Supplementary Information

Controlling PEDOT:PSS electropolymerization for label-free optical recording of bioelectric potentials

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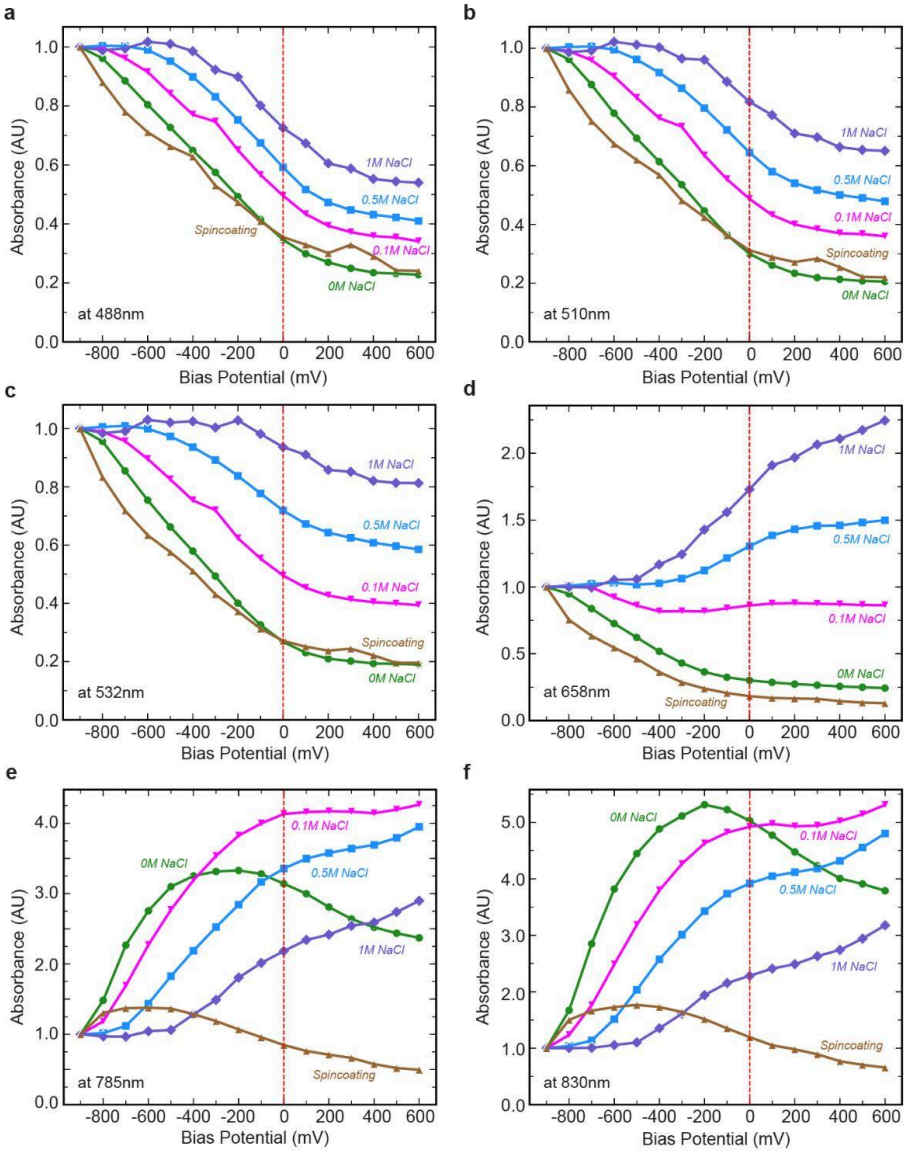
Supplementary Text

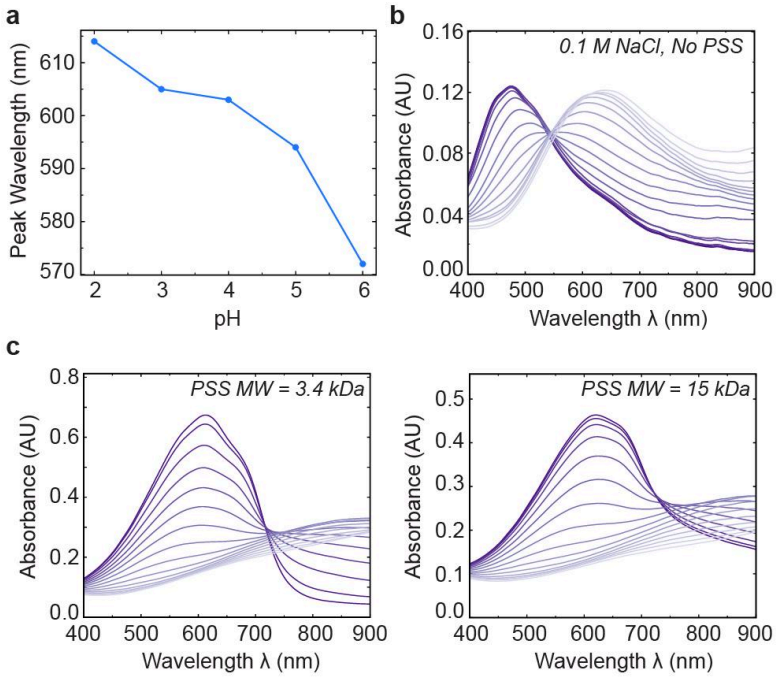
1. Surface treatment of indium tin oxide (ITO)-coated glass

The surface morphology of ITO glass using different surface treatment methods was characterized by atomic force microscopy (AFM) (**Supplementary Figure 3a**). Untreated clean ITO glass (dish soap water, acetone, isopropyl alcohol) exhibits relatively smooth surfaces (RMS roughness of ~0.6 nm) and largest grain size. UV-Ozone treatment leads to slightly reduced grain size but an increased RMS roughness of ~0.8 nm. Oxygen plasma treatment results in a more fragmented surface morphology with the smallest grain size but highest RMS roughness of ~1.0 nm. Details of ITO glass treatments before electropolymerization are described in the Methods section.

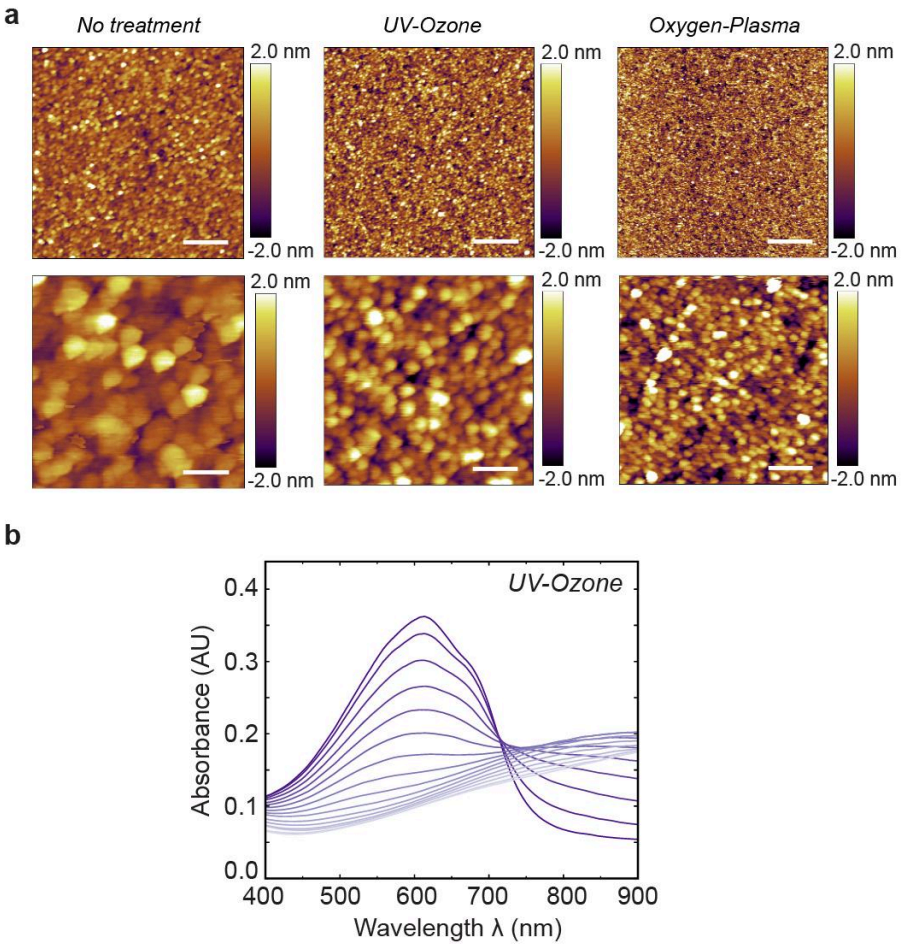
Supplementary Figures



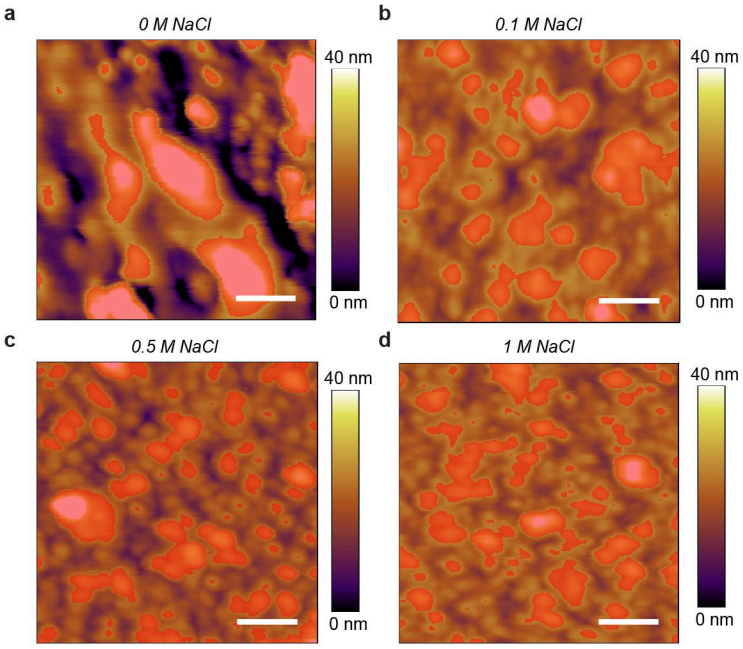
Supplementary Figure 1. Voltage-dependent absorbance change of PEDOT:PSS thin films at different wavelengths. Voltage-dependent absorbance changes of PEDOT:PSS films electropolymerized under different NaCl concentrations at commonly-used laser wavelengths: (a) 488 nm, (b) 510 nm, (c) 532 nm, (d) 658 nm, (e) 785 nm, and (f) 830 nm. The dashed vertical lines indicate 0 mV (vs. Ag/AgCl). A reverse in the voltage-dependent absorbance change trend is observed at higher laser wavelengths. Data for spin-coated PEDOT:PSS film from commercial suspension is included for comparison.



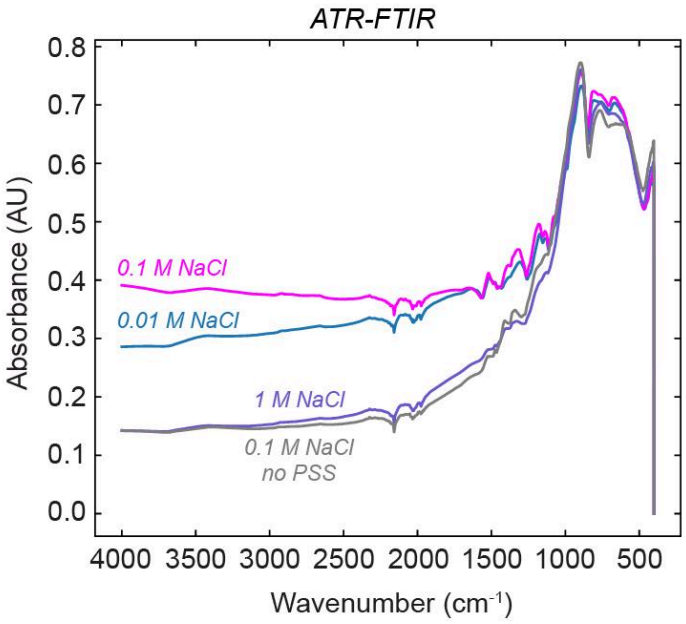
Supplementary Figure 2. Influence of pH, NaCl, and PSS molecular weight on the spectroelectrochemistry of electropolymerized PEDOT:PSS films. (a) π-π* absorption peak wavelength as a function of electrolyte pH during electropolymerization. (b) Vis-NIR spectroelectrochemistry of PEDOT:Cl films electropolymerized with 0.1 M NaCl without PSS. (c) Vis-NIR spectroelectrochemistry of PEDOT:PSS films electropolymerized with 3.4 kDa and 15 kDa PSS (0 M NaCl). All measurements were performed from −900 mV to +600 mV versus Ag/AgCl in HEPES-buffered Tyrode's solution.



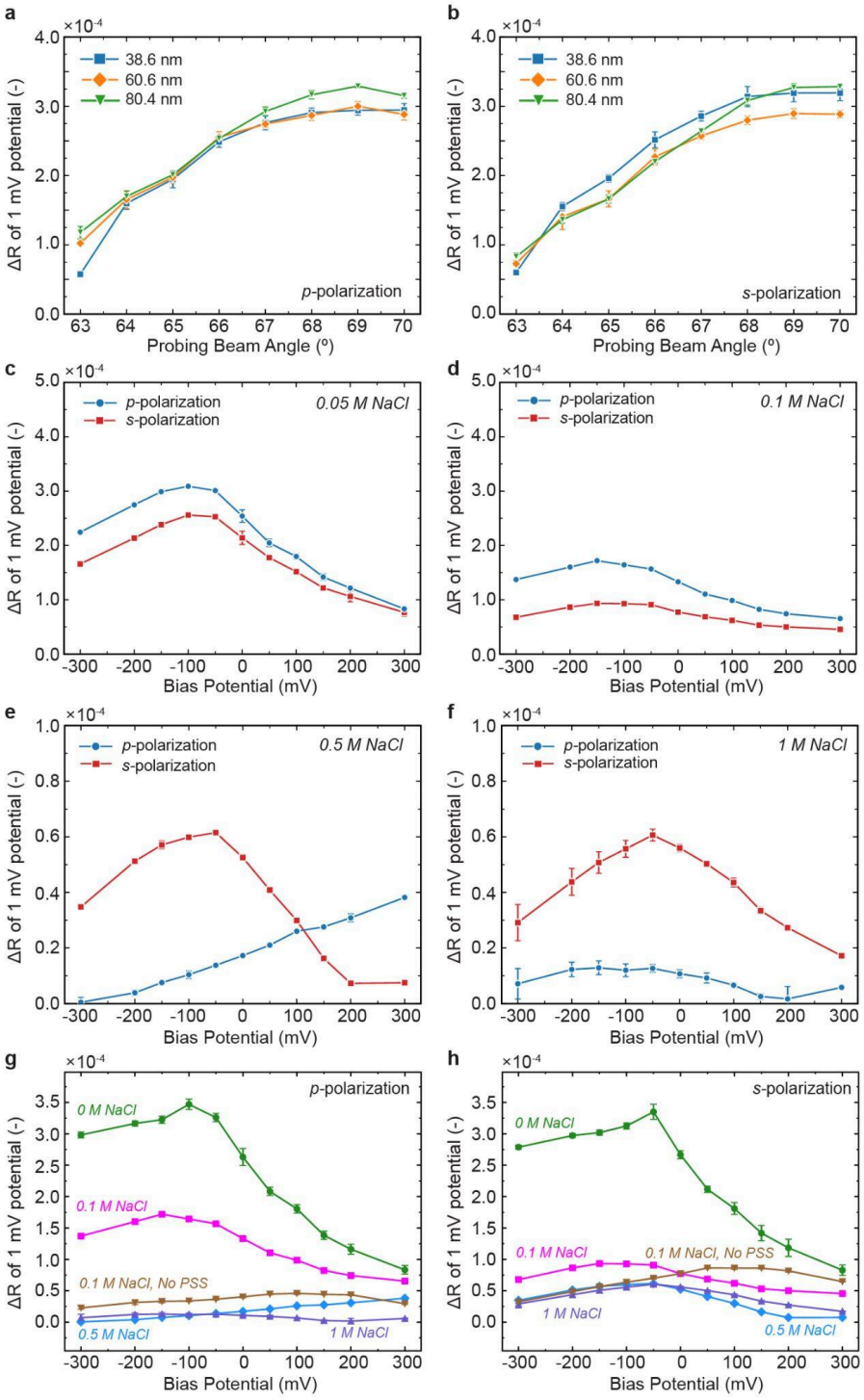
Supplementary Figure 3. Influence of ITO glass surface treatment on the spectroelectrochemistry of electropolymerized PEDOT:PSS films. (a) Atomic force microscopy (AFM) images of ITO glass substrates under different surface treatment conditions. Scale bar = 1 μm (top row) and 200 nm (bottom row). (b) Vis-NIR spectroelectrochemistry of PEDOT:PSS films electropolymerized on UV-Ozone-treated ITO glass with 0 M NaCl.



Supplementary Figure 4. Grain analysis on AFM images. A 75% rank was used as a fixed threshold for all samples. The area covered with red masks are suggested as "grains" in this analysis. PEDOT:PSS thin films electropolymerized with (a) 0 M, (b) 0.1 M, (c) 0.5 M, and (d) 1 M NaCl shows mean equivalent radii of 48.2 nm, 37.9 nm, 25.9 nm, and 26.8 nm, respectively.

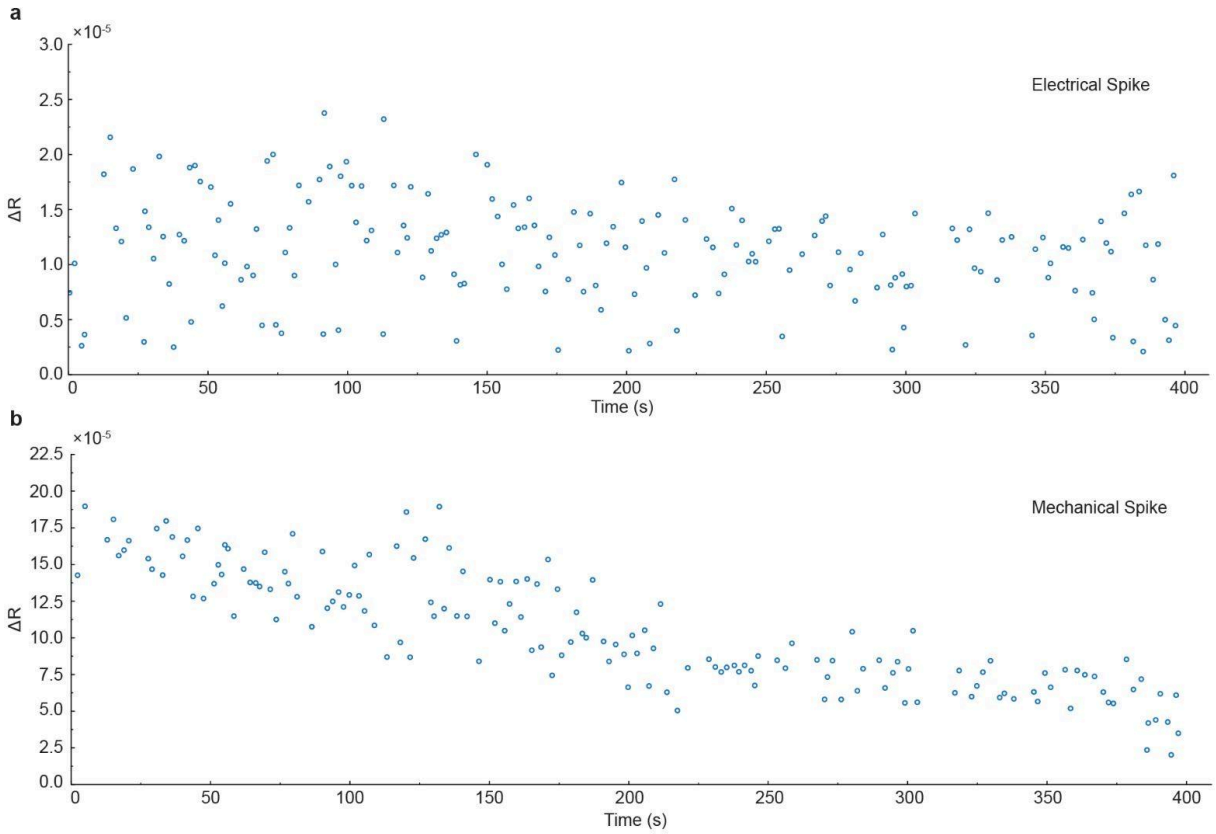


Supplementary Figure 5. ATR-FTIR spectra of PEDOT:PSS films electropolymerized under different NaCl concentrations. Characteristic bands are observed at ~1520 cm^{-1}, corresponding to C=C/C–C stretching of the thiophene ring. The region between ~1100-1250 cm^{-1} is dominated by C–O–C stretching vibrations of the ethylenedioxy groups with contributions of $–SO_3^-$ from PSS. Features around ~970-1000 cm^{-1} are mainly attributed to C–S stretching modes of the thiophene ring[1]. Qualitatively, 1 M NaCl and 0.1 M with no PSS conditions show largely reduced contributions from PSS. A baseline drift across the spectra is observed, arising from the wavelength-dependent infrared absorption of the underlying ITO glass substrate.



Supplementary Figure 6. Influence of probing beam incident angle, film thickness, and bias potential on ECORE signal in response to 1 mV, 1 Hz squarewave potential. Reflectance change (ΔR) as a function of probing beam incidence angle for PEDOT:PSS films with different thicknesses when measured using (a) *p*-polarized and (b) *s*-polarized light. Bias-potential dependence of ΔR measured under *p*-polarized and *s*-polarized light for PEDOT:PSS thin films electropolymerized with (c) 0.05 M, (d) 0.1 M, (e) 0.5 M, and (f) 1 M NaCl. ΔR of electropolymerized PEDOT:PSS and PEDOT:Cl films in

response to 1 mV, 1 Hz squarewave potential measured using (g) *p*-polarized and (h) *s*-polarized light under different bias potentials. Data are presented as mean ± SD.



Supplementary Figure 7. Electrical and mechanical spike amplitudes of E10 chicken hearts recorded by ECORE with blebbistatin. Reflectance change, ΔR, as a function of time for (a) field potential spikes and (b) mechanical contraction spikes recorded from isolated E10 chicken hearts after 15 min incubation with blebbistatin. Each point represents a detected individual peak.

Supplementary Tables

Sample	PEDOT 2p 3/2	PEDOT 2p 1/2	$PEDOT^+$ 2p 3/2	$PEDOT^+$ 2p 1/2	PSS 2p 3/2	PSS 2p 1/2	R.S.F (S)	Cl^- 2p 3/2	Cl^- 2p 1/2	C-Cl 2p 3/2	C-Cl 2p 1/2	R.S.F (Cl)
0.1 M, no PSS	10627.6	5313.8	5098.7	2549.4	1650.4	825.2	1.677	1101.3	550.7	5709.6	2854.8	2.285
0.01 M	3133.3	1566.7	2958.4	1479.2	7430.0	3715.0	1.677	0.0	0.0	155.8	77.9	2.285
0.05 M	5143.0	2571.5	3899.0	1949.5	7872.1	3936.1	1.677	0.0	0.0	829.5	414.8	2.285
0.1 M	4092.3	2046.2	3395.4	1697.7	7786.7	3893.4	1.677	46.2	23.1	722.7	361.4	2.285
0.5 M	3803.6	1901.8	2778.5	1389.3	6838.1	3419.1	1.677	670.5	335.3	1275.2	637.6	2.285
1 M	4162.7	2081.4	3102.1	1551.1	9953.7	4976.9	1.677	0.0	0.0	1673.0	836.5	2.285

Supplementary Table 1. Fitted XPS peak areas of PEDOT:PSS films electropolymerized under different NaCl concentrations. Peak areas corresponding to PEDOT (2p), $PEDOT^+$ (2p), PSS (2p), and Cl-related species (Cl^- 2p and C–Cl 2p) are listed for each sample, including a PSS-free control. Relative sensitivity factors (R.S.F.) for both elements used for quantification are also listed.

Sample	PSS/PEDOT	Cl/PEDOT	Cl/PSS
0.1 M, no PSS	0.105	0.318	3.029
0.01 M	1.220	0.019	0.015
0.05 M	0.871	0.067	0.077
0.1 M	1.040	0.075	0.072
0.5 M	1.039	0.217	0.209
1 M	1.370	0.169	0.123

Supplementary Table 2. Atomic ratios derived from XPS analysis of PEDOT:PSS films. Calculated ratios of PSS/PEDOT, Cl/PEDOT, and Cl/PSS for films electropolymerized under different NaCl concentrations, including a PSS-free control.

References

1. Sriprachuabwong, C. *et al.* Inkjet-printed graphene-PEDOT:PSS modified screen printed carbon electrode for biochemical sensing. *J. Mater. Chem.* **22**, 5478–5485 (2012).