Water-resistant conformal hybrid electrodes for aquatic endurable electrocardiographic monitoring

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2020

Ji, S., Wan, C., Wang, T., Li, Q., Chen, G., Wang, J., Liu, Z., Yang, H., Liu, X. & Chen, X. (2020). Water-resistant conformal hybrid electrodes for aquatic endurable electrocardiographic monitoring. Advanced Materials, 32(26), 2001496-. https://dx.doi.org/10.1002/adma.202001496

https://hdl.handle.net/10356/147122

https://doi.org/10.1002/adma.202001496

Supporting Information

Water-resistant conformal hybrid electrodes for aquatic endurable electrocardiographic monitoring

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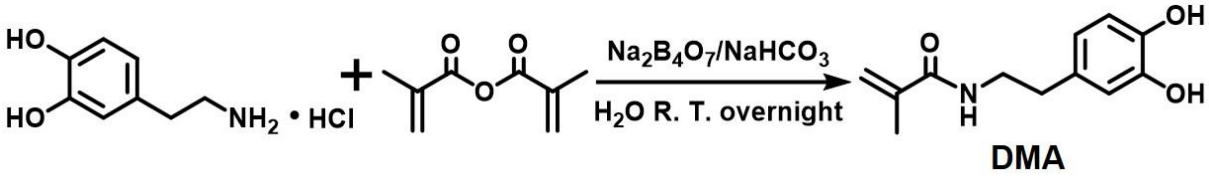
Methods

Preparation of Au/PDMS films: PDMS films were prepared from Sylgard 184 Silicone Elastomer Kit (Dow Inc.). A mixture of precursor and crosslinker at 10:1 ratio was spin coated on a fluorinated silicon wafer at 800 rpm for 60 s, and cured 60 ^{o}C for 5 h. The prepared PDMS films were around 70 μm thick. Au nanolayers were deposited by a vacuum thermal evaporator (Nano 36, Kurt J. Lesker) under 2×10^{-6} Torr with a deposition rate of 0.3 Å/s. The Au source was purchased from Kurt J. Lesker and the purity was 99.99%. The deposition time was controlled to get 80 nm thick gold layers.

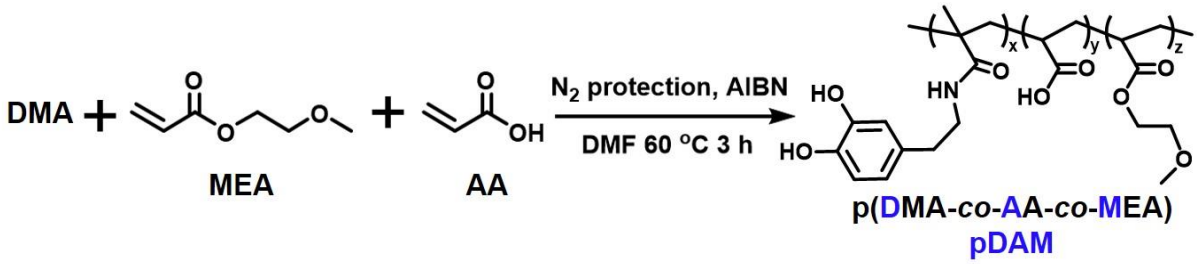
Synthesis of dopamine methacrylamide (DMA) monomer: DMA monomer was synthesized according to the previously reported method.[S1] 10 g of sodium tetraborate and 4 g of sodium bicarbonate were dissolved in 100 mL deionized water and bubbled with nitrogen for 20 min. With continuous nitrogen flow, 5 g of dopamine hydrochloride (26.4 mmol) was dissolved in the solution. Then 5 mL of methacrylate anhydride (94 % purity, 29.1 mmol) in 20 ml THF was added dropwise, during this process the pH was kept above 8 with the addition of 1 M sodium hydroxide. The mixture was stirred overnight at room temperature. The reaction mixture was washed twice with 50 mL ethyl acetate, and then the pH of the aqueous solution was changed to less than 2 and extracted with 50 mL of ethyl acetate three times. The ethyl acetate layers were combined and dried over sodium sulfate, evaporated to reduce to around 30

mL. Then the solution was dropped into 300 mL hexane with vigorous stirring under an ice bath. The product was purified by dissolving the solid in 30 mL hot ethyl acetate and recrystallized from 300 mL ice bathed hexane. 3.6 g of grey solid was produced, yield 65 %. ^{1}H-NMR (400MHz, DMSO-d/TMS): 8.73 (s, 1H, -C_6H_3(O*H*)(OH)), 8.62 (s, 1H, -C_6H_3(OH)(O*H*)), 7.92 (s, 1H, -CH_2N*H*(C=O)-), 6.62 (d, 1H, -C_6*H*H_2(OH)$_2$), 6.57 (d, 1H, -C_6*H*H_2(OH)$_2$), 6.42 (m, 1H, -C_6*H*H_2(OH)$_2$), 5.61 (s, 1H, -C(=O)-C(-CH_3)=C*H*H), 5.30 (s, 1H, -C(=O)-C(-CH_3)=CH*H*), 3.22 (m, 2H, C_6H_3(OH)$_2$-CH_2C*H*$_2$NH-), 2.55 (t, 2H, C_6H_3(OH)$_2$-C*H*$_2$$CH_2$NH-), 1.84 (s, 3H, -C(=O)-C(-C*H*$_3$)=CH_2).



Scheme S1. The synthesis of DMA monomer.

Polymerization of pDAM and control polymers: The polymers were synthesized via similar procedures with different monomer feeds (Table S1). Taking pDAM as example: 0.70 g DMA (3.2 mmol), 0.90 mL MEA (7.0 mmol), 0.75 mL AA (10.9 mmol), and 100 mg azobisisobutyronitrile (AIBN, 0.61 mmol) were dissolved in 10 mL DMF. The solution was degassed through three times of pump–freeze-thaw cycles, and filled with nitrogen. Then the mixture was heated to 65 ^{o}C for 3 h, and the solution became gel during polymerization. The gel was dissolved by adding 20 mL methanol, and the solution was dropped into ice bathed diethyl ether to precipitate the polymer. The polymer was dissolved in 20 mL methanol and precipitated in ice bathed diethyl ether again for purification. After drying in vacuum, 1.36 g grayish solid was collected, yield 60 %. Gel permeation chromatography was carried out on a Waters 2414 Index Detector with DMF as eluent. See Figure S2 for GPC and ^{1}H NMR results.



Scheme S2. The synthesis of pDAM polymer.

Table S1. Monomer feed for different polymers

	DMA	MEA	AA	AIBN
pDAM	0.70 g	0.90 mL	0.75 mL	100 mg
pDM	0.35 g	0.90 mL	-	50 mg
pDA	0.35 g	-	0.75 mL	60 mg
pMA	-	0.90 mL	0.75 mL	40 mg*

* With 80 mg AIBN, the produced pMA was liquid and not suitable for the test. Thus the initiator/monomer ratio was halved for pMA.

Fabrication of pDAM/Au/PDMS electrodes: The electrodes were fabricated by drop casting pDAM methanol solution on the gold surface of Au/PDMS films and drying at r. t. for 6 h. The concentration of pDAM solution was ~200 mg/mL. With 250 μL pDAM solution per cm^2 on the surface, a thickness of ~80 μm was achieved. By changing the amount, the thickness of the polymer layer was controlled.

Preparation of PDMS-skin model: The PDMS films were prepared with a mixture of precursor and crosslinker at 30:1 ratio. The mixture was poured into a mold with mimetic skin surface structures and cured at 80 °C for 4 h. The elastic modulus was only 80 kPa, which was also similar to skin.

Measurement of mechanical and electrical properties: The mechanical properties were tested by a mechanical tester (C42, MTS Systems Corporation) in tensile stretch mode. Tensile tests were conducted at a speed of 5 mm/min with a 40 mm × 5 mm rectangular samples and

initial gauge lengths of 20 mm. The elastic modulus was calculated using the first 0.2 % strain region. The resistance of Au/PDMS films and the change during stretching were recorded by a semiconductor parameter analyzer (Keithley 4200-SCS, Tektronix). For the measurement of resistance change under cyclic strains, 30% strain was applied to a 40 mm × 5 mm rectangular sample with an initial gauge length of 20 mm using the mechanical tester at a speed of 0.5 mm/s while the resistance was recorded continuously. The impedance on the skin was measured by an electrochemical workstation (ZAHNER ZENNIUM) with a range from 1 Hz to 1 MHz and a voltage of 220 mV. The measurements were carried out by pasting electrode pairs with a circle shape (diameter: 16 mm) with a center-to-center distance of 5 cm on forearm skin. Commercial gel electrodes were also tested for comparison (Chunfeng YD-50 Ag/AgCl gel electrodes).

Normal adhesion measurements: The measurements were carried out on PDMS-skin model in air or underwater with a custom-built equipment and testing program (C42, MTS Systems Corporation). The electrode parts were attached to a 3D printed tips which was a round shape with 14 mm diameter, and fixed by super glue overnight before test. A 100 mm × 50 mm rectangular shaped PDMS-skin model with 5 mm thickness was pasted to a glass petri dish (diameter 150 mm, 15 mm deep to fill in water) through double-sided tape and the edge was further fixed by waterproof tapes. The petri dish was fixed to a flat metal platform of the tester by double-sided tape. For the test, the sample (circle shape with 14 mm diameter) was pressed to the PDMS film till 1 N load and pulled off till failure. The load was recorded and used for calculation of adhesive strength.

Pasting and peeling off of electrodes to skin: The skin surface was cleaned by water before pasting electrodes, no special preparation was needed. For commercial gel electrodes (Chunfeng YD-50 Ag/AgCl gel electrodes) which were designed for dry skin, water on skin

needed to be wiped off for best performance. For our electrodes, the residue water after cleaning skin had little effect on their performance; but the skin was also wiped dry to keep the same condition as the commercial ones. When in water or wet, our electrodes were not easy to peel off and partial polymer residue might stay on the skin. After step out of water and dry for 30 min, the electrodes became easy to peel off with totally no residue and could be re-used. One of the reasons is after drying the modulus of pDAM layer increased, becomes stiffer and easier to peel off. And the skin and PDMS-skin model surface are both hydrophobic without strong coordination sites for catechol groups, during drying the polymer chain movement may cause dissociation between adhesive catechol groups and skin and further restrict their interaction, leading to easier peel off. If the electrodes were peeled off after drying, there was no residue and no sign of irritation after wearing the electrode on the chest for ~2 h.

Recording of ECG signals: The ECG signals were recorded by a Heal Force PC-80B ECG Monitor with three electrodes. Two electrodes were pasted on each forearm to detect ECG signals, and one reference electrode was pasted on the belly. Commercial electrodes (Chunfeng YD-50 Ag/AgCl gel electrodes) or pDAM/Au/PDMS electrodes were used. For experiments in water, both arms were immersed in water in the same container. For water impact, a water flow with 2.0 L/min from a pipe of 6.0 mm diameter was directly drawn to the electrodes on arms. The tests on human skin were approved by Institute of Review Board, Nanyang Technological University (approval number: IRB-2017-08-035-01). The test subject was a male at age of 28.

Recording of ECG signals during swimming: The water-resistant electrode pair was pasted on the chest and connected to the wearable device which was fabricated based on a Zeetion H1 ECG device. The device was fixed on a belt, and collected signals were transferred to an application in smartphone in real-time. For signal recording, the subjected swam in breaststroke

style for 15 min. And for recording the video, the subject swam in backstroke to show the pasted electrodes.

Supplementary Figures

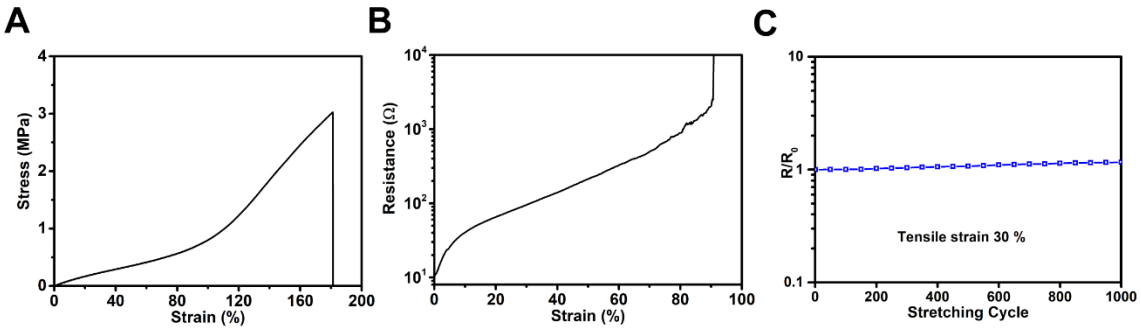


Figure S1. Characterization of Au/PDMS film. The (A) stretchability and (B) resistance change of Au/PDMS film during stretching. (C) The resistance of Au/PDMS at 0 % strain during cyclic stretching from 0 % to 30 % strain.

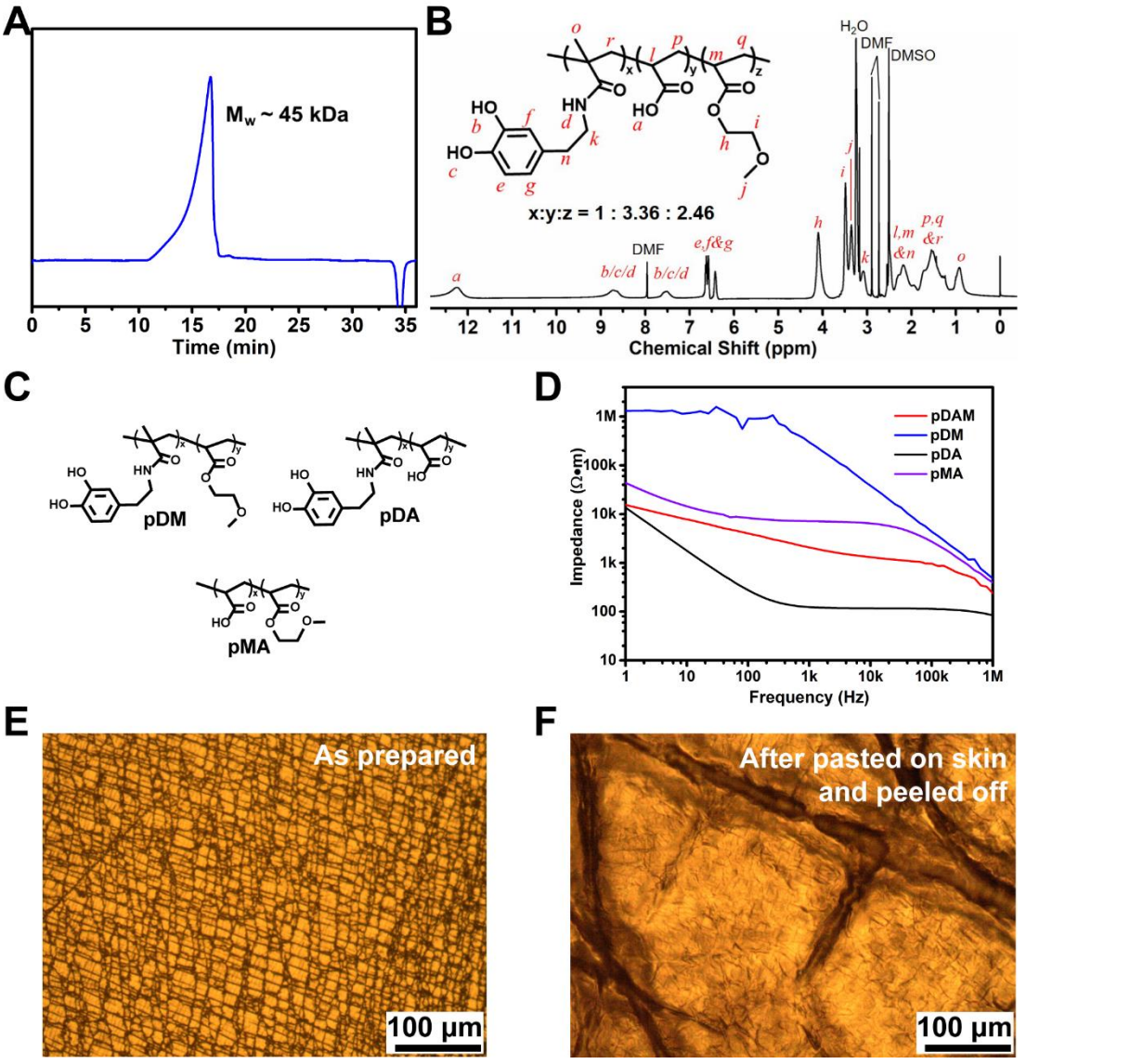


Figure S2. Characterization of the synthesized polymer. (A) GPC trace and (B) ^{1}H NMR spectrum of product pDAM. The composition was calculated by the integration of proton *e,f&g* (for DMA), *a* (for AA), and *h* (for MEA). (C) Structures of control polymers synthesized from different monomer pairs. (D) The impedance of synthesized polymers. All polymers were immersed in pure water for 10 s before the test. Microscopic image of polymer coating surface of pDAM/Au/PDMS electrode (E) as prepared, (F) after pasted on the skin and peeled off.

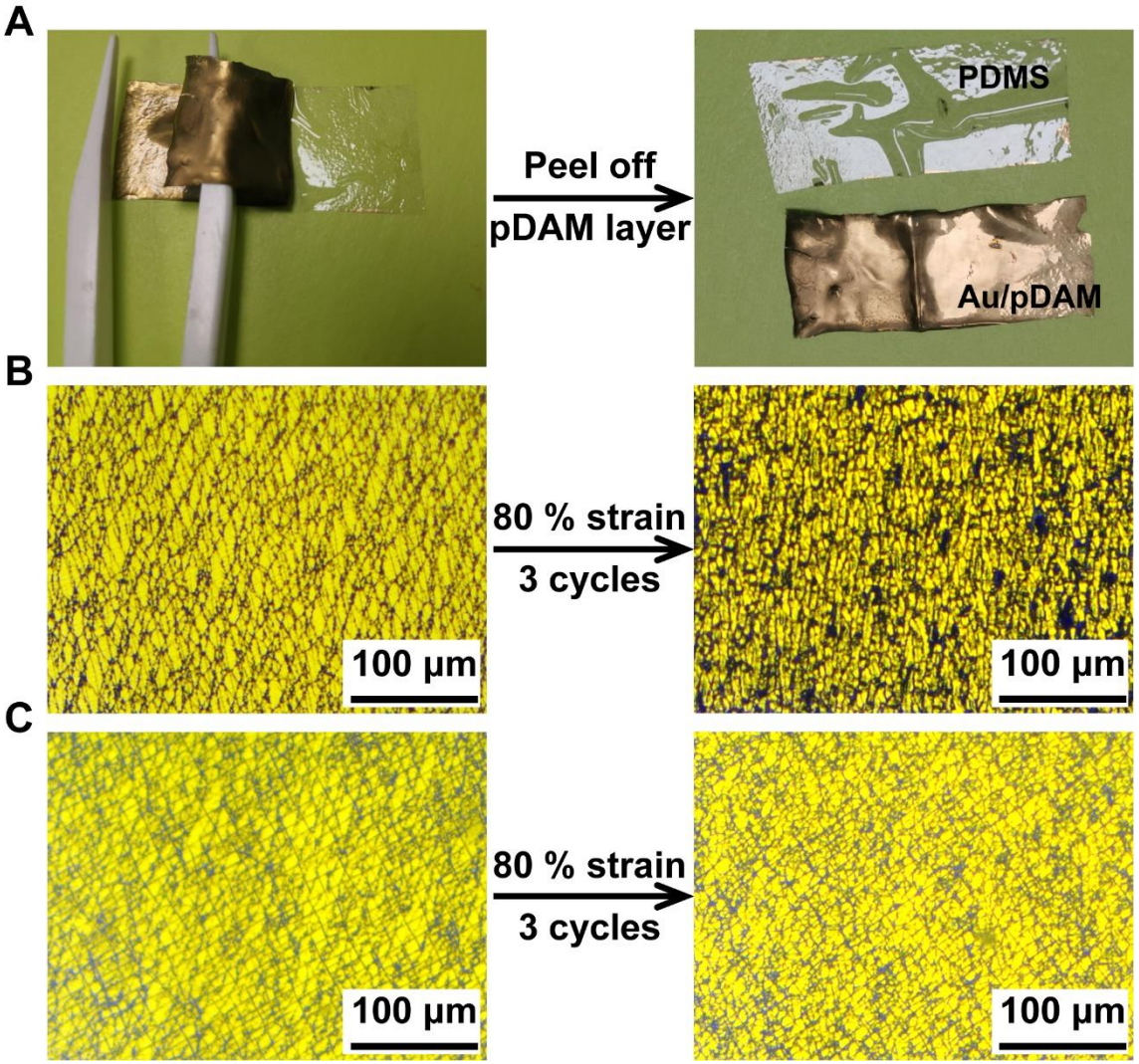


Figure S3. Adhesion between pDAM and Au layers. (A) When force peeling off the pDAM layer from the electrode, Au layer would be peeled along with pDAM, indicating a much stronger adhesion between Au and pDAM than Au and PDMS. Microscopic image of Au/PDMS film (B) and pDAM/Au/PDMS film (C) before and after stretching to 80 % strain for 3 cycles. Both Au layer showed increased cracking after stretching, the addition of pDAM layer didn't result in worse.

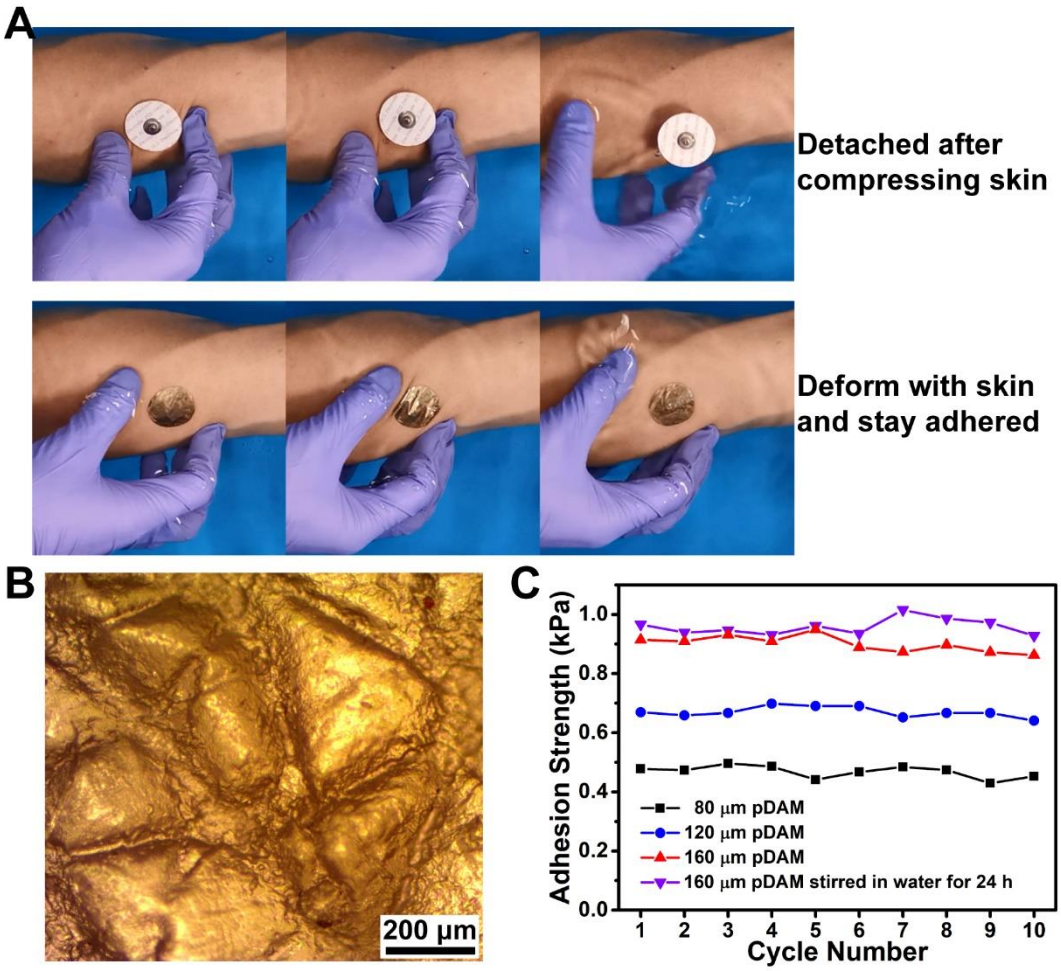


Figure S4. Test of adhesion strength. (A) Photos of compressing commercial electrode (above) or pDAM/Au/PDMS electrode (below) on the arm in water. The commercial electrodes detached from the skin when compressed, while pDAM/Au/PDMS electrodes deformed with skin and stay adhered. (B) The surface structure of PDMS-skin model. (C) The cycled adhesion test on PDMS-skin model in water with different pDAM amount on Au/PDMS films.

With increasing pDAM amount, the adhesion strength increased. The thickness of 160 μm was selected by following reasons: the adhesion strength of 160 μm pDAM was similar to commercial gel electrodes in air (Figure 2A) and was better for comparison; there were filaments formed after the 6th test cycle for 160 μm pDAM which indicated good adhesion but decreased stability, with more pDAM filaments formed easier so the thickness was not further increased for following tests.

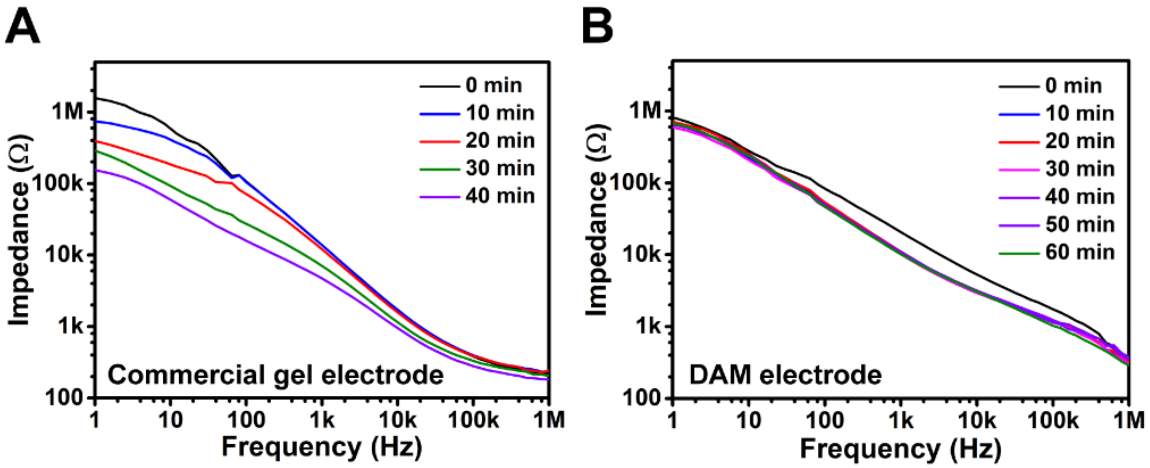


Figure S5. The skin interfacial impedance change of (A) commercial gel electrodes and (B) pDAM/Au/PDMS electrodes during water immersion. The distance between the electrode pair was 5 cm, the contact area of electrodes to skin was around 210 mm^2.

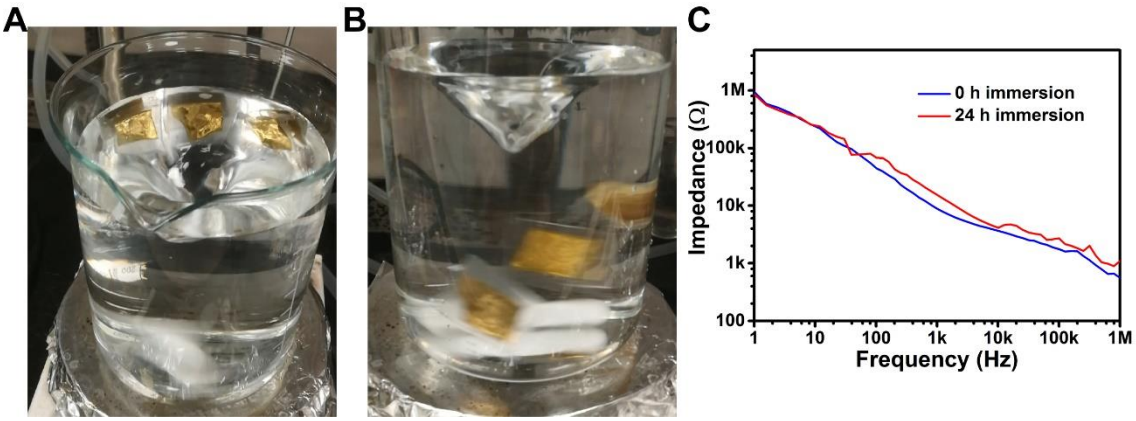


Figure S6. Stability of electrodes under extreme condition. pDAM/Au/PDMS electrodes were pasted on PDMS-skin model and stirred in water at 300 rpm for 24 h. (A) The PDMS films were fixed on the beaker by tapes in the beginning. (B) The PDMS films had detached from the beaker during the stirring due to loss of adhesion of the tape and kept stirred to the end. (C) The impedance of the electrodes before and after the immersion and stirring.

References

[S1] H. Lee, B. P. Lee, P. B. Messersmith, *Nature* **2007**, *448*, 338.