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Conducting Polymer Microelectrodes Anchored to Hydrogel Films

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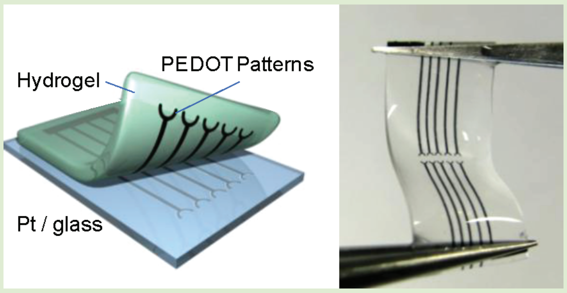
Supporting Information

ABSTRACT: We report the fabrication of totally organic hydrogel-based microelectrodes of poly(3,4-ethylenedioxythiophene) (PEDOT), which exhibit a lowered sheet resistivity of about 100 $\Omega/\square$. The preparation process starts with the electrodeposition of conductive PEDOT (ca. 20 S cm^{-1}) on Pt microelectrodes. After laminating hydrogels onto the PEDOT-modified Pt electrode substrates, a second PEDOT (low conductivity) layer was electrodeposited to anchor the first PEDOT film to the hydrogel. Finally, the hydrogel sheet with PEDOT micropatterns was peeled off by taking advantage of the electroactuation property of PEDOT. The process proved to be versatile, allowing the use of most natural and synthetic hydrogels including agarose, collagen, polyacrylamide, and so on.



Conducting polymers (CPs) such as poly(3,4-ethylenedioxythiophene) (PEDOT) are attractive electrode-coating materials, having the advantages of biocompatibility and low electrical impedance.[1−3] They have been utilized for implanted electronics[4−6] and in vitro devices for culturing cells.[7−11] In contrast to these conventional metal-supported CP electrodes, we have attempted to prepare an autonomous CP microelectrode on a hydrogel substrate that contains ~80% H_2O in order to develop a totally organic, flexible, and molecularly permeable electrode. All of the existing printing methods using screens, inkjet systems, or microstamps, require the drying of fluid inks and, thus, cannot be used for printing on a moist gel substrate. Recently, we found that the electrodeposition of PEDOT into an agarose film produces such a gel-based electrode, which is soft enough to contract synchronously with the motion of muscle cells.[12] However, the sheet resistivity of that PEDOT electrodes formed in the agarose (ca. 10 k$\Omega/\square$) was unfortunately higher than expected.[13] Apparently, dendritic growth through the hydrogel matrix[5] resulted in a larger surface area (manifested by a larger double layer capacitance) but a lower electrical conductivity due to the sparse structure. An improvement in the conductive property of the PEDOT/hydrogel electrodes should expand their possible applications.

We report herein an improved process to prepare more conductive PEDOT micropatterns on hydrogels. As shown in Figure 1a, the dense PEDOT film was first electropolymerized on Pt microelectrodes. Owing to the absence of hydrogel, we can freely employ appropriate polymerization conditions. For example, the use of CH_3CN as solvent leads to highly conductive PEDOT, as described later; the polymerization from aqueous EDOT solutions would have advantages for the biofunctionalization of PEDOT such as enzyme immobilization.[3,14] Next, as illustrated in Figure 1b,c, after forming agarose or laminating a precured other hydrogel onto the PEDOT-modified electrode substrates, a second PEDOT layer was electropolymerized from aqueous EDOT solution to anchor the first conductive PEDOT film to the hydrogel matrix. The process we previously reported[12] depended only on this sparse PEDOT for electrode preparation. Finally, the hydrogel film with PEDOT micropatterns was peeled from the Pt electrode substrate (Figure 1d) by taking advantage of the electrochemical elastic actuation of PEDOT (±0.5 V vs Ag/AgCl).[15,16]

Figure 2 shows photographs of typical specimens after the peeling process with different polymerization charges of the second PEDOT, proving its importance for nondisruptive peeling. The 1 × 1 cm Pt electrodes on glass substrates were first coated with a 300 mC PEDOT film. Next, a melted 2.8 wt % agarose solution was poured over the substrate and gelated by cooling in room temperature (2 mm thickness). Then a second PEDOT layer was electropolymerized at charges of (a) 0, (b) 100, and (c) 200 mC. Finally, twin cycles of electrochemical elastic actuation was applied for inducing stress at the polymer/electrode interface, leading to eventually

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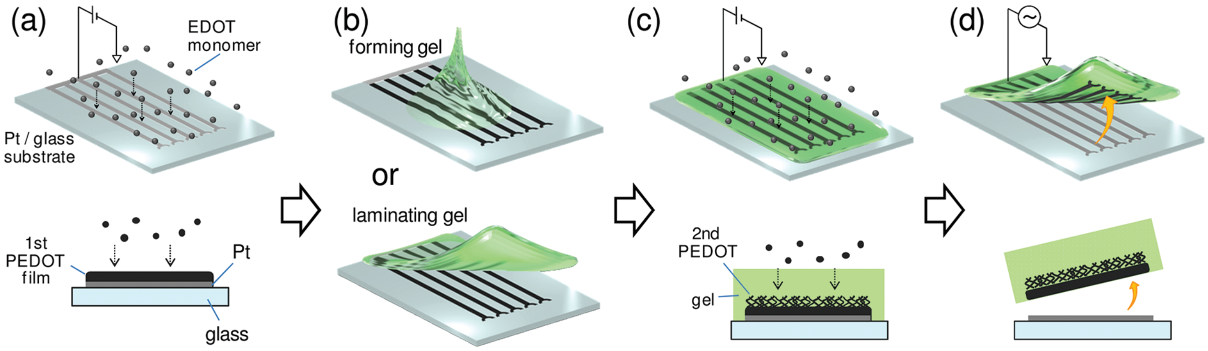

Figure 1. Schematic illustrations of the fabrication process for a conducting polymer/hydrogel electrode: (a) PEDOT was electropolymerized on a Pt microelectrode substrate; (b) a hydrogel sheet was formed or laminated on the substrate; (c) PEDOT was again polymerized; (d) then a PEDOT/hydrogel electrode was peeled from the substrate after electrochemical elastic actuation.

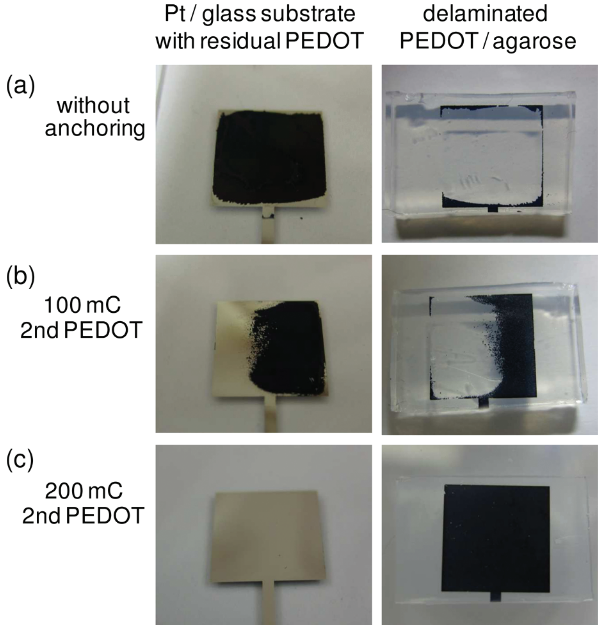

Figure 2. Photographs of Pt/glass substrates and agarose sheets after the peeling process with twin redox cycles (±0.5 V vs Ag/AgCl). The polymerization charge of the first PEDOT films was 300 mC and (a) 0, (b) 100, and (c) 200 mC for the second PEDOT layers. The polymerization was potentiostatic at 1.0 V vs Ag/AgCl in 0.1 M $LiClO_4$ aqueous solution of EDOT.

detachment. In the case without the second PEDOT deposition, a clean transfer of the pattern has never achieved (Figure 2a). The second PEDOT of 100 mC resulted in an irregular, partial transfer (Figure 2b). On the other hand, the second PEDOT of 200 mC ensured 100% transfer every time (Figure 2c), indicating that a sufficient amount of a second dendritic PEDOT layer (more than 200 mC) can serve as an effective anchor to connect the first PEDOT film and the hydrogel matrix. It is worth noting that a prior hydrophilic modification of the glass substrates with aminosilane is also necessary for nondisruptive peeling; we immersed Pt/glass substrates in 20 mM 3-aminopropyltriethoxysilane/heptane for 6 h for forming the self-assembling monolayer of aminosilane on the surface of the glass part of the substrates. Without these treatments, the naturally impure glass surface often causes anisotropic lateral growth of the polymer from the Pt electrode along the surface of the surrounding glass, resulting in adhesion between the CP and the glass substrate.[11]

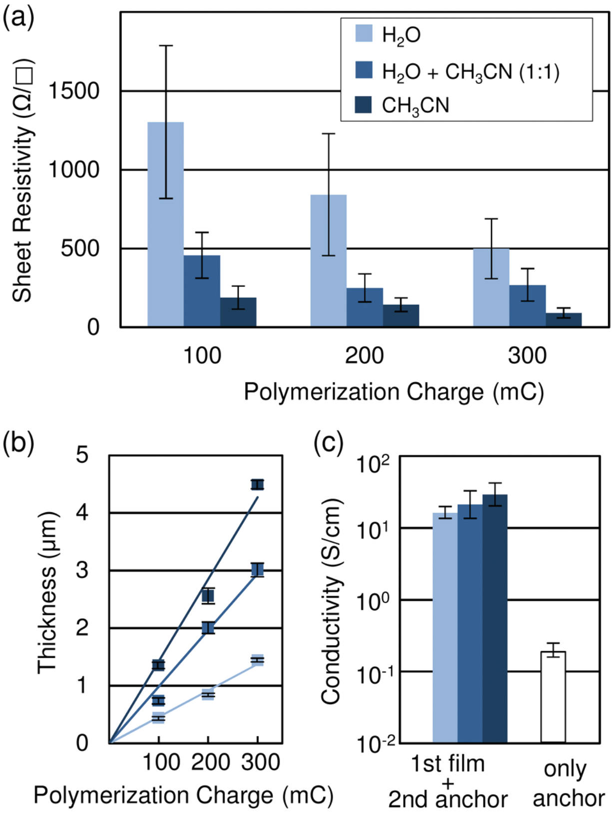

Figure 3. (a) Sheet resistivity of the PEDOT patterns (1 × 1 cm) transferred to agarose films as functions of polymerization charge of the first PEDOT film (100, 200, and 300 mC) and the solvents used for the polymerization (H_2O, CH_3CN, and their 1:1 mixture). The mean values (±standard deviation) of at least three independent specimens are given. The polymerization was potentiostatic at 1.0 V in each solution containing 50 mM EDOT and 0.1 M $LiClO_4$. The charge for second PEDOT layer was 300 mC. (b) Thickness of the first PEDOT films measured by a surface texture analyzer (DEKTAC 150). (c) Conductivity of the PEDOTs calculated by using their thickness. The conductivity value in the case without the first PEDOT film (only the second PEDOT anchor) is also shown.

With the polymerization charge of the second PEDOT fixed at 300 mC, we studied next the sheet resistivity of the peeled PEDOT patterns by changing the polymerization conditions of the first PEDOT films. The resistivity measurements were conducted under wet conditions by the two-point probe method around 0.4 V versus Ag/AgCl, where the PEDOT is in

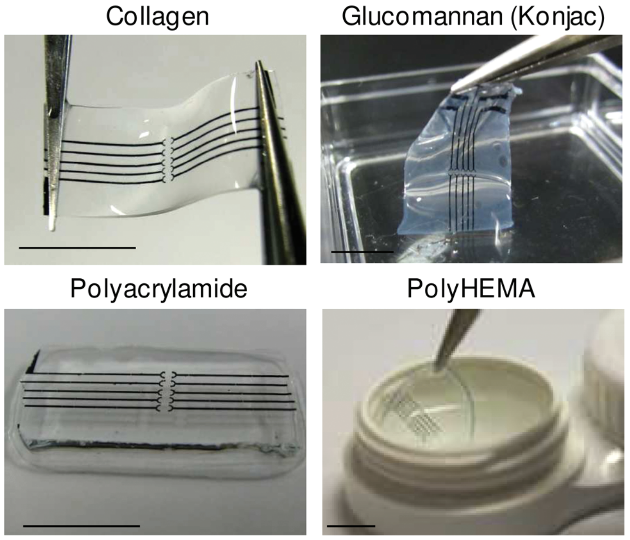

Figure 4. Photographs of the PEDOT microelectrodes anchored to the preliminarily molded hydrogel films of collagen (0.3 mm thick), glucomannan (1 mm thick), polyacrylamide (1 mm thick), and a commercial soft contact lens made of poly(2-hydroxyethyl methacrylate). Scale bar: 5 mm.

the oxidized form. The ohmic property was checked by varying the bias between the probes. Figure 3a shows that increasing the polymerization charge up to 300 mC decreased the sheet resistivity to less than 500 Ω/□, a value 2 orders of magnitude lower than that (ca. 10 kΩ/□) of the PEDOT electrode prepared by our previous process without the first PEDOT film.[12] In particular, the PEDOT film prepared using CH_3CN solvent showed the lowest resistivity, about 100 Ω/□. Presumably, polymerization at greater than 300 mC will further decrease the sheet resistivity. As shown in Figure 3b, the thickness of the first PEDOT film, measured by a surface texture analyzer, were found vary with solvents used, probably due to difference in the Coulombic efficiency of electrodeposition. The 300 mC/cm^2 polymerization led to a thickness of about 1.5 μm in H_2O, 3.0 μm in H_2O/CH_3CN, and 4.5 μm in CH_3CN, respectively. Figure 3c depicts the conductivity of the transferred PEDOTs calculated taking account of their thickness. The conductivity values of the present PEDOT electrodes reach the range of 10^1 S/cm, regardless of the kind of solvent, the value being comparable to the generally known conductivity of the PEDOT.[13] For reference, the second PEDOT layer grown in agarose showed a thickness of about 5 μm for 300 mC/cm^2,[12] as also judged from the cross section (Supporting Information, Figure S1). Because the conductivity of the second PEDOT layer grown in agarose was in the range of 10^{-1} S/cm, its contribution to the net conductivity is small; it functions simply as an anchor between the first PEDOT film and the hydrogel.

The process used to prepare PEDOT micropatterns was versatile, being also successful with precured films of other kinds of natural hydrogels (collagen, glucomannan) and synthetic hydrogels (polyacrylamide, poly(2-hydroxyethyl methacrylate)), as shown in Figure 4. In addition, the PEDOT patterning process is adaptive to the variations of elasticity, thickness and shapes of the hydrogels. For example, even a commercial soft contact lens can be used as the substrate for PEDOT electrodes. Although the structural and electrical characters of the second PEDOT would be somewhat different by the hydrogels used, they functioned well as the anchor for nondisruptive peeling of the first PEDOT, as with the case of agarose. Among the hydrogels we studied, only the fibrin gel could not be used as the substrate for PEDOT electrodes. The electrostatic and chemical conditions in fibrin may inhibit the polymerization of the second PEDOT.

The hydrogel-based CP micropatterns discussed here represent a totally organic, moist, flexible, and molecularly permeable electrode that can be combined with cells and tissues without disturbing the physiological conditions including the continuous supply of O_2 and nutrients. Such properties are ideal for use as in vivo and in vitro electrodes for stimulation and recording. Besides such cellular applications, these improved conductivity CP/gel electrodes should be applicable to a variety of hydrogel-based electronic systems such as iontophoretic drug delivery.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The optical microscope image of the cross section of PEDOT/agarose electrode. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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