group. The aforementioned results indicated that M100 hydrogel is biocompatible to be applied to the skin applications.
Seamless Interfaces and Conformal Adhesion with Skin. A robust, seamless interface between skin and bioelectronics is essential for stable and accurate acquisition of biosignals such as bioelectrical signals, especially in wet/water applications. However, commercial Ag/AgCl gel electrodes are not suitable for sensing in water. First, there still exist micro-gaps at the skin–electrode interface, and water can diffuse into these micro-gaps (Figure 5a). Second, Ag/AgCl gel severely swell in water. They will lead to adhesion loss, unstable conductivity, mechanical property degradation, and unreliable detection result from the unreliable interfacial condition.\(^1\) In contrast, M100 hydrogel-based electrodes can achieve seamless adhesion with skin and create a stable skin–electrode interface benefited from their wet adhesion, anti-swelling, and conformal contact with skin (Figure 5b). Then, the Ag/AgCl gel electrode and M100 hydrogel were mounted on porcine skin, followed by submerging into water dyed with methylene blue (Figure 5c–f). As shown in Figure 5c, the commercial gel swelled significantly and turned fragile after 20 h soaking. Moreover, a distinct color was observed both at surface of the gel and porcine skin (Figure 5e), presenting the permeation of the water into the skin–electrode interface. While no dyed areas were observed on the surface of M100 hydrogel and the area of porcine skin where the hydrogel pasted on (Figure 5f), indicating no colored water entered the interface. It should be noted that M100 hydrogel’s surface displayed imprints of the rough skin dermatoglyph when hydrogel was peeled from the porcine skin, indicating conformal adhesion to skin.

Additionally, cross-sectional SEM images of interfaces (i.e., porcine skin and Ag/AgCl gel, porcine skin and M100 hydrogel) were represents respectively in Figure 5g,h. There existed apparent micro-gaps at the interface between Ag/AgCl gel and porcine skin (Figure 5g), which confirmed the previous assumptions. While there were no micro-gaps at the hydrogel–skin interface (Figure 5h), demonstrating conformal and seamless contact between M100 hydrogel and skin. This conformal contact and seamless adhesion are essential for skin-interfaced biosignal sensing, which can avoid the above-mentioned issues of Ag/AgCl electrodes. This conformal and seamless hydrogel–skin interface was attributed to the low modulus and good adhesion strength of M100 hydrogel, which can also lower skin interfacial contact impedance. Figure 5ij showed the contact impedance under dry and wet (sweat) adhesive conditions, respectively, where the M100 hydrogel exhibited the lowest contact impedance. Such a conformal contact was considered to be the main reason for low contact impedance. Additionally, abundant Al\(^3+\) inside the M100 hydrogel served as an ionic conducting layer. The high compliance of the hydrogel was also boosting the induced charge density at the interface. The addition of MXene also further increased the electrical conductivity of M100 hydrogel, resulting in low contact impedance than A2 hydrogel. Besides, when adhered on sweating skin, M100 and A2 hydrogels exhibited much lower impedance than commercial Ag/AgCl gels, owing to their wet adhesion ability. Comparisons of the performance with reported wet/submerged adhesion hydrogels are displayed in the Table S1, showing excellent overall performance of the M100 hydrogel.

DLH Applied as Electrodes for Electrophysiological Monitoring. Benefitting from the significant performance including strong adhesion, low modulus, as well as the seamless and conformal contact with skin, DLH was utilized as the electrophysiological electrodes for ECG and electromyogram (EMG) monitoring. As shown in Figure 6a, a pair of DLH electrodes or Ag/AgCl gel electrodes were attached to each hand, and a third electrode serving as a reference electrode was placed to the lower chest for ECG recording. The performance of both electrodes adhered in air, in wet and underwater conditions was assessed. For ECG signals recorded in air without arm motion (static condition) and with arm motion (moving condition) (Figure 6a), the corresponding ECG signals are given in Figure 6b,c. Under static conditions in air, DLH electrodes can record comparable ECG signals to those of Ag/AgCl gel electrodes. Notably, ECG signals recorded by DLH electrodes were more stable during motion condition.
than those of the Ag/AgCl electrodes due to DLH electrodes’ conformal contact with the skin.

For ECG signals recorded in wet conditions (Figure 6c), owing to Ag/AgCl electrodes can hardly adhere on the surface of wet skin, failing in capturing ECG signals without assisting with pressing. In contrast, DLH electrodes can stably record ECG signals even in wet skin, which were comparable to those in air. Besides, for ECG signals recorded underwater in both static and moving conditions (Figure 6b), ECG signals captured can be found in Figure 6d,e, respectively. It should be noted that the underwater ECG capture involved first attaching Ag/AgCl electrodes to skin before submerging them into water, while DLH electrodes were directly attached to skin underwater. In static condition underwater, ECG signals obtained by Ag/AgCl electrodes exhibited significant fluctuations in T-wave peak than DLH electrodes, indicating water permeation at the interface between skin and Ag/AgCl electrodes. In addition, it is obvious that the signals recorded by Ag/AgCl electrodes fluctuate a lot under moving conditions, and the motion artifacts of Ag/AgCl electrodes were significantly worse than those of DLH electrodes. Since DLH electrodes showed an elastic modulus that was closer to skin than that of Ag/AgCl electrodes, they could deform with skin and maintain consistent tight contact while moving and in water.\textsuperscript{12,34} Attributed to their stable conformal and seamless adhesion, DLH electrodes outperformed Ag/AgCl gel electrodes both in air and underwater conditions.

EMG signals were captured on the forearm with electrodes by gripping with 20, 40, and 60 LB grip ringcollars, respectively (Figure S8a). The amplitudes of EMG signals increased as the gripping force escalated and also showed good repeatability (Figure S8b,c). EMG signals captured by Ag/AgCl electrodes have a much larger baseline deviation than that of DLH electrodes, which were considered a non-conformal contact between the skin and Ag/AgCl electrodes. Besides, the DLH electrode can operate on wet skin, benefiting from wet adhesion capability. To mimic the wet conditions such as sweaty skin, different amounts of deionized water (10 mg per spray) were sprayed onto the skin before EMG capture (Figure 7a). Figure 7b–d correspond to EMG signals obtained after one, two, and three sprays, respectively. It should be noted that Ag/AgCl electrodes were fixed with tape due to their poor wet adhesion. With the addition of the sprays, DLH electrodes remained tightly adhered on skin under wet conditions and displayed high quality and stability in capturing EMG signals, which were comparable to those under dry conditions. For
better comparison, SNR and baseline deviation were utilized to further assess the performance of various electrodes. Under dry conditions, the SNR of the DLH electrode (28.0 dB) was comparable to or even slightly higher than that of the Ag/AgCl electrode (25.3 dB) (Figure 7e). Besides, the SNR of DLH electrodes (28.3, 27.1, and 27.6 dB) remained high even after one, two, and three sprays. In contrast, the SNR of the Ag/AgCl electrode (18.5 dB) degraded significantly after one spray, owing to the hydration layer formed at the skin–electrode interface. After two sprays, however, the SNR of the Ag/AgCl electrode increased slightly instead. This can be explained by the swelling of Ag/AgCl gel under wet conditions, which gradually filled part of the gap between the skin and electrode. As can be seen in Figure 7f, the baseline deviation of Ag/AgCl electrodes under dry conditions was 0.059 ± 0.055 mV, and the baseline fluctuation increased significantly after one spray, reaching 0.011 ± 0.058 mV. In contrast, the baseline deviation of DLH electrodes was only 0.026 ± 0.012 mV for dry adhesion and exhibited relatively gentle baseline fluctuation (0.023 ± 0.012, 0.026 ± 0.012, and 0.019 ± 0.007 mV) after different sprays, indicating the stability of EMG signals obtained by DLH electrodes. Notably, it can be concluded that DLH electrodes allow the realization of higher and more stable EMG signal quality under both dry and wet skin conditions than Ag/AgCl electrodes.

**DLH Applied as a Strain Sensor for Human Activity Monitoring and Underwater Communications.** Benefiting from the outstanding performance, including good tissue adhesion, low modulus, stable electrical conductivity, strain-sensitivity, and anti-swelling properties, DLH can also be employed as a strain sensor for human activities monitoring and underwater communications. The high sensitivity of the DLH-based strain sensor is shown in Figure 8a, the gauge factor (GF) were 4.7, 13.1, 32.3, and 63.0 in the strain ranges of 0–500, 500–1200, 1200–1800, and 1800–2300%, respectively. As shown in Figure 8b, the response and recovery times of the strain sensor were 100 and 120 ms, respectively. Additionally, the sensor also displayed a stable and consistent response to frequency variations at 100% strain (Figure 8c). Stability tests showed only a slight variation in sensitivity after 500 cycles (Figure 8d). By attaching DLH-based strain sensor in air to different joints of the human body including fingers, wrists, elbows, and knees, human daily activities can be monitored by real-time converting the strain into electrical signals (Figure S9a–d). Besides, the strain sensor can also be utilized for monitoring human health states, including pulse and respiratory monitoring (Figure S9e,f). For instance, after the sensor was adhered to the finger joints, the resistance of the sensor varies as the fingers bended and remained almost constant as the fingers kept static. When straightened once more, it quickly returned to its initial value.

By virtue of the properties of anti-swelling and wet/underwater seamless adhesion, DLH-based strain sensor can be used as a strain sensor to monitor human motions underwater. For diving activity, hand gestures can hardly be visible by diving partners owing to the low visibility.
underwater. Fatalities do occur especially in the lack of reliable underwater communication techniques, thus it is imperative to instantly communicate with partners in dangerous situations. Here, the DLH-based strain sensor was mounted on the finger joints and utilized as an efficient underwater communication device. Morse code was employed for underwater communication because of its universality and adaptability, which conveys information according to sequences of dots and dashes (Figure 9a). The relative resistance variation by finger bending and straight with different time intervals can be considered as dots and dashes. As shown in Figure 9b–e, different words such as “SOS”, “HELP”, “COME”, and “LOST” were easily transmitted underwater through finger bending. Therefore, the DLH-based strain sensor shows great potential in next-generation underwater communication.

## CONCLUSIONS

In conclusion, we proposed an adhesive/hydrophilic and a non-adhesive/hydrophobic multifunctional DLH hydrogel inspired by natural skin in this work. This hydrogel possesses various abilities including anti-swelling (~3.8%), self-healing, underwater tissue-specific adhesion, and biocompatibility. Based on a varied of dynamic reversible non-covalent bonds, the hydrogel showed attractive mechanical properties, including a high stretchability of ~2400%, a low elastic modulus of ~4.5 kPa, and anti-puncturing. The hydrogel has remarkable underwater adhesion strength (388.1 kPa) with porcine skin through synergistic interactions, including hydrogen bonding, electrostatic attraction, and mechanical interlocking. The hydrogel has been demonstrated to have seamless and highly conformal adhesion to skin in aquatic conditions, which shows a stable skin–hydrogel interface. Furthermore, this multifunctional hydrogel, DLH hydrogel, was adhered to skin for high-quality ECG and EMG signal monitoring, demonstrating lower contact impedance and higher SNRs than commercial Ag/AgCl gel electrodes under dry, wet, and underwater adhesion conditions. Using a strain sensor, its ability for human activity monitoring and underwater communication was also demonstrated. This multifunctional hydrogel therefore shows great promise in underwater sensing and health monitoring.

## METHODS

### Materials

Chitosan (CHI, BR level) with a viscosity of 50–800 mPa·s was purchased from Sinopharm Chemical Reagent Co., Ltd., China. Acrylic acid (AA, AR level), Al(NO₃)₃·9H₂O (AR level), TPO (97%), and ethyl acetate (EA, AR level) were purchased from Shanghai Aladdin Biochemical Technology Co., Ltd., China. (3-aminopropyl) triethoxysilane (APTES, 99%) and STA (40%, 54–57 °C) were supplied by Shanghai Macklin Biochemical Co., Ltd., China. Dimethylsilicone oil (viscosity 500 mPa·s) was obtained from Dow Corning Co., Ltd., USA. Multilayered Ti₃C₂Tx nanosheets were purchased from Beike 2D Materials Co., Ltd., Beijing. Commercial Ag/AgCl gel electrodes were obtained from HealForce Biomedical Technology Co., Ltd., China. Deionized (DI) water was used in all the experiments. All the reagents were used without further purification.

### Synthesis of Adhesive Hydrogel

The designed amounts of AA (1.5, 1.8, 2.2, or 2.5 g) and CHI (0.1, 0.15, 0.2, or 0.3 g) were added and evenly dispersed into 6 mL of deionized water under constant stirring for 1 h. Next, Al(NO₃)₃·9H₂O (0.1, 0.15, 0.2, or 0.25 g) was added, and the mixture was stirred for 20 min to reach complete dissolution. Then, multilayered Ti₃C₂Tx nanosheets (0 g, 50 mg, 100 mg, 150 mg, or 200 mg) and 80 mg TPO were dispersed into the above mixture under stirring for 20 min and treated by ultrasonication.
for 10 min. The obtained solution was degassed to remove the bubbles and dissolved oxygen. Finally, the precursor solution was sealed in transparent plastic molds, and the polymerization was conducted under UV light (wavelength, 365 nm) for 1 h. The PCAM adhesive hydrogels were obtained by removing the molds. The PCAM comprised of 1.5 g AA, 0.1 g CHI, 0.15 g Al(NO\textsubscript{3})\textsubscript{3}·9H\textsubscript{2}O, and 0.05 g MXene in the prepolymer is named 1.5P−0.1CHI−0.15Al−0.05M. For convenience, 1.5P−0.1CHI−0.15Al−0.05M, 1.5P−0.1CHI−0.15Al−0.1M, 1.5P−0.1CHI−0.15Al−0.15M, 1.5P−0.1CHI−0.15Al−0.2M, and 1.5P−0.1CHI−0.15Al−0.25M hydrogels are shortened as A2, M50, M100, M200, and M250, respectively.

Synthesis of DLH Hydrogel. Hydrophobic-layer-coated DLH hydrogel was obtained by treating PCAM adhesive hydrogel with a hydrophobic modification. Briefly, 0.2 M APTES/EA solutions and 0.15 M STA/EA solutions were obtained by ultrasonication. Then, the plasma-pretreated adhesive hydrogel was instantly submerged in the APTES/EA solution for 20 min, followed by taking out the APTES-decorated hydrogel (M100-A) and dried for 5 min in the air. Due to the interaction between the hydrolysate of siloxane groups and the −OH on the hydrogel surface, APTES can be decorated on the hydrogel surface during this process. Next, the decorated hydrogel was removed from the STA/EA solution after being immersed for 20 min and dried for 5 min, as a result, the hydrogel with a hydrophobic coating layer (M100-AS) was prepared. Finally, the M100-AS hydrogel was put into the silicone oil for 20 min at room temperature, and the oil could be coated on the surface through hydrophobic interactions. Once taken out, carefully wipe the excess oil on the hydrogel surface with filter paper, and the DLH hydrogel was obtained.

Materials Characterization. Helios 5 CX DualBeam (Thermo Scientific) was employed for surface morphology characterization and elemental mappings, which contains SEM and energy dispersive X-ray spectroscopy (EDS). FTIR (FTIR-650, Gangdong Tech., China) was utilized to characterize the chemical compositions. The electrode−skin impedance was measured by an electrochemical workstation (CHI 604E).

Mechanical Testing and Measurement of Adhesion Force. Hydrogel samples used for mechanical tests were sliced into pieces with a size of 15 mm × 20 mm × 1.0 mm. A force gauge (ESM301, Mark-10) was used to assess the hydrogels’ stress−strain curves with a loading speed of 50 mm min\textsuperscript{−1}. By and by evaluating the linear portion of the stress−strain curve, the elastic modulus was obtained. The lap−shear test was utilized to measure the adhesion strength of hydrogels. Briefly, by sandwiching a hydrogel (l = 25 mm, w = 20 mm) between two pig skins, and then placing in static at room temperature for 30 min prior to tensile tests, the adhesion strength of the hydrogel to porcine skin was measured with a loading speed of 5 mm min\textsuperscript{−1} at room temperature. The adhesion strengths of the hydrogel to other substrates were tested by the same procedure. The standard 90°-peeling test (ASTM D 2861) was carried out to evaluate the interfacial toughness of hydrogel on various substrates. Hydrogels with a size of 70 mm × 25 mm × 1.5 mm were attached to the substrate and left there for 30 min at room temperature before the peeling test. To prevent the hydrogel from breaking during the peeling process, a support layer was employed together with the hydrogel to limit the stretchability during the peeling process. The peeling speed was set as 50 mm min\textsuperscript{−1}. For underwater adhesion test, a slight difference was that the adhesion process was conducted in water and remained underwater for 2 min before being taken out from the water. Each test was conducted by at least three samples.

Cytotoxicity Assays. Before cytotoxicity tests, A2 and M100 hydrogels were first immersed in deionized water for 2 days and replaced with fresh water every 8 h to remove unreacted acrylic monomers. In brief, for the acquisition of extracts, a 50 mg sample of the hydrogel was placed in a sterile Petri dish with 5 mL of anhydrous ethanol and subsequently sterilized under UV light for 1 h. Excess alcohol was removed from the hydrogel by evaporation, and the hydrogel was then washed with sterile phosphate-buffered saline. The sterilized hydrogels were placed in 1 mL of complete medium and incubated at 37 °C for 24 h to obtain the extracts. The cytotoxicity of the hydrogels was determined by culturing human fibroblasts with the extracts of the hydrogels. Human fibroblasts were cultured in 24-well culture plates containing the extract for 1, 2, and 3 days. Live/dead cells were stained with calcein-AM and PI fluorescent dyes after 3 days and visualized by confocal laser scanning microscopy.

Data Acquisition and Analysis. The ECG and EMG signals were recorded by a Heal Force PC-80B monitor and a Sicharay EMG recorder. The resistance data during the stretching and human motion monitoring of the strain sensor were recorded by Keithley DMM6500.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsami.2c21595.

Blowing up into a balloon of the hydrogel (MP4)
Underwater specific adhesion (MP4)
Robust adhesion of hydrogel to porcine skin (MP4)
Experimental details for characterizations and tests of hydrogel (PDF)

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