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Water-resistant conformal hybrid electrodes for aquatic endurable electrocardiographic monitoring

Shaobo Ji, Changjin Wan, Ting Wang, Xijiang Liu, Qingsong Li, Geng Chen, Jianwu Wang, Zhiyuan Liu, Hui Yang, and Xiaodong Chen**

Dr. S. Ji, Dr. C. Wan, Dr. T. Wang, Dr. Q. Li, Dr. G. Chen, Dr. J. Wang, Dr. Z. Liu, Prof. X. Chen
Innovative Center for Flexible Devices, School of Materials Science and Engineering, Nanyang Technological University, 50 Nanyang Avenue, 639798, Singapore
Dr. H. Yang
Tianjin Key Laboratory of Molecular Optoelectronic Sciences, Department of Chemistry, School of Science, Tianjin University, Tianjin, 300072, China
Dr. X. Liu
College of Chemistry and Chemical Engineering, Shanghai University of Engineering Science, NO. 333 Longteng Road, Shanghai, 201620, China
E-mail: chenxd@ntu.edu.sg; yanghui2018@tju.edu.cn

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Underwater vital signs monitoring of respiratory rate, blood pressure, and heart's status is essential for healthcare and sports management. Real-time electrocardiography (ECG) monitoring underwater could be one solution for this. However, the current electrodes used in ECG are not suitable for aquatic applications since they may lose their adhesiveness to skin, stable conductivity, or/and structural stability immersing into water. Here, we report the design and fabrication of water-resistant electrodes to repurpose stretchable electrodes for applications in aquatic environment. The electrodes are composed of stretchable metal polymer composite film as the substrate and dopamine-containing polymer as a coating. The polymer was designed to possess underwater adhesiveness from dopamine motif, water stability from main scaffold, and ionic conductivity from carboxyl groups for signal transmission. Stable underwater conductivity and firm adhesion to skin allowed the electrodes to collect reliable ECG signals under various conditions in water. We show wearable devices incorporated with the water-resistant electrodes could acquire real-time ECG signals during swimming, which could be used

for revealing heart condition. These water-resistant electrodes realized underwater detection of ECG signals and could be used for health monitoring and sports management during aquatic activities.

Underwater vital signs monitoring, including real-time electrocardiography (ECG), respiratory rate, blood pressure, etc. is important for healthcare and helpful in sports management, especially ECG monitoring for lifesaving. Heart attacks have become the second leading cause of death for divers with increasing population attending swimming and diving.[1] Aquatic ECG can realize underwater monitoring of vital signals, allowing preventive measures to be taken before a heart attack occurs and a help alarm to be sent in case of an attack.[2] However, to obtain stable and reliable signals underwater, ECG electrodes must be both conductive and adhesive to the skin in water, which is still a challenge. Commercial gel electrodes lose their adhesion in water, and even if they were pasted on the skin before entering water, there are still microvoids at the interface due to skin surface structure. Water can penetrate to the skin-electrode interface, leading to decreased adhesion and unstable detection with the changing interfacial environment (**Figure 1**A). The attempted researches to acquire ECG from skin in water was focused on current collection, the electrodes were fixed only by tapes or rubber bands.[3] The unstable fixation and electrodes without adhesion nor stretchability led to motion artifacts during movement and the signals could only be monitored in static status. On the other hand, in recent years stretchable and conformal electrodes for dry applications have been developed, they could be integrated with wearable devices to detect biosignals from the skin for decentralized self-monitoring of health conditions.[4] With these electrodes, ECG can be recorded during body motion, but only in the air. The very limited example from them for monitoring ECG in water was carried out with a swimsuit to fixate the electrodes.[5]

The stretchable electrodes are based on different substrates, some of them show excellent biocompatibility along with water solubility, such as silk based electrodes,[6] which are not suitable for underwater applications. A popular kind of stretchable substrate is polydimethylsiloxane (PDMS) films coated with microcracked gold nanolayer (Au/PDMS),[7] their mechanical stability and conductivity are both not affected by water, which makes they a good candidate for aquatic applications. However, due to their hydrophobicity, Au/PDMS cannot adhere to skin in water. To repurpose the water-resistant Au/PDMS for underwater applications, there is a need for introducing an additional layer that is adhesive underwater to bridge the film and skin. Because an extra layer adds resistance to the sensing circuit (Figure 1B), the polymer must possess certain conductivity to ensure minimum resistance.[8] Thus, even though currently developed dopamine-containing polymers demonstrated underwater adhesiveness,[9] extra efforts are needed to make them more than just adhesives for application in electrode systems.

Here, we report the use of an ionic conductive dopamine-containing polymer to create water-resistant electrodes for underwater ECG monitoring. Dopamine methacrylamide (DMA), acrylic acid (AA) and methoxyethyl acrylate (MEA) monomers were co-polymerized to form a random co-polymer, p(DMA-*co*-AA-*co*-MEA) (pDAM), which was then drop cast onto the gold surface of Au/PDMS films to form water-resistant pDAM/Au/PDMS electrodes (Figure 1C). The dopamine-containing motif, DMA, provided the underwater adhesion, while AA conferred ionic conductivity as it deionizes in water, allowing the adhesive polymer to detect and transfer electrophysiological signals. MEA prevented the destruction of pDAM by forming a water-stable scaffold. The electrodes adhered tightly to skin in the presence of water and had stable conductivity. Upon drying, the electrodes could be peeled off easily without leaving any residue on the skin and re-used. As the polymers from these monomers showed good biocompatibility, no skin irritation was observed in 2 h.[10] The electrodes could be used to collect stable and reliable real-time skin interfacial ECG signals in water and during swimming.

In a typical experiment, the Au/PDMS films were prepared by depositing 80 nm thick gold layer onto 70 μm thick PDMS films. The films without the adhesive pDAM polymer can be stretched up to 180% strain, have a low electrical resistance of 13.3 ± 1.4 Ω/sq, is conductive up to 90% strain, and is stable over 1000 cycles of stretching at strains 0 to 30% (Figure S1). These characteristics are suited for collecting electro biosignals, but the Au/PDMS films are not adhesive in water. To make them adhesive, we drop casted polymerized pDAM onto the gold surface of the Au/PDMS films. The resulting pDAM/Au/PDMS films were both conductive and adhesive underwater, which are crucial for aquatic ECG applications. All three monomers of the pDAM layer were essential for the water-resistant electrode (Figure 1D and Figure S2C, D). The pDM control polymer without ionizable carboxyl groups showed low conductivity while the unstable pDA polymer chains led to lowered adhesion in water. The pMA controls that lacked the dopamine motif detached easily with minor surface wetness.

With a dry layer of pDAM (160 μm thick), the elastic modulus of pDAM/Au/PDMS decreased from 928 kPa to 798 kPa (Figure 1E). After wetting the pDAM, the modulus further decreased to 420 kPa. The pDAM/Au/PDMS films attached stably on skin because the elastic modulus began to approach that of skin (less than 100 kPa).[11] Compared to Au/PDMS films, pDAM/Au/PDMS films showed significantly lowered skin interfacial impedance (Figure 1F). Microscopic images confirmed the lowered impedance was due to good contact between the skin and the adhesive pDAM layer. After pasting the pDAM/Au/PDMS film and peeling them off the skin, the transparent and flat as-prepared pDAM surface (Figure S2E) showed imprints of rough patterns from the skin (Figure S2F), indicating good contact had been formed. Such an intimate contact lowers impedance. The adhesion between pDAM layer and Au layer was higher than Au-PDMS adhesion, but would not affect the Au layer after stretching due to the lower modulus than PDMS (Figure S3). Because water was necessary for ionic conductivity of pDAM, all tests were done after immersing the polymer in water for 10 s.

For underwater use, the adhesion and stability of the electrodes in the presence of bulk water are crucial. To test this, we attached commercial polyacrylate based gel electrodes and our pDAM/Au/PDMS electrodes (abbr. DAM electrodes) on different human arms and immersed the arms in water. When the skin surrounding the electrodes was compressed, the commercial gel electrodes rapidly detached from the skin due to poor adhesion whereas the stretchable and adhesive DAM electrodes deformed along the skin and remained attached (**Figure S4**A). We measured adhesion strength by attaching the electrodes on surface patterned PDMS (elastic modulus ~ 80 kPa) – a substrate as the model for human skin (Figure S4B) – and measured the force required to detach the electrodes from the substrate. In air, DAM electrodes had only a slightly better adhesion strength than commercial gel electrodes (**Figure 2**A). After immersion in water, the adhesion strength of commercial gel electrodes dropped significantly to less than 1% of its adhesion strength in air while DAM electrodes retained its high strength. The DAM electrodes also showed good recyclability in water; their adhesion strength remained stable even after 10 cycles of pasting and peeling underwater (Figure 2B and S4C).

Besides underwater adhesion, the DAM electrodes were also stable in water. Benefitting from the water-insoluble MEA scaffold, DAM electrodes attached on PDMS-skin model in the dry state and then immersed in water for 24 hr showed only a 10% weight increase (calculation based on the weight of pDAM layer) (Figure 2C) and remained tightly adhered to the PDMS films. In contrast, under the same conditions, commercial gel electrodes swelled and detached after 50 min of static immersion in water. Although the outer ring tape of the electrodes could isolate the gel from water initially, water penetrated the surface structures over time (Figure 1A), loosening the adhesion of the outer ring tape and causing the gel to swell. With increasing swelling rates, the electrodes eventually detached (Figure 2C). These results showed that the pDAM coating stabilizes the electrode material and offers firm underwater adhesion.

We further tested the electrical properties of the DAM electrode. Commercial gel electrodes and DAM electrodes were immersed in water for different durations and their interfacial impedance in water was measured. The impedance of commercial gel electrodes decreased significantly with immersion time, dropping one order of magnitude after 40 min (Figure 2D and **S5**A). This loss of impedance is due to water entering the interface between the gel and skin, which is consistent with the adhesion results. The changing conductivity could lead to unreliable and unstable signals, especially during swimming as water will flow through the interface. Unlike commercial gel electrodes, the interfacial impedance of DAM electrodes was highly stable. The slight decrease seen at the beginning is due to the swelling of water (Figure 2D and S5B). Thereafter, the impedance remained nearly constant up to 40 min of immersion. It benefited from the sealing effect of DAM electrodes due to underwater adhesion and conformal properties, providing a stable environment at the interface between electrodes and skin (Figure 2E). To visualize the water penetration, commercial gel electrode and DAM electrode were pasted on PDMS-skin model and immersed in water containing water soluble red food dye (E122, 0.2 % v/v). After immersion for 30 min, obvious color could be seen at the interface between commercial gel electrode and PDMS-skin model, while no colored water entered the interface of DAM group (Figure 2F). The appearance of water at the interface led to decreased adhesion, unstable conductivity, and swelling caused structural instability. They made commercial electrodes not stable and not reliable when used in water, while DAM electrodes could avoid these problems.

Experiments under extreme conditions were also carried out to further demonstrate their long-term adhesion and stability. We attached DAM electrodes on PDMS-skin model and stirred them in water at 300 rpm for 24 h before the tests (Figure S6A, B). The electrodes adhered so tightly to the PDMS films that the adhesion strength could not be tested in the wet state (above 5 kPa, the PDMS films fixed by tapes detached from the sample stage). The enhanced adhesion is likely due to the continuous impact of water pressing the electrodes firmly

onto the PDMS films. After drying the electrodes for 2 hr at room temperature, they could be peeled and tested. The DAM electrodes maintained their adhesion strength and recyclability (Figure S4C) without any significant change in electrical properties even after 24 hr stirring in water (Figure S6C).

To explore the performance of the DAM electrodes, we used them to collect ECG signals. Commercial gel electrode or DAM electrode pairs were attached on human forearms and ECG signals were collected continuously for 60 min in water (**Figure 3**A). Despite limited arm motion, commercial gel electrodes detached from the skin within 20 min. ECG signals from pDMA/Au/PDMS electrodes remained stable even after 60 min of continuous immersion in water. In air under static state, signals from DAM electrodes were comparable to those from commercial gel electrodes (Figure 3B). During motion, however, their signals were more stable than commercial electrodes largely due to conformal contact with the skin.

For underwater recording of ECG signals, three different conditions were examined: without arm motion (static), with arm motion (moving), and with water flow impacting the electrodes (impacted) (Figure 3C). Because most underwater circumstances involve the flow of water, the water impact scenario reflects an open water environment. For better comparison, the data were processed to quantify their quality and stability (see Figure 3A for details). A number close to 1/3 for the T/R peak indicates good quality while a smaller deviation between T and P peaks indicates better stability, which reflects the effect of motion artifacts. ECG signals recorded in water by commercial gel electrodes showed lower quality and poorer stability than signals recorded in air (Figure 3D, E). The T/R ratio and TP deviation for commercial electrodes decreased even upon simple immersion in water. When arms were moved, the TP deviation for commercial electrodes increased slightly due to skin deformation resulting from the movement. However, in the presence of water impact, TP deviation increased significantly. Skin deformation and water flowing into the skin-electrode interface can affect conductivity, resulting in the unstable signals seen with commercial electrodes.

Unlike the commercial electrodes, DAM electrodes collected stable and high-quality underwater ECG signals. For all tested underwater conditions, the T/R ratio approached 1/3, confirming their quality. The TP deviations were also similar to those recorded in air and much lower than commercial electrodes. All ECG signals recorded by DAM electrodes were comparable to control signals (acquired by commercial gel electrodes in air under static conditions). Because the elastic modulus of DAM electrodes was closer to skin than commercial electrodes, they could deform with skin and achieve constant tight contact during motion and water impact. Such stable adhesion allowed the DAM electrodes to perform much better in water than commercial gel electrodes.

We further tested the electrodes in a swimming pool. As shown in **Table 1**, commercial gel electrodes could not attach to skin underwater. When applied on wet skin, the electrodes detached within 30 s upon entering the pool. On very dry skin, they fell off within 8 min during swimming. Because they detach so readily, commercial gel electrodes are not suitable for real-time monitoring of ECG signals in the pool. In contrast, DAM electrodes remained on the skin for over 40 min during swimming, whether they were pasted on wet skin or underwater. This good attachment allowed us to use DAM electrodes to measure ECG signals in the pool.

We integrated the DAM electrodes with a wearable device to obtain real-time ECG signals during swimming (**Figure 4**A and Supporting Video). The device collected ECG signals from the chest via a two-electrode system and transferred the signal to an application in a smartphone wirelessly. With this setup, we recorded ECG signals before, during and after swimming (Figure 4B-E). Upon entering the pool, the device began recording ECG signals (Figure 4B). During swimming, the ECG signals showed slightly different wave shapes and a much higher heart rate than the resting state (Figure 4C). After swimming and resting in water, the wave shape and heart rate returned to the original state (Figure 4D). Signals collected continuously during a 15-min swim was stable (Figure 4E). These results show that the electrodes maintained good enough adhesion and contact with the skin for continuous ECG

monitoring. No abnormality was observed from these ECG signals, indicating the subject had a healthy heart. Current wearable devices that measure heart rate mainly rely on optical sensors, which are highly inaccurate and not functional in water. Some devices can provide heart rate information through ECG monitoring, such as Apple Watch, but cannot function during swimming. With our electrodes, continuous heart rate can be recorded underwater and any variability in the heart rate can be used to warn users of potential risks of heart attacks (Figure 4F).[12]

Water-resistant electrodes were fabricated for monitoring and recording aquatic electrophysiological signals. The electrodes were based on stretchable Au/PDMS films and a dopamine-containing ionic conductive polymer layer. The polymer was designed to combine underwater adhesion and ionic conductivity for aquatic applications. The electrodes had excellent long-term stability and could bind to skin more strongly underwater than commercial gel electrodes. The ECG signals recorded using these water-resistant electrodes were stable and insensitive to the impact of water flow. A wearable device was also developed with these electrodes to acquire real-time ECG signals during swimming, the data of which could potentially be used to warn the user of potential risks of heart attacks. The polymer coating strategy is also applicable to other electrode materials and devices, and can expand their application scenarios from dry to aquatic environments.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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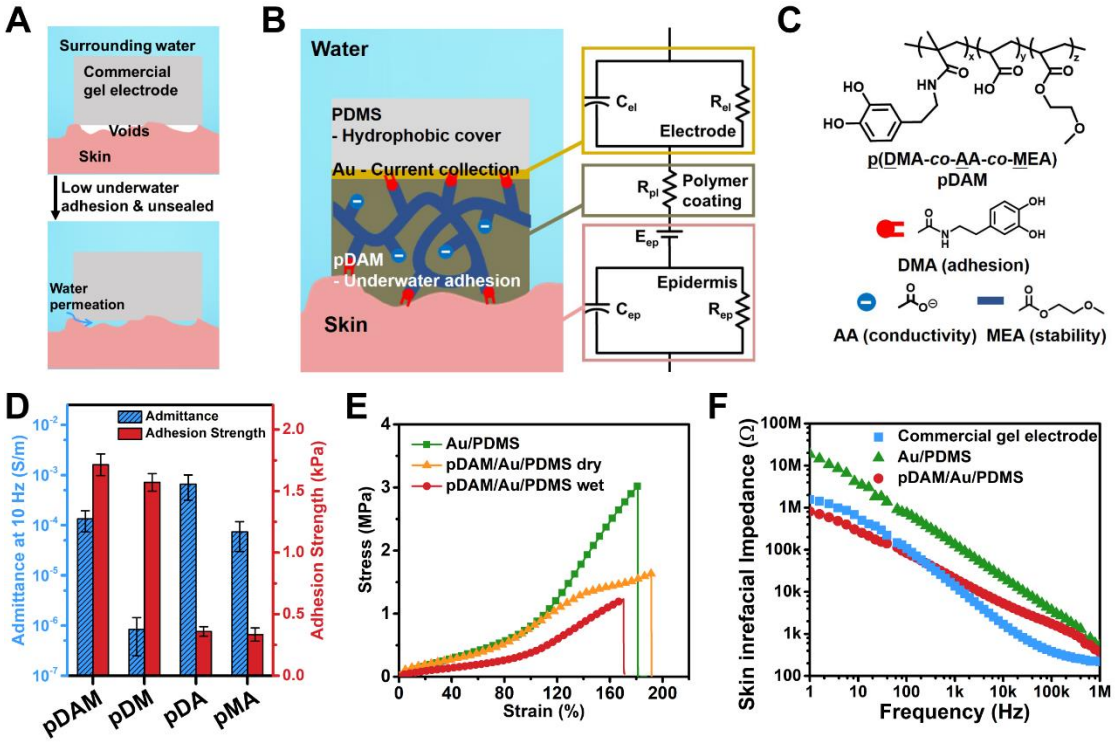

Figure 1. Illustration and properties of the multilayer water-resistant pDAM/Au/PDMS films. (A) Voids exist at the commercial gel electrode-skin interface due to skin surface structure, which allows water in and cause decreased adhesion. (B) Schematic showing the water-resistant pDAM polymer coating bridging the Au/PDMS electrode and skin (left), and the corresponding circuit (right). C_{el} and R_{el} are the capacitance and resistance of the electrode and C_{ep} and R_{ep} are that of the epidermis; E_{ep} is potential across the epidermis; R_{pl} is additional resistance caused by the polymer coating. Adhesion and conductivity of the polymer coating are both crucial for achieving low R_{pl}. (C) Chemical structures of the dopamine-containing ionic conductive random co-polymer, p(DMA-*co*-AA-*co*-MEA) (pDAM), and the corresponding symbols used in **B**. Calculated from ^{1}H NMR in Figure S2, x:y:z = 1:3.36:2.46. (D) Graph of admittance (at 10 Hz) and adhesion strength in the presence of water for pDAM and control polymers, pDM, pDA, pMA. Only pDAM is both highly adhesive and conductive in water. Error bars represent standard deviation of 4 independent tests. (E) Tensile stress-strain curves of Au/PDMS film, Au/PDMS with 160 μm pDAM layer under dry and wet state. Mechanical strength of wet pDAM/Au/PDMS resembled skin, which enables conformal adhesion on skin. (F) Skin interfacial impedance for pDAM/Au/PDMS was significantly lower than Au/PDMS films but similar to commercial gel electrodes. The distance between electrode pair was 5 cm, the contact area of all types of electrodes to skin was around 210 mm^2 per electrode.

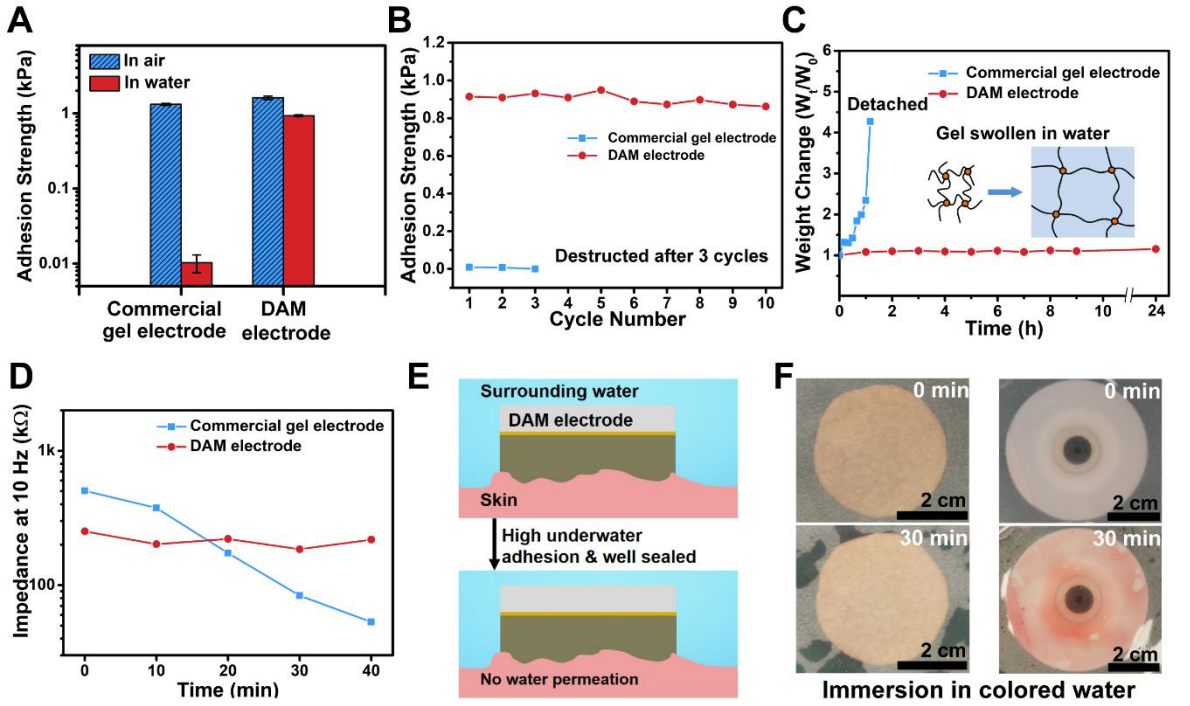

Figure 2. Underwater adhesion and stability of pDAM/Au/PDMS electrodes (DAM electrodes) containing 160 μm thick pDAM. (A) Adhesion strength tested on PDMS-skin model in air and in water. DAM electrodes retained its high adhesion strength after immersion in water whereas commercial gel electrodes showed significant deterioration. Error bars represent the standard deviation of 4 independent tests. (B) Adhesion strength during underwater paste and peel off cycles. DAM electrode showed high and stable adhesion for 10 cycles while commercial ones adhered poorly and destructed after 3 cycles. (C) Graph showing weight change of electrodes attached to PDMS-skin model during water immersion. DAM electrodes showed only a 10% increase in weight, while commercial ones swelled considerably and detached from the substrate in 50 min. (D) Skin interfacial impedance for DAM electrode remained stable whereas commercial gel electrode deteriorated significantly with immersion time (see Figure S5 for full spectra). The distance between electrodes pair was 5 cm, the contact area of both types of electrodes to skin was around 210 mm^2 per electrode. (E) Illustration of sealing effect and prevention of water permeation of DAM electrode pasted on skin. (F) DAM electrode (left) and commercial gel electrode (right) pasted on PDMS-skin model and immersed in water containing red food color.

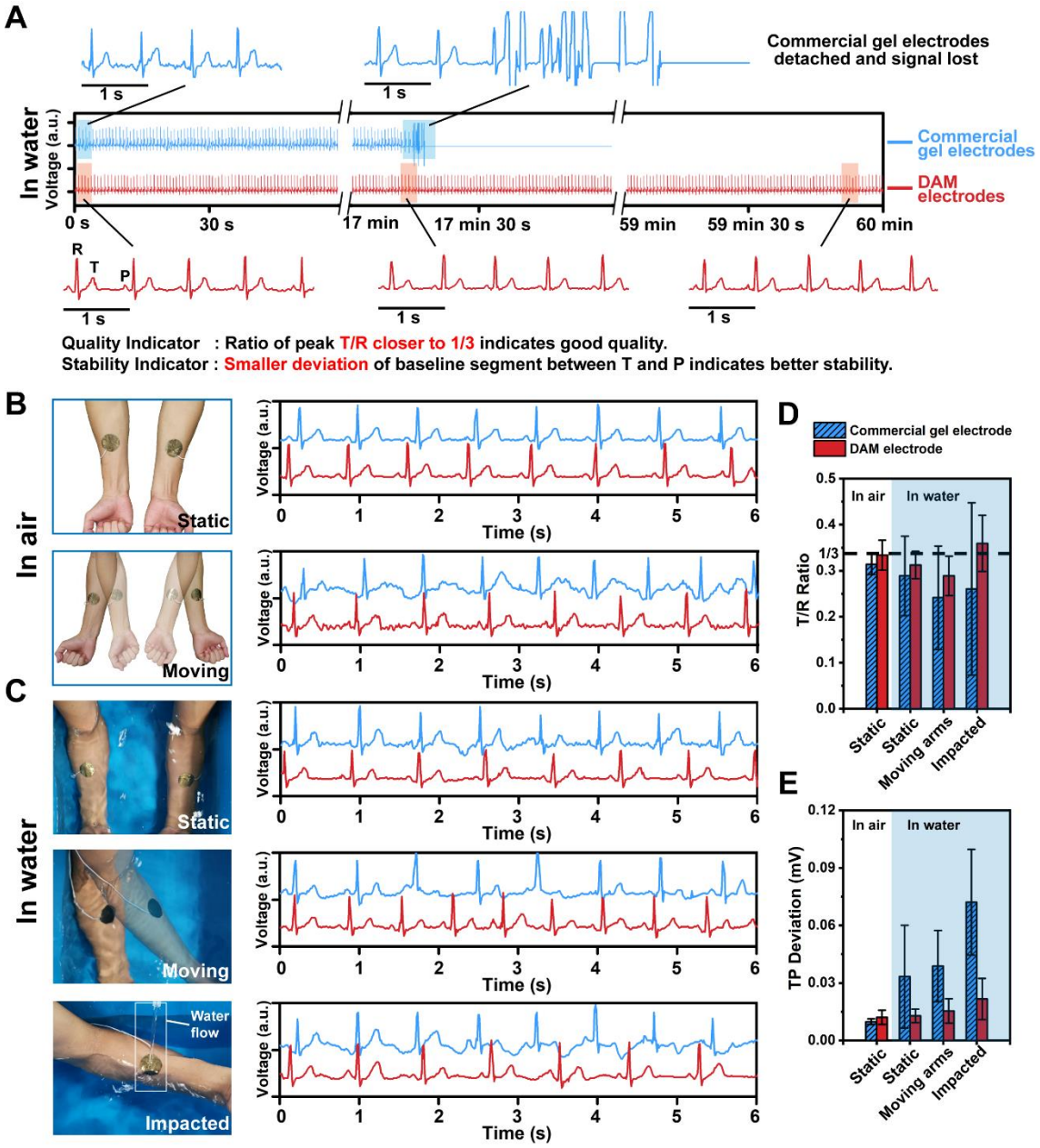

Figure 3. Performance of DAM electrode compared to commercial gel electrodes. (A) In water, commercial gel electrodes detached from the skin and suffered signal loss while DAM electrodes remained attached and continued collecting stable signals. T/R ratio and deviation of the TP segment were used to quantify the quality and stability of the acquired signals, respectively. B,C, ECG signals recorded in air (B) and water (C). Corresponding photos show the recording conditions. To introduce impact, water flow was applied with a flow rate of 2.0 L/min from a pipe with a 6.0 mm inner diameter. D,E, Graphs showing T/R peak ratio (D) and deviation of TP segment (E) for commercial electrodes and DAM electrodes under different recording conditions. T/R peak ratio approaching 1/3 indicates good signal quality while a lower TP deviation indicates signal stability. DAM electrodes outperformed commercial electrodes in water.

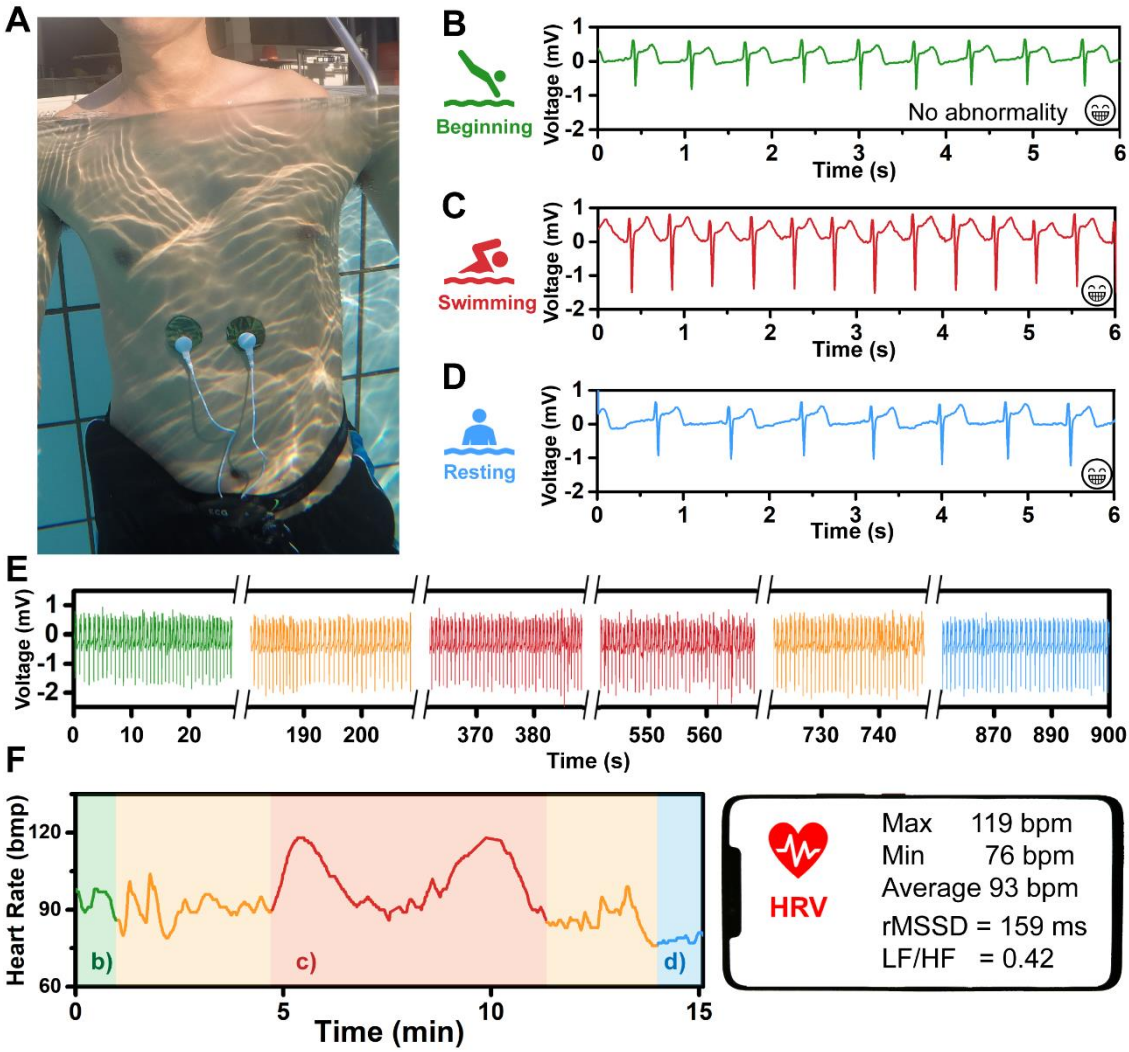

Figure 4. Real-time recording of ECG signals during swimming using a wearable device fabricated with DAM electrodes. (A) Photo of the device with DAM electrodes in water. Signals are received and recorded by a smartphone wirelessly through Bluetooth. B-D, ECG signals recorded by the device in water before swimming (B), during swimming (C), and in water after swimming and resting (D). (E) Continuous recording in water for 15 min showed the signals remained stable. (F) Continuous heart rate record from ECG waves (left) and heart rate variability (HRV) for 15 min of swimming (right). HRV showed the maximum, minimum, and average heart rate; root means square of the successive differences (rMSSD), and low-frequency power to high-frequency power ratio (LF/HF). Color codings in the figure: green, in water before swimming; yellow, low intensity swimming out of lane; red, swimming in lane; blue, in water at the edge of pool.

Table 1. Duration before detachment of electrodes from the skin in the swimming pool.

Electrode	Pasting condition	Duration before detachment
Commercial gel electrodes	underwater	0 s
	to wet skin	< 30 s
	to dry skin	< 8 min
DAM electrodes	underwater	> 40 min

Water-resistant stretchable electrodes are fabricated with a specially designed polymer. The polymer is underwater adhesive to bridge the electrode and skin, and ionic conductive to transmit electrophysiological signals. The conformal electrodes realize reliable ECG detection when moving body or being impacted with water flow, which enables stable wireless real-time ECG collection during swimming with a wearable device.

Keyword
underwater adhesion, on-skin electrode, healthcare, electrocardiography monitoring

S. Ji, C. Wan, T. Wang, X. Liu, Q. Li, G. Chen, J. Wang, Z. Liu, H. Yang*, X. Chen*

Water-resistant conformal hybrid electrodes for aquatic endurable electrocardiographic monitoring