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Electronic Supplementary Information

Water stability and orthogonal patterning of flexible micro-electrochemical transistors on plastic

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Experimental details:

Polyethylene terephthalate (PET) substrates were cleaned by sequential sonication in acetone, isopropanol and de-ionized (DI) water, (10 min for each step), dried using nitrogen flow and laminated on a cleaned glass wafer pre covered with a 300 μm polydimethylsiloxane (PDMS) layer (spin-coated at 500 rpm for 40 s), which served as an adhesive layer to ensure flatness and rigidity during the successive patterning steps. Au source/drain contacts (40 nm thickness with 4 nm Cr/Ti as adhesion layer), with distances ranging from 100 μm to 5 μm, were patterned by photolithography, metal deposition and lift-off using SPR 220.3 (MicroChem) as the photoresist (ca. 2.5 um), AZ-726 (Micro Chemicals) as the developer (4 min immersion) and PG 1165 (MicroChem) as the stripper. PEDOT:PSS OECT channels were patterned using a subtractive process consisting of film deposition, photolithography, etching and lift off. PEDOT:PSS films were first deposited on the Au-patterned PET substrates after a 10 min UV-ozone treatment of the substrate. The films were spin coating for a mixture containing filtered Clevios PH1000 (previously filtered through a 0.45 um cellulose syringe filter), the conductivity enhancer glycerol (5 v/v.%) and occasionally dodecylbenzenesulfonic acid (DBSA, 0.5 v/v.%) and 3-glycidoxypropyltrimethoxysilane (GOPS, 1 v/v.%). Prior to spin coating the mixtures were homogenized in a planetary Thinky Mixer (ARM-310) for 5 min at 2000 rpm. After spin coating, the films were immediately dried on a hotplate at 100 °C for 20 min. The negative-tone OSCoR 4000 fluorinated photoresist (Orthogonal, Inc.) was then spin-coated on the PEDOT:PSS film (1000 rpm for 30 seconds), baked on a hotplate (90 °C, 1 min) and exposed to the UV light of the mask aligner (for ca. 1 second) through a photomask. After a post-exposure baking (85 °C, 1 min), the unexposed photoresist was developed using a double-puddle method (30 seconds etch): the developer (Developer 103, Orthogonal, Inc.) was dropped on the sample covered with the photoresist and left on it for 25 s to react, then the spin-coating was started to remove the developer. This process was repeated two times. The unprotected PEDOT:PSS was then etched by an oxygen reactive ion etching (RIE) plasma for 1 min (150W, 125 mTorr and 10 standard cubic centimeters per minute, sccm) and the exposed photoresist remaining on the patterned PEDOT:PSS film was removed by a three minutes stripping process (Stripper 700, Orthogonal, Inc.). Subsequently, a further photolithography step (same procedure as mentioned above) was used to cover the Au electrodes with photoresist in order to prevent direct contact between Au and the electrolyte. At the end of the fabrication process, the devices were soaked in DI water for 10 min to remove water soluble contaminants from the PEDOT:PSS films. This procedure yielded transistors featuring channel lengths ranging from 5 μm to 100 μm and channel with of 80 μm and 400 μm. Finally, the PET foil is peeled-off PET from PDMS/glass substrates. For device characterizations, a glass well was attached on the channel area using PDMS layer to confine the electrolytes and then the samples were placed in an oven at 80 °C for 20 min to solidify the PDMS. The OECTs were characterized by recording source–drain current (I_{ds}) versus time (t), versus drain voltage (V_{ds}) or gate voltage (V_g). A high surface area (1000~2000 m^2g^{-1}) activated carbon was used as the gate electrode. Before depositing PEDOT:PSS films on glass (CORNING) substrates, the glasses were pre-cleaned with Acetone, IPA and DI water in sonication bath for 10-min each, followed by a UV treatment for 10-min. For the CV measurements, we used a three electrode configuration where a PEDOT:PSS film on plastic acted as the working electrode, Pt foil as the counter electrode and aq. Ag/AgCl as the reference electrode. The scan rate was 100 mV/s.

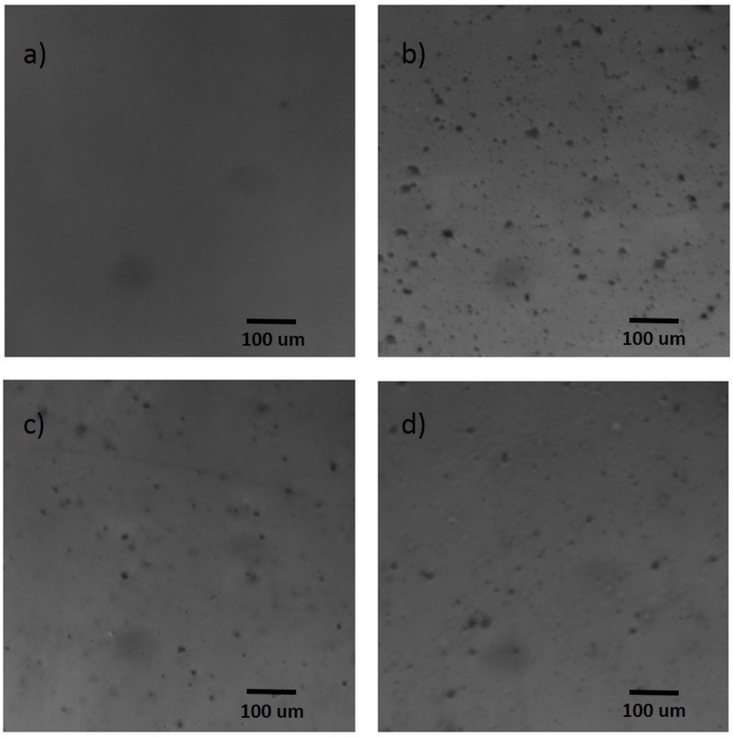

Fig. S1. Film morphologies of a) PEDOT:PSS: 5 v/v.% glycerol on glass substrate; b) pure PET substrate; c) PEDOT:PSS: 5 v/v.% glycerol on PET substrate; and d) PEDOT:PSS: 5 v/v.% glycerol on PET substrate after 1 day water immersion. PEDOT:PSS: 5 v/v.% glycerol film on glass is not shown since it delaminated after 1 day water immersion.

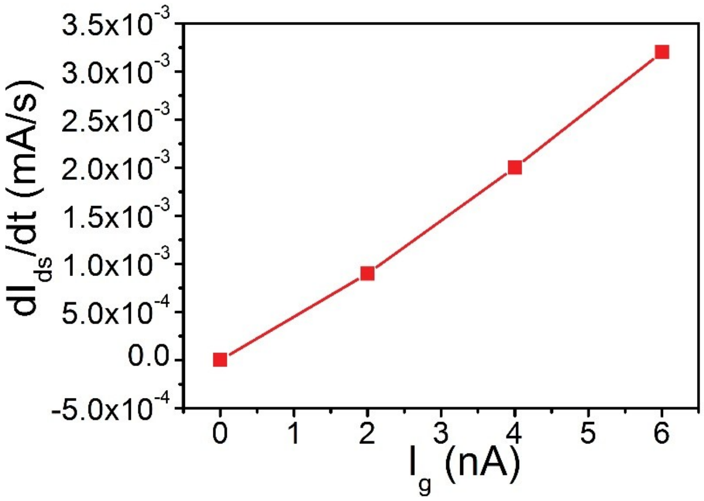

Fig. S2. Derivative of I_{ds} with respect to time as a function of I_g. The line is a fit to Eq. (1).[1] The data are from the OECT with channel length (L) of 100 um and a channel width of 400 µm. The V_{ds} was -0.2 V. Hole mobility of PEDOT:PSS on plastic can be obtained via Eq. (2) and (3).[1] The extracted mobility is 0.25 $cm^2V^{-1}S^{-1}$.

$$I_{ds}(t, I_g)=I_{ds0}-I_g(f+\frac{t}{\tau_e}) \qquad (1)$$

$$dI_{ds}/dt=-\frac{I_g}{\tau_e} \qquad (2)$$

$$\tau_e=L^2/\mathbf{u}V_{ds} \qquad (3)$$

where t is the time, I_{ds0} is the source-drain current prior to application of a gate current (I_g), f is a proportionality constant to account for the spatial non-uniformity of the de-doping process, τ_e is the electronic transit time, L is the channel length of OECT and V_{ds} is the source-drain voltage. u denotes the hole mobility of PEDOT:PSS film.[1]

Table.S1. Changes in thickness, sheet resistance and conductivity of PEDOT:PSS films on plastic after water immersion. The PEDOT:PSS films were deposited by spin-coating a mixture containing 20 ml Clevios PH1000 and 1 ml glycerol at 500 rpm for 10s and 1500 rpm for 40s.

Films on plastic	Before water immersion	After 1 day water immersion
Thickness (nm)	142±8	118±11
Sheet resistance (ohm/sr)	115±3	150±12

Conductivity (S/cm)	614±20	567±22

Reference:

1. D. A. Bernards and G. G. Malliaras, *Advanced Functional Materials*, 2007, **17**, 3538-3544.