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Patterning of Stretchable Organic Electrochemical Transistors

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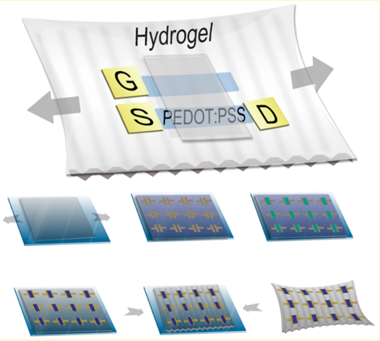
Supporting Information

ABSTRACT: The fabrication of stretchable electronic devices is presently rather challenging on account of both the limited number of materials showing the desired combination of mechanical and electrical properties and the lack of techniques to process and pattern them. Here we report on a fast and reliable transfer patterning process to fabricate high-resolution metal microelectrodes on polydimethylsiloxane (PDMS) by using ultrathin Parylene films (2 μm thick). By combining transfer patterning of metal electrodes with orthogonal patterning of the conducting polymer poly(3,4-ethylenedioxythiophene) doped with polystyrenesulfonate (PEDOT:PSS) on a prestretched PDMS substrate and a biocompatible "cut and paste" hydrogel, we demonstrated a fully stretchable organic electrochemical transistor, relevant for wearable electronics, biosensors, and surface electrodes to monitor body conditions.



INTRODUCTION

Stretchable electronic devices, based on materials combining high electrical conductivity with mechanical elasticity, are of great interest for applications in wearable electronics and bioelectronics. They can be placed on textiles, three-dimensional objects, and soft biological tissues such as skin, heart, brain, and muscles to monitor electrical and mechanical signals as well as body conditions.[1] Significant progress in the development of stretchable electronic devices has been achieved in recent years. Devices showing attachable,[2] implantable,[3] self-healing,[4] and dissolvable features[5] have been used for several in vitro or in vivo applications. Rogers and co-workers developed high-performance stretchable integrated circuits by buckling ultrathin inorganic films.[6,7] Bao and co-workers explored stretchable electronic skin,[8] capacitive pressure sensors,[9] and solar cells[10] based on conducting polymers and carbon nanotubes. Lacour and co-workers proposed a strategy to increase the stretchability of metal films and electronic interconnects on elastomer surfaces.[11,12] Someya and co-workers reported stretchable ultralightweight transistors[13] and stretchable displays.[14] Other groups also reported stretchable devices based on nanomaterials, such as carbon nanotubes,[15] graphene,[16] ionic conductors,[17] and liquid metals.[18]

The large majority of stretchable electronic devices are currently fabricated on the organosilicon compound polydimethylsiloxane (PDMS).[19] PDMS offers a number of unique and attractive features, such as optical transparency, biocompatibility, ease of process, and a moderate elastic modulus, which permits conformable surface coverage of a wide variety of surfaces.[20] The key steps for the fabrication of high-resolution stretchable electronic devices (e.g., transistors) on PDMS are the patterning of the metallic contacts and the electroactive material. In principle, several techniques can be used for these processes, such as shadow masking, elastomer stamp, printing, and photolithography. Shadow masking, although very simple, presents several drawbacks, such as limited lateral resolutions (tens of microns), diffusion of material below the mask features, mask clogging after a few uses (especially for small features) and contact with substrate leading to materials damage. Besides that, this technique is unsuitable for alignment of multilayer patterning. The use of elastomer stamps requires critical control of the adhesion between the carrier stamp and donor/acceptor substrates, which sometimes produces low yield due to variation of the contact area.[21] As a result, transferred patterned metallic electrodes onto soft substrates using this method have minimum feature sizes of tens of micrometers.[22] Printing techniques (e.g., inkjet or screen printing), although very promising to produce large-scale patterns on PDMS, still have limited lateral resolution (typically above 20 μm).[23,24] In addition, ink formulation and alignment of multilayer patterns remain very challenging. Photolithography, on the other hand, yields high resolution on multilayer patterns with high throughput, without contact with the substrate. However, on PDMS and other elastomers, the use of photolithography results in low yield, due to poor adhesion of the photoresist on elastomer surfaces,[25] swelling of the elastomer induced by organic solvents, and when chemical etching is used, diffusion of corrosive chemicals into the porous PDMS matrix, an undesirable effect for bioelectronics devices to be interfaced with living systems.[26−29] Therefore, an alternative high-fidelity process to pattern high-resolution features on stretchable substrates is highly desirable.

In this work, we propose high-fidelity processes to pattern both metal electrodes and organic electroactive materials on PDMS with high resolution. Metal electrodes, with a channel

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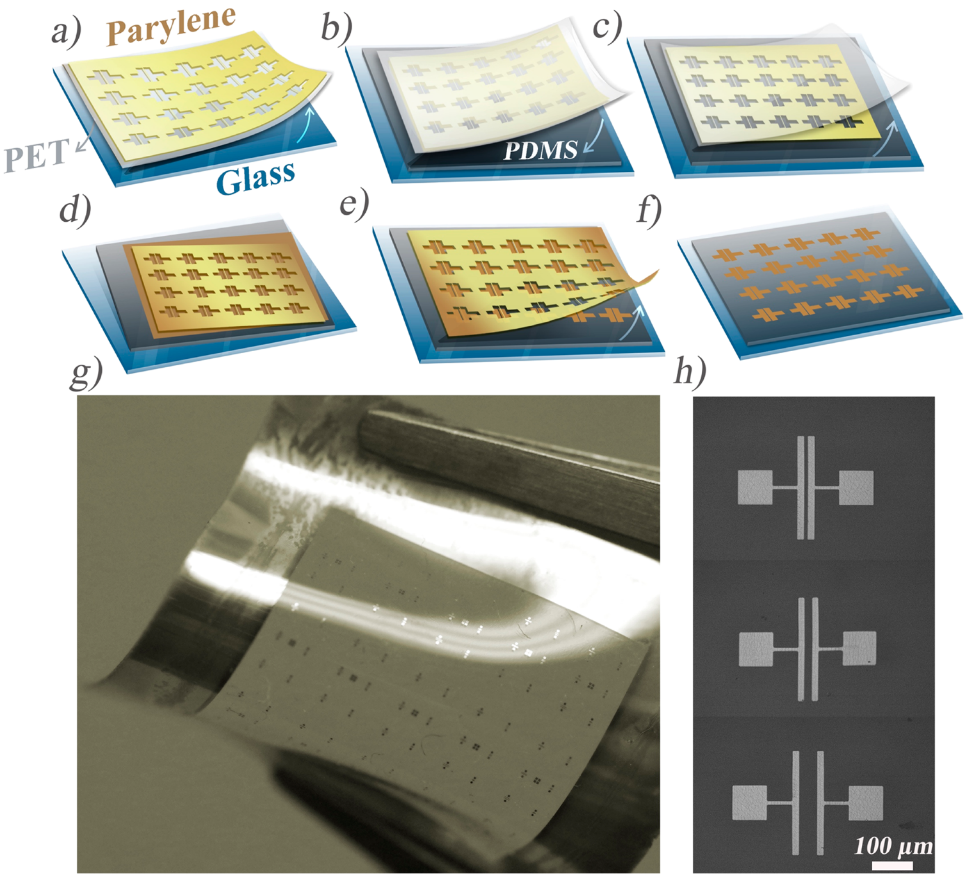

Figure 1. Parylene transfer process used to fabricate microelectrode arrays on PDMS. (a) Detaching PET (CTAB-treated)-carried Parylene patterns from glass; (b) laminating of the PET/Parylene onto freshly prepared PDMS; (c) detaching PET, leaving Parylene patterns on PDMS; (d) metal deposition; (e) lift-off of the Parylene film; (f) electrode arrays on PDMS; (g) PDMS patterned with Au electrodes with substrate dimension of 15 mm × 15 mm; and (h) Au microelectrodes with channel lengths of 5, 20, and 50 μm.

length as short as 5 μm, were realized using Parylene transfer patterning, whereas the organic electroactive material was patterned by unconventional orthogonal photolithography. By taking advantage of those two patterning techniques and of a "cut and paste" hydrogel as stretchable electrolyte, we demonstrated a fully stretchable organic electrochemical transistors (OECTs). The biocompatibility of all device components make our technology viable for in vivo bioelectronics.

■ RESULTS AND DISCUSSION

We fabricated organic electrochemical transistors (OECT) on PDMS by using a combination of Parylene pattern transfer and orthogonal photolithography. We demonstrated both microscale devices, with channel lengths as low as 5 μm, and fully stretchable devices, featuring larger dimensions to facilitate probing.

Thin films of the chemically stable and biocompatible polymer Parylene (ca. 2 μm thickness, comparable to photoresist thickness) can be used as seamless sacrificial masks to pattern microbioelectronic devices, such as organic neural pixels[30] and OECTs,[31−33] used for in vivo recording of brain activity[34] or treatment of neuropathic pain.[35] However, Parylene patterning on PDMS is challenging due to the strong adhesion between these two materials, which makes difficult the removal (lift-off) of the parylene the Parylene mask after material deposition.[36] To circumvent this problem and pattern the metallic electrodes on PDMS, we first deposited a thin Parylene film (2 μm) on a flexible polyethylene terephthalate (PET) sheet attached to a glass substrate to ensure its flatness during the photolithography process (Figure 1 and experimental part). We created patterns corresponding to the desired microelectrode geometry on the Parylene layer by photolithography and reactive ion etching. Successively, we detached the PET sheet carrying the patterned Parylene from the glass support (Figure 1a) and gently attached it to freshly prepared PDMS (Figure 1b). Because of the higher adhesion force of Parylene onto PDMS with respect to the surfactant-treated PET (Figure 1c), detaching of the PET sheet leads to the transfer of the patterned Parylene film to the PDMS, thus creating a seamless mask for metal deposition. After Au deposition (Figure 1d), we mechanically peeled off the patterned Parylene from the PDMS (Figure 1e), leaving the desired Au pattern on the PDMS (Figure 1f). Notably, the Parylene film is not damaged by this process and can therefore be reused (see Figure S1). We would like to stress that this fabrication process permitted us to pattern electrodes with distances as short as 5 μm (Figure 1g and Figure 1h) with a yield close to 100% (see Video S1). Moreover, the process is totally dry and is carried out at room temperature, thus being viable for large-scale, roll-to-roll production of devices on elastomers.

After patterning of the contacts, we performed patterning of the organic active material, in our case the conducting polymer, poly(3,4-ethylenedioxythiophene) polystyrenesulfonate (PEDOT:PSS). Conventional photolithography is not suitable for

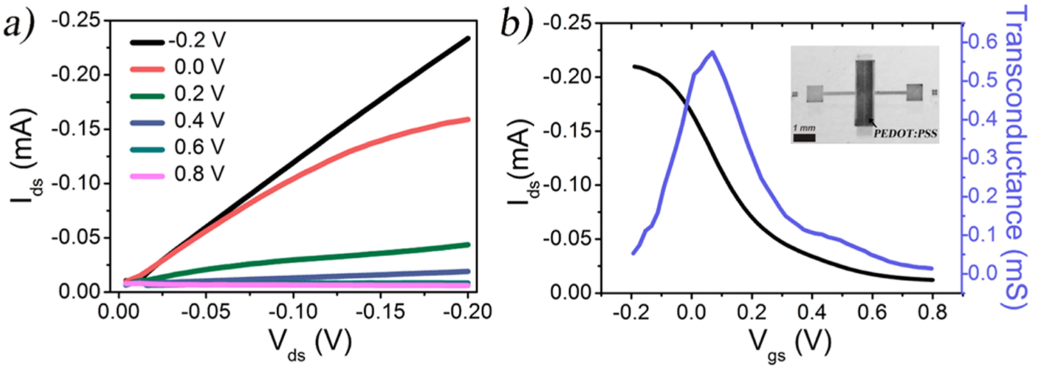

Figure 2. Electrical characteristics of PEDOT:PSS micro-OECTs on PDMS. (a) Output (V_{gs} varying from −0.2 to 0.8 V) and (b) transfer characteristics (V_{ds} = −0.2 V) with associated transconductance. Optical micrograph of the patterned OECT with channel width of 4000 μm, channel length of 10 μm, and channel thickness of about 400 nm (inset). The dark region corresponds to the patterned PEDOT:PSS film.

this purpose because exposure to photoresists, solvents, and developers leads to chemical deterioration of organic electronic materials.[31] Here, we patterned the PEDOT:PSS film on PDMS via orthogonal photolithography, which is based on fluorinated photoresists, developers, and strippers that are totally inert to organic materials,[37−41] by adapting a process we recently developed for PET flexible substrates.[37] Combining Parylene pattern transfer and orthogonal lithography, we fabricated the first microscale OECTs on PDMS, featuring channel lengths as small as 5 μm (inset of Figure 2b). The OECT fabrication was completed by exposing the PEDOT:PSS channel to a 0.01 M aqueous solution of CTAB (confined within a PDMS or glass well), with a high surface area activated carbon (AC) gate electrode immersed in it. As shown in our previous work, the combination of AC gate and CTAB electrolyte leads to high current modulation in OECTs.[42] Our devices show the typical behavior of PEDOT:PSS OECTs working in depletion mode (Figure 2a). The device performance remained stable for successive cyclic transient measurements (Figure S2). From the transfer curves (Figure 2b), we extracted a maximum transconductance (i.e., I_{ds} sensitivity to V_g variations) of about 0.6 mS (at V_{gs} = 0.1 V), a value comparable to those typically measured for devices on more conventional glass[43] or plastic substrates.[37] Micro-OECTs on PDMS with relatively high transconductance are promising as conformal devices for in vivo (bio) sensing applications[34,44] and for detection of electrically active single cells, whose dimensions are in the range 1−10 μm.[44]

Although the ON/OFF ratio can be increased by increasing the PEDOT:PSS film thickness (Figure S3), it remains lower than that obtained on glass or PET substrates,[37,42] indicating a more difficult doping/dedoping of PEDOT:PSS, likely due to a higher concentration of impurities at the PEDOT:PSS/PDMS interface.[45]

Patterning of OECTs on stretchable PDMS substrates can be exploited to obtain fully stretchable OECTs (i.e., devices with stretchable electrodes, channel, and electrolyte). Stretchable transistors based on organic semiconductors, such as pentacene[14] and poly(3-hexylthiophene) (P3HT),[46] have been recently reported. However, these materials cannot compete with PEDOT:PSS for in vivo bioelectronics due to their lower sensitivity (transconductance) and instability in air and water. A possible strategy to achieve stretchable devices is to use intrinsically stretchable materials for all the device components. However, although intrinsic stretchability can be achieved for PEDOT:PSS (via blending with soft polymers[47] or plasticizers[48]), the same is not possible for evaporated metallic electrodes. An advantageous approach to achieve stretchable devices is the buckling method. As first shown by Whitesides et al.,[49] deposition of high-modulus thin films on expanded (prestretched) PDMS substrates leads to the formation of buckled (wavy) films upon relaxation. The buckled structure permits all the components on PDMS to be stretched up to the value of the prestrain, without considerable degradation of the active components. To verify the effect of the prestretching, we measured the variation of the current flowing in buckled PEDOT:PSS films upon stretching the PDMS substrate along the longitudinal direction of the film (current versus strain, Figure 3c). Our data demonstrates that PEDOT:PSS films show an unchanged current flow up to applied strain

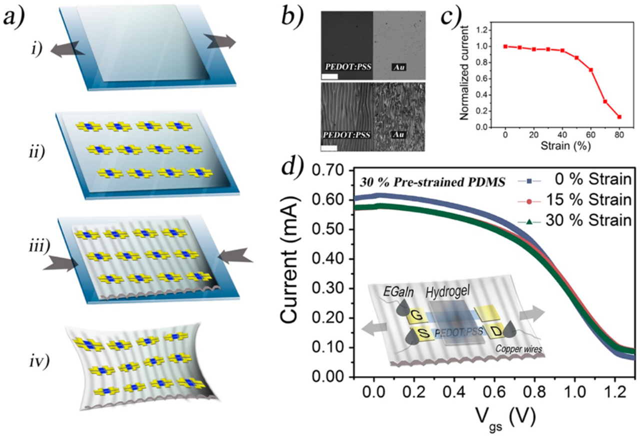

Figure 3. (a) Fabrication of stretchable OECT, using Parylene transfer and orthogonal patterning, carried out on 30% prestrained PDMS: (i) Prestretching PDMS substrate; (ii) Au patterning via Parylene transfer and PEDOT:PSS patterning via orthogonal photolithography; (iii) stretchable OECTs obtained upon PDMS relaxation; (iv) detachment of PDMS from glass substrate; (b) optical images of PEDOT:PSS and Au film surface morphology showing a transition from smooth to buckled morphology after release of prestretched PDMS; (c) prestretching effect on the stain-current profile of the PEDOT:PSS channel on PDMS; PEDOT:PSS films (with 5 % (v/v) glycerol and 1 % (v/v) Capstone FS-30) deposited on 30% prestretched substrate; d) transfer characteristics (V_{ds} = −0.5 V) of stretchable OECTs at 0%, 15%, and 30% strains. The inset shows the schematic representation of our OECT configuration. The distance between the PEDOT:PSS gate and channel is 200 μm. The channel and the gate electrode are both 8 mm long and 2 mm wide.

percentages close to the initial prestretching (i.e., films deposited on 30% prestretched substrates show an unchanged current flow up to about 30% applied strain). We therefore carried out device patterning on a PDMS substrate prestretched by 30% of initial length (the maximum strain human skin can undergo[50]), which resulted in buckled OECTs upon releasing the prestrain (Figure 3a−c). In agreement with previous literature,[48] optical microscopy images show that the application of larger strains (i.e., 45% and 60%) leads to the formation of cracks in PEDOT:PSS films (Figure S4), in turn resulting in a current decrease. Imaging of the bucked Au contacts shows that no cracks are formed in the films within 30% strain, and microcracks appear at larger strains[12] (Figure S5). To permit the measurement of the strain-dependent behavior of our buckled OECTs on PDMS, we employed devices using a planar PEDOT:PSS gate, parallel to the PEDOT:PSS channel. A polyacrylamide-based stretchable hydrogel containing sodium chloride (NaCl) was used as the electrolyte (see experimental part and Video S2).[51,52] The channel and electrode dimensions were increased from micrometer to millimeter scale, to facilitate hydrogel assembling onto the device electrical and electrical probing during device stretching.[46,53] The strain-dependent OECT electrical characteristics were measured in the following order: no strain applied, application of 15% strain and, finally, application of 30% strain. As shown in Figure 3d, the devices operate at low voltage range (0−1.2 V), demonstrating that the stretchable hydrogel can efficiently induce reversible PEDOT:PSS doping/dedoping. Significantly, the OECT shows identical transfer (Figure 3d) and transconductance (Figure S6) characteristics under 0%, 15%, and 30% applied strains. These results demonstrate the potential of our stretchable OECTs toward in vivo conformable sensing applications. For larger applied strains (50% and 65%), the transistor performance deteriorates (Figure S7), in line with morphological changes observed by optical microscopy (Figure S4). The long-term cyclic stability test shows a decrease in the source-drain current after multiple cycles (Figure S8), which could be related to changes in PEDOT:PSS morphology and the viscoelastic properties of the PDMS substrate, in agreement with previous findings for P3HT on PDMS.[46]

■ CONCLUSIONS

We have developed a new process to pattern metal microelectrodes on PDMS substrate based on Parylene transfer pattern. This process permits the high fidelity transfer of microscale patterns, with a totally dry process, from flexible substrates onto stretchable substrates such as PDMS, which are challenging to pattern by conventional lithography. Parylene pattern transfer of metal contacts together with conducting polymer patterning with orthogonal photolithography have been used to fabricate microscale OECTs on PDMS. Fully stretchable OECTs were developed by employing these pattern processes on a prestretched PDMS substrates and by using a cut-and paste stretchable acrylamide-based hydrogel as the electrolyte.

These results pave the way to the development of new technologies for conformal/implantable healthcare devices for in vivo bioelectronic studies, electronic skins, or wearable sensors, and they help to overcome some of the challenges associated with fabrication of stretchable devices, especially those requiring both high resolution and biocompatibility. In addition, the high fidelity and scalability of the Parylene transfer pattern makes it a reliable way to fabricate thin film electrodes or driving circuits on elastomers, with possible applications in next generation large-area stretchable displays and wearable electronics. Further high-impact applications of our technology can be achieved by integrating stretchable OECTs with flexible/stretchable light sources (e.g., OLEDs) for the fabrication of tactile sensors and interfacing stretchable electrodes to the human body to detect electromyography or electrocardiography signals.

■ EXPERIMENTAL SECTION

Materials. Polydimethylsiloxane (PDMS, Sylgard 184 silicone elastomer kit) was purchased from Dow Corning. Polyethylene terephthalate (PET) sheets were purchased from Policrom Inc. (Bensalem, PA, U.S.A.). Parylene (Parylene C) was purchased from SCS coating. The PEDOT:PSS aqueous suspension (Clevios PH1000) was purchased from Heraeus Electronic Materials GmbH (Leverkusen, Germany). Glycerol (99.5+ % purity) was purchased from Caledon Laboratories Ltd. (Georgetown, ON). Capstone FS-30 was purchased from Alfa Chemicals. The fluorinated photoresist kit, including a negative tone chemically amplified photoresist (OSCoR 4000), a developer (Orthogonal developer 700), and a stripper (Stripper 103), was supplied by Orthogonal Inc. (Rochester, NY, U.S.A.). Hexadecyltrimethylammonium bromide (or cetyltrimethylammonium bromide, CTAB), sodium chloride, the liquid metal alloy EGaIn and acrylamide used for hydrogel synthesis were purchased from Sigma-Aldrich Canada Ltd. (Oakville, ON). CTAB solutions were prepared by dissolving CTAB salt in deionized water.

Parylene Patterning. PET sheets were cleaned by sequential sonication in acetone, isopropanol, and deionized (DI) water (10 min for each step), dried using nitrogen flow and laminated on glass slides precoated with a PDMS adhesion layer, to ensure PET flatness and rigidity during the following lithography steps. To facilitate Parylene peel-off at the end of the process, a CTAB solution (0.005 M) was spin coated on the PET substrate prior to Parylene coating. Within 30 min after CTAB spin coating, 2 μm of Parylene (Parylene C, SCS coating) was deposited. The photoresist SPR 220.3 (Micro Chemicals Ltd.) was spin coated on the Parylene layer, and then the samples were exposed to the UV light of a mask aligner (Karl Suss MA6) and developed in the developer AZ-726 (Micro Chemicals Ltd.). Next, the unprotected Parylene was etched with an oxygen plasma in a RIE chamber (ENI OEM-6 apparatus). After the etching process, the remaining photoresist was stripped using PG 1165 (Micro Chemicals Ltd.) and the PET with the patterned Parylene layer on top was detached from the PDMS. A similar procedure was used to pattern Parylene film on glass and silicon.

Preparation of PDMS Substrates. Glass slides were cleaned using acetone, isopropyl alcohol, and DI-water and dusted off using a nitrogen gun. They were then spin coated with CTAB solution (0.005 M) acting as an antiadhesive for the PDMS peel-off at the end of the process. Next, the premixed PDMS (base:curing agent ratio of 10:1) was spin coated on the glass substrates at 500 rpm for 30s. Afterward, the samples were cured at 85 °C for 40 min in an oven. Finally, the PDMS substrates (thickness of about 300 μm) were detached from the glass slides using tweezers.

PEDOT:PSS Processing, Patterning, and Device Fabrication. OECTs were fabricated by first defining Parylene patterns on PDMS. After the Parylene film transfer onto PDMS (see main text), 4 nm of Cr and 40 nm Au were deposited using E-beam evaporation. After metal deposition, the patterned Parylene film was manually peeled from PDMS, leaving the microelectrode arrays on PDMS.

PEDOT:PSS aqueous suspensions (PH 1000) were first stirred for 3 min and then mixed with glycerol (5 v/v%) and Capstone FS-30 (1 v/v%) in a centrifugal mixer (Thinky M310) at 2000 rpm for 5 min. Glycerol is used to enhance film a conductivity and 1 Capstone FS-30 to enable the wetting on PDMS. The detailed effects of the Capstone FS-30 on PEDOT:PSS film conductivity, chemical composition, and morphology are shown in Figures S9−S11.

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The resulting suspension was then spin coated on PDMS substrates pretreated with UV/O_3 for 20 min. After drying of the PEDOT:PSS film on a hot plate at 100 °C for 30 min, the negative-tone OSCoR 4000 fluorinated photoresist was spin coated (1000 rpm, 30s) on the PEDOT:PSS film and baked on a hot plate (90 °C, 1 min). The samples were then exposed to the UV light of the mask aligner (Karl Suss MA-6/BA-6) through a photomask for 5 s. After postexposure baking (85 °C, 1 min), the unexposed photoresist was developed using a "puddle" method: the developer (Orthogonal 103) was dropped on the samples for 25 s, and then the spin coater was started. The unprotected PEDOT:PSS film was then etched by an oxygen reactive-ion etching (RIE). The exposed photoresist remaining on the patterned PEDOT:PSS film was removed by a 3 min stripping process (using Orthogonal 700 stripper). For the micro-OECT, a PDMS well was placed on the micro-OECT to confine the electrolyte (a 10^{-3} M CTAB aqueous solution), and a high-surface-area (1000−2000 m^2g^{-1}) activated carbon was used as the gate electrode. For the stretchable OECT, an acrylamide-based hydrogel (i.e., pasted on the channel and gate) was used as the stretchable electrolyte, and a PEDOT:PSS film was used as the planar gate electrode. Devices operated at 50% and 65% applied strain used gallium indium (EGaIn, liquid metal) electrodes and a 0.01 M NaCl solution as the electrolyte.

Hydrogel Synthesis. To prepare our stretchable hydrogel, we adapted to our application a procedure reported in the literature.[51] We prepared a mixture of acrylamide 2.2 M (3.1 g) and NaCl 0.1 M (0.12 g) in 20 mL of Milli-Q water. After dissolution of the monomer and of the salt, which took approximately 15 min, the solution was cooled in an ice bath, and then the cross-linking agent (*N*,*N*′- methylenebis-(acrylamide): 6 mg), the thermo-initiator (ammonium persulfate: 19 mg), and the accelerator of polymerization (*N*,*N*,*N*′,*N*′-tetramethyl ethylene diamine: 6 μL) were added while stirring. The transparent solution was then drop-casted onto a glass substrate. The samples were then gelled on a hot plate at 80 °C for 10 min. The hydrogel thin film obtained in this way is transparent and stretchable, and subsequently, it could be cut into the desired shapes with a razor blade and then pasted onto the PDMS substrates.

Characterization of PEDOT:PSS Films and Devices. Film thickness measurements were performed with a Dektak 150 profilometer. The sheet resistance of PEDOT:PSS films was measured by Jandel four-point probe equipment with a Keithley 2400 voltage−current source measure unit. The prestretching effect was evaluated by measuring the current flowing in PEDOT:PSS films between two eutectic gallium indium (EGaIn, liquid metal) electrodes, as a function of the applied tensile strain percentage for PEDOT:PSS films on PDMS. The films are 10 mm wide, 35 mm long, and about 400 nm thick. The applied strain percentage is defined as $[(L' - L)/L] \times 100\%$ where L and L' denote, respectively, the relaxed and stretched lengths of the PDMS substrate. The current is normalized with respect to the value measured for unstretched films. The transistor electrical characteristics were measured with Agilent B2900A, controlled with Quick IV Measurement software, and the strain was either applied in situ with an Instron E-3000 tensile tester or with a LabVIEW software-controlled tensile tester. The OECT electrical measurements (output, transfer, transient) were performed using an Agilent B2902A source-measure unit controlled by LabVIEW software.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.7b00181.

> Optical images of delaminated Parylene film from PDMS, transient behavior of micro-OECTs on PDMS, PEDOT:PSS thickness effect on the OECT ON/OFF ratio, optical images of Ti/Au and PEDOT:PSS films at different strains, OECT transconductance, transfer and stability curves at different strains, XPS of PEDOT:PSS films with Capstone FS-30, and the effect of Capstone FS-30 addition on PEDOT:PSS film morphology and conductivity (PDF)
>
> Video S1: shows the fabrication process, which permitted pattern electrodes with distances as short as 5 μm and a yield close to 100% (MPG)
>
> Video S2: shows a stretchable electrochemical transistor featuring a PEDOT:PSS channel, a PEDOT:PSS gate electrode, Au source/drain electrodes and an polyacrylamide-based stretchable hydrogel containing sodium chloride as the electrolyte (MPG)

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Notes

The authors declare no competing financial interest.

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