Conducting Polymer Electrodes Printed on Hydrogel

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Abstract: We report herein the micropatterning of poly(3,4-ethylenedioxythiophene) (PEDOT) on a hydrogel, agarose, to provide a fully organic, moist, and flexible electrode. The PEDOT/agarose electrodes were prepared through two electrochemical processes: electropolymerization of PEDOT into the hydrogel and electrochemical-actuation-assisted peeling. We also present a typical application of the PEDOT/agarose electrode to the cultivation of contractile myotubes.

Conducting polymers such as poly(3,4-ethylenedioxythiophene) (PEDOT) and polypyrrole (PPy) are attractive electrode materials that have the advantages of biocompatibility, high capacitance, and flexibility. They have been utilized in biomedical devices,[1] including implanted electronics[2] and in vitro devices for culturing cells.[3]

We report herein the micropatterning of PEDOT by electropolymerization on a hydrogel, agarose, to provide a fully organic, moist, and flexible 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. We also present a typical application of a PEDOT/agarose electrode prepared in this manner to the cultivation of contractile myotubes; the electrodes are soft enough to effectively support the successive contraction of the myotubes.

The PEDOT/agarose electrodes were prepared through two electrochemical processes: electropolymerization of PEDOT into the hydrogel and electrochemical-actuation-assisted peeling (Figure 1). The melted 2.8 wt % agarose solution was poured over a Pt microelectrode fabricated on a glass plate. After gelation of the agarose (typical thickness 2 mm), electropolymerization was conducted on the gel-covered electrode in the aqueous monomer solution. As explained below, we found that the successive volume change of the PEDOT induced by redox cycles is effective for nondestructive peeling of the soft gel film from the master electrode.

Figure 2a shows a typical set of time courses of current and charge during the potentiostatic electropolymerization at 1.0 V vs Ag/AgCl in an aqueous solution containing 50 mM EDOT and 100 mM KNO$_3$. The time lag before the start of current flow is a result of the time required for the diffusive supply of monomer through the gel sheet. As shown in Figure 2b,c, the pattern of the master Pt electrode (b) was reprinted onto the gel sheet by the electropolymerized PEDOT (c). The print resolution depends on the polymerization time (polymerization charge). In the case of polymerization for 60 min, it can be seen that the PEDOT pattern became ∼10 μm thicker than the Pt master electrode, indicating that the PEDOT grew ∼5 μm from the electrode. The growth in the vertical direction into the gel film was also ∼5 μm, as judged from the cross-section
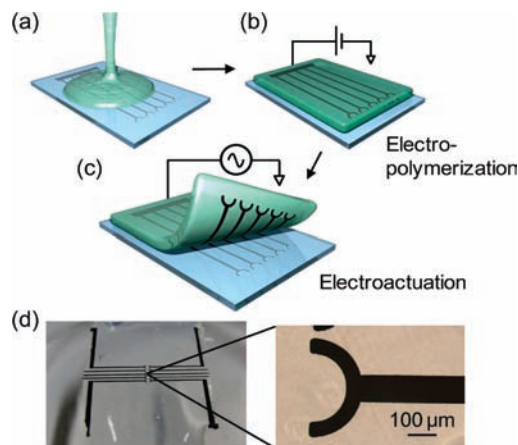

Figure 1. (a−c) Schematic illustrations of the fabrication of a conducting polymer/hydrogel electrode: (a) the melted agarose solution is poured onto a Pt microelectrode substrate; (b) PEDOT is electropolymerized into the gel and then (c) electrochemically actuated several times for peeling. (d) Photograph of the PEDOT microelectrode array on the gel sheet.

observation (Figure 2d). Such isotropic polymer growth was ensured by the previous hydrophilic modification of the glass plate with aminosilane molecules, without which the hydrophobic or naturally impure glass surface often caused anisotropic polymer growth along the substrate surface.[4]
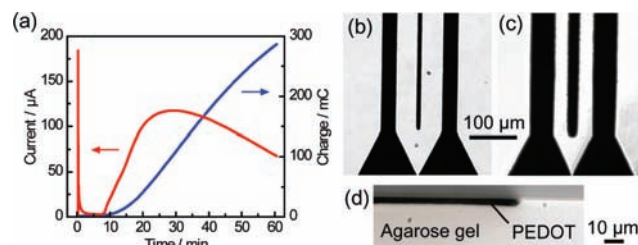

Figure 2. (a) Typical time courses of current and charge during the electropolymerization at 1.0 V vs Ag/AgCl in 50 mM EDOT + 100 mM KNO$_3$ aqueous solution. Electrode area: 45 mm^2. (b−d) Photographs of (b) a Pt master electrode on a glass plate, (c) a peeled PEDOT/agarose electrode surface, and (d) a cross section. Polymerization time: 60 min.

For the PEDOT printed on the agarose sheet by polymerization for 60 min, the surface resistance was measured under wet conditions using a four-point probe method and found to have an average value of 11.0 kΩ/□ (standard deviation = 2.7 kΩ/□, n = 11), which is in agreement with previous reports.[5] The prepared PEDOT/agarose electrode can be stored in water for more than a month.

The electropolymerized PEDOT film adhered to the Pt master electrode, and therefore, mechanically aggressive peeling collapsed the soft hydrogel (Figure 3a). Figure 3b shows that electrochemical

elastic actuation of PEDOT ($\pm$0.5 V vs Ag/AgCl) was effective in nondestructively peeling the soft gel from the master electrodes. As shown in Figure 3c, thinner polymers (smaller polymerization charge) required several successive actuation cycles, while thicker polymers could be peeled using a single actuation cycle. This conducting polymer is known to change its volume by $\sim$30% during oxidation and reduction because of the reversible incorporation of hydrated dopant ions.[6a] Such a volume change may induce stress (depending on the thickness of polymer) at the polymer/electrode interface and cause detachment of the film. In fact, similar peeling events have been a practical problem for bimorph conducting polymer actuators.[6b]
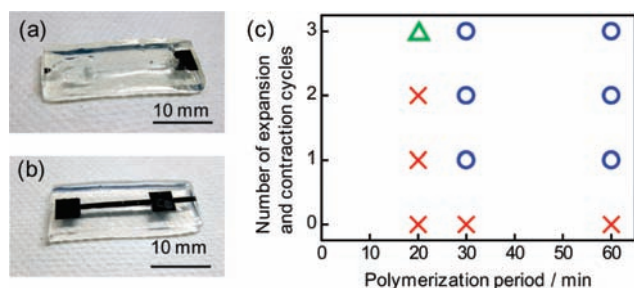

Figure 3. (a, b) Photographs of (a) collapsed and (b) successfully peeled PEDOT/agarose electrodes. (c) Plot of success and failure of the peeling for various polymerization periods (*x* axis) and electroactuation cycles (*y* axis) (*n* = 3). Success rate: ○, 100%; ×, 0%; △, 66% (2 out of 3).

Such a fully organic, moist, flexible electrode should have many unique applications, such as an in vivo lapping electrode[7] and in vitro cell cultivation. As an important example, we demonstrate herein the advantage of the present electrode for the electrical stimulation of C2C12 myotubes. A culture system of contractile myotubes is required for research on type-2 diabetes, a condition that is closely associated with defective glucose uptake in skeletal muscle.[8] Recently, we were able to prepare contractile C2C12 myotube line patterns embedded in a fibrin gel and show that the fibrin-supported myotubes maintain higher contractile activity for a longer period of time than do myotubes adhered on a conventional culture dish.[9] Figure 4a illustrates how, in the present study, the cell-embedded fibrin sheet was set on the PEDOT/agarose electrode, which was connected to an electric stimulator. A periodic voltage pulse (6 V, 0.6 s) was applied at 1 Hz to induce the cellular contraction, and the motion of the myotubes and PEDOT electrodes were analyzed.

As shown in Figure 4b and in the movie in the Supporting Information, the electrical stimulation supplied through the PEDOT electrode induced contraction of the muscle cells. Importantly, the PEDOT electrode also contracted synchronously with the motion of the cells. The smaller displacement of the hydrogel electrode than of the myotubes is presumably due to slipping between the sheets. Another important feature of the PEDOT electrode is its higher capacity, which makes it advantageous for noninvasive stimulation without electrolysis.[3]

The present strategy for preparing PEDOT/agarose electrodes can be applied to other kinds of hydrogels, such as collagen and fibrin. It may also be important that PEDOT can be electropoly-
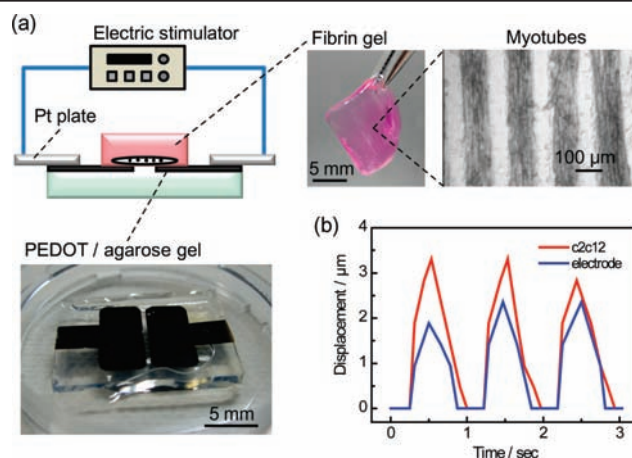

Figure 4. (a) Experimental setup for stimulation of myotubes. A fibrin gel sheet containing the micropatterned C2C12 myotubes is laid on the PEDOT/agarose electrode. (b) Time course of contractile displacements of C2C12 myotubes (red) and the PEDOT hydrogel electrode (blue). Details regarding these experiments are provided in the Supporting Information.

merized on a precured gel sheet attached to the electrode substrate. For example, a double-sided hydrogel electrode (Figure S1 in the Supporting Information) can be prepared in this way. Such variations of the technique will be reported in the near future.

Supporting Information Available: Details of myotube stimulation, a photograph of a double-sided hydrogel electrode, complete ref 7, and a movie of cell contraction (MPG). This material is available free of charge via the Internet at http://pubs.acs.org.

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