Supporting Information

# Scaling of capacitance of PEDOT:PSS: volume or area?

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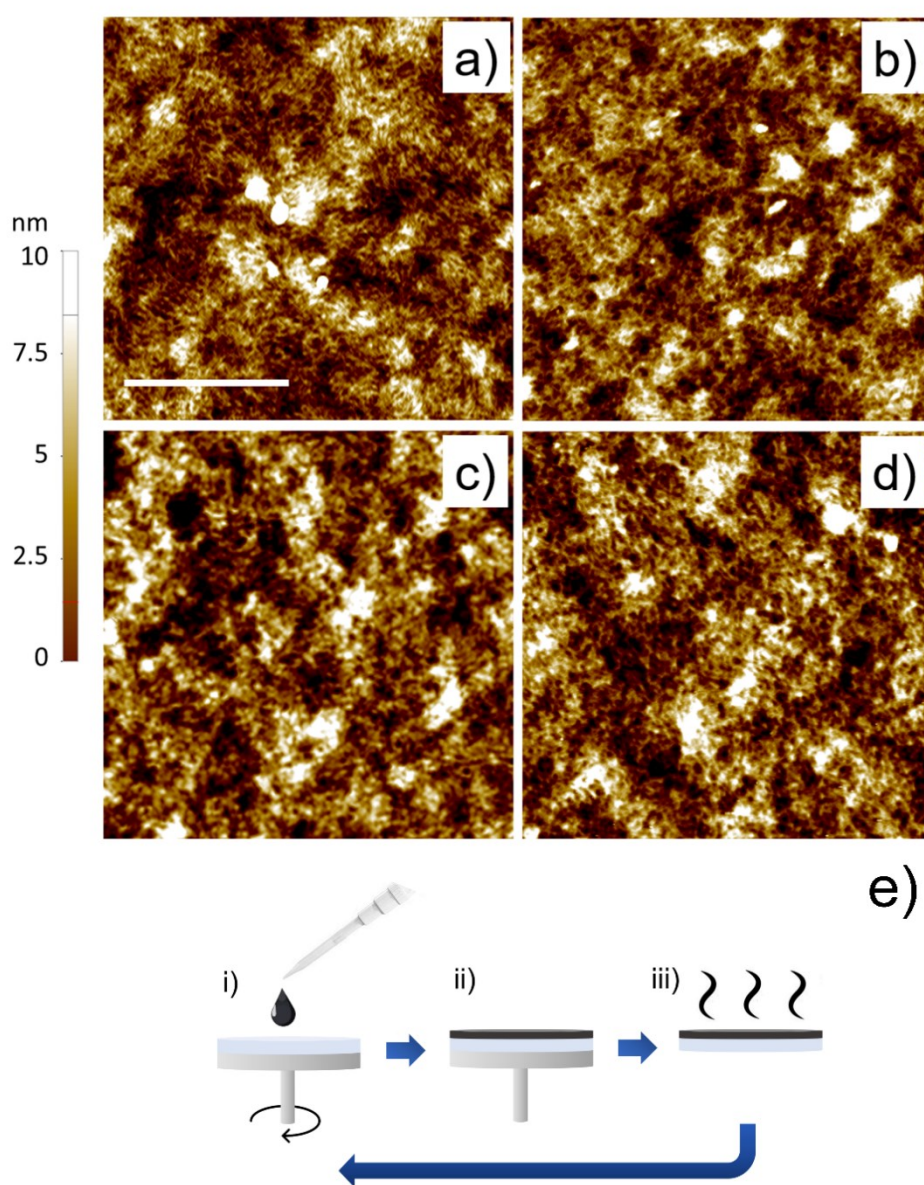
**Figure S1.** AFM topographic images of group a) A, b) B, c) C and d) D (scale bar is 1 μm); e) Sketch of the iterated spin coating and baking steps.
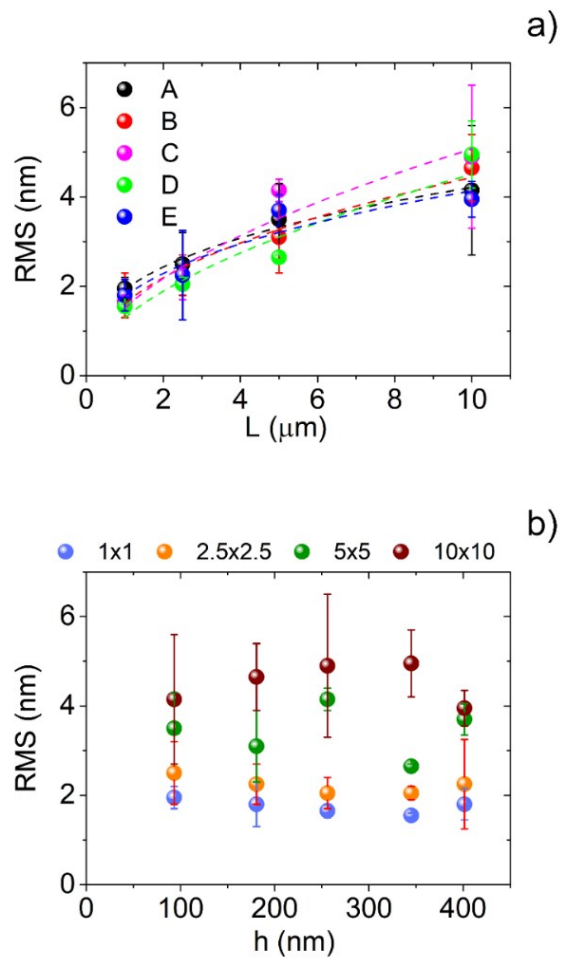
**Figure S2.** RMS roughness of PEDOT:PSS films vs a) scan size L (the dashed lines represent the fitting curve obtained with a power law equation RMS=A L$^{\alpha}$, and b) film thickness h at the different scan size investigated (top, unit is $\mu m^2$).

**a)**

**b)**

**c)**

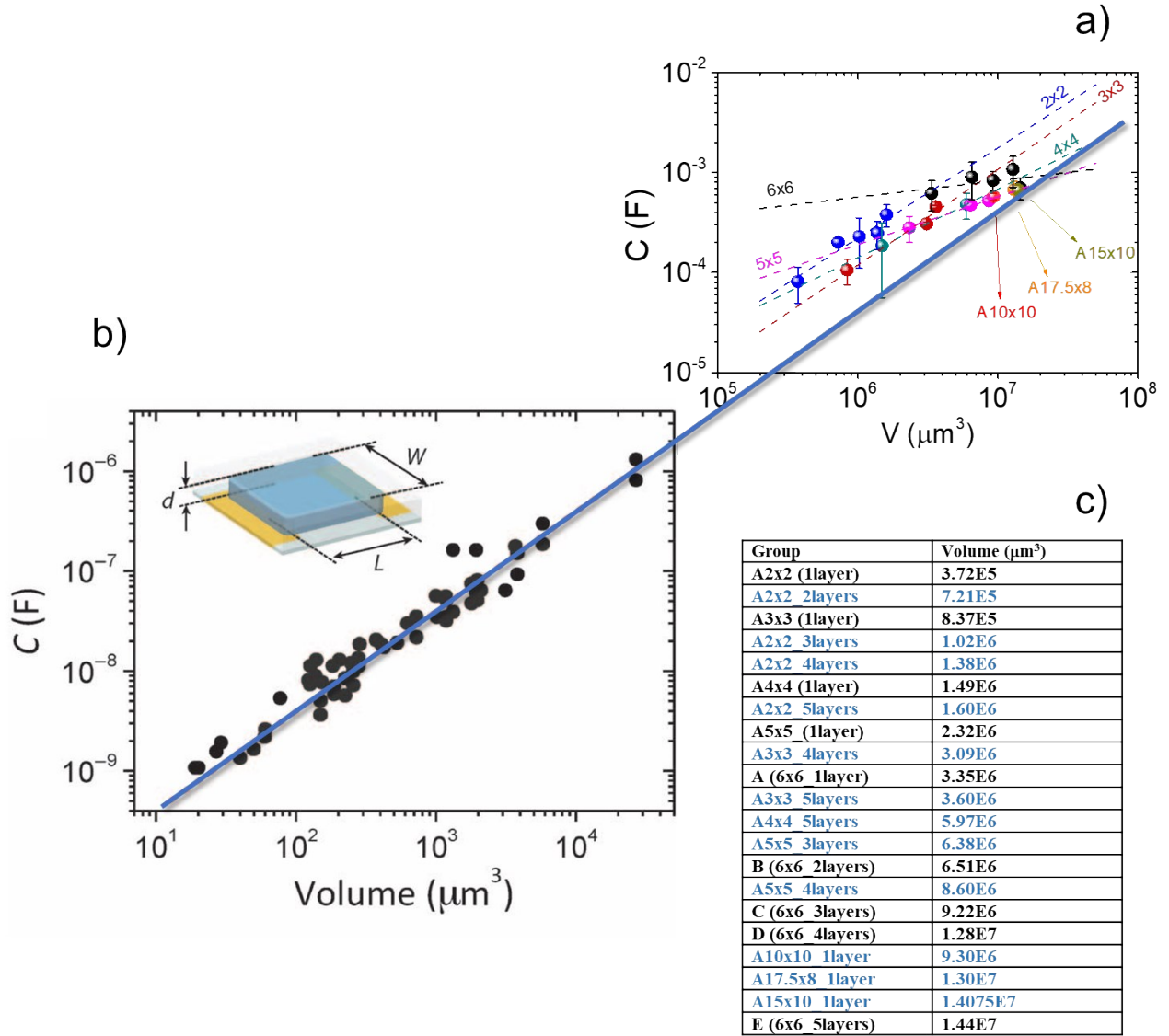| Group | Volume (µm³) |
|---|---|
| A2x2 (1layer) | 3.72E5 |
| A2x2_2layers | 7.21E5 |
| A3x3 (1layer) | 8.37E5 |
| A2x2_3layers | 1.02E6 |
| A2x2_4layers | 1.38E6 |
| A4x4 (1layer) | 1.49E6 |
| A2x2_5layers | 1.60E6 |
| A5x5_(1layer) | 2.32E6 |
| A3x3_4layers | 3.09E6 |
| A (6x6_1layer) | 3.35E6 |
| A3x3_5layers | 3.60E6 |
| A4x4_5layers | 5.97E6 |
| A5x5_3layers | 6.38E6 |
| B (6x6_2layers) | 6.51E6 |
| A5x5_4layers | 8.60E6 |
| C (6x6_3layers) | 9.22E6 |
| D (6x6_4layers) | 1.28E7 |
| A10x10_1layer | 9.30E6 |
| A17.5x8_1layer | 1.30E7 |
| A15x10_1layer | 1.4075E7 |
| E (6x6_5layers) | 1.44E7 |

**Figure S3**. a) Log-log plot of capacitance vs volume for the PEDOT:PSS electrodes investigated in the present study compared to previously published data for PEDOT:PSS exhibiting smaller volume (b; reprinted and modified from Ref. 16. © The Authors, some rights reserved; exclusive licensee American Association for the Advancement of Science. Distributed under a Creative Commons Attribution NonCommercial License 4.0 (CC BY-NC) http://creativecommons.org/licenses/by-nc/4.0/). The continuous blue line is a guide-for-the-eye line that extends the original (linear) fit to the volume range investigated in our work. Additional data from PEDOT:PSS electrodes showing different area/thickness combination (new samples are marked in bold in panel (c)) have been included. Dashed lines in a) represent the power low fittings ($C = a \cdot V^b$) clustered by geometric area. The capacitance scaling of the PEDOT:PSS groups with volumes smaller than the critical volume $V_c$ (i.e. 2x2 and 3x3) closely follows that reported in ref. 16 ($b \sim 1$), being $0.90 < b < 0.96$. On the contrary, PEDOT:PSS groups with volume spanning across $V_c$ showed a decreasing exponential term, ranging from 0.69 (A4x4) to 0.16 (A6x6, i.e. A, B, C, D and E samples), hinting to the crossover towards a saturation regime at volumes $> V_c$. The fact that the capacitance of groups 2x2 and 3x3 increased with number of deposition steps is a strong evidence in support of the hypothesis that no resistive interfaces were created between one layer and the other by multiple deposition steps.
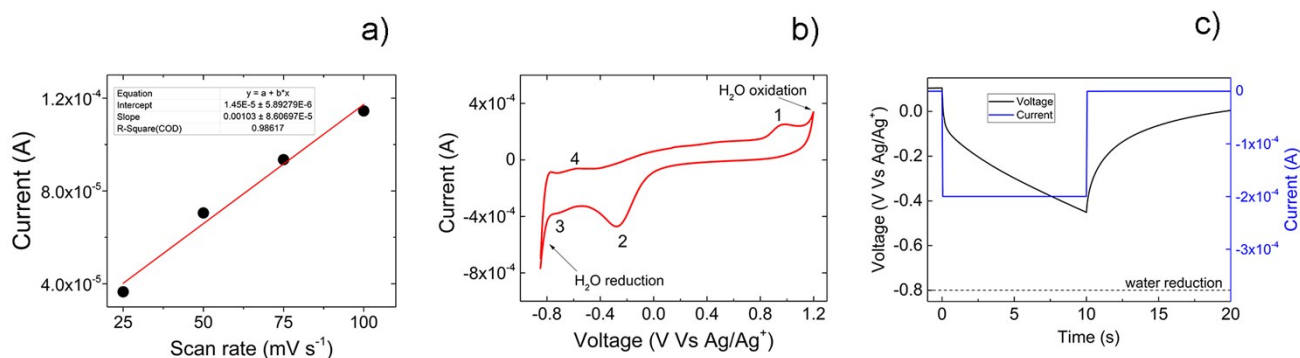
**Figure S4.** Electrochemical characterization of the Pt foil used as CE in this study. a) The capacitance of the Pt CE was extracted by performing CV analysis in saline at different scan rate (25-50-75-100 mV/s) setting the Pt foil as WE, a standard Ag/AgCl (3M KCL) electrode as RE and a high surface area Pt mesh electrode (https://www.advent-rm.com/fr-FR/Products/Pure-Metals/Platinum/Form/WOVEN-Mesh-Gauze/Line/PT5425) as CE. The capacitance of the Pt CE used in this work resulted ~1 mF, thus comparable to that of the largest PEDOT:PSS volumes. In addition, to demonstrate that the potentials supplied by the CE fall well inside the electrolyte stability window, the CV curve of the Pt CE (acquired in saline at 50 mV/s) was first examined (b). The CV exhibits distinct peaks associated with the oxidation and reduction of surface oxide (peaks 1 and 2, respectively) and hydrogen-atom plating and stripping (peaks 3 and 4, respectively). The stability water window falls within the voltage interval -0.8 V and + 1.1 V. The amount of charge that was injected on the WE (PEDOT:PSS) during the experiments reported in the main text, was calculated from the time integral of CV plots for the voltage sweep from 0 V to +0.6V (corresponding to the anodic charging step of the capacitor). The maximum amount of injected charge was estimated to be ~1 mC. Thus, the potential supplied by the CE used in our manuscript was monitored through a chronopotentiometric experiment in the same experimental condition. In particular, to verify that by the polarization at the CE falls within the stability window of the aqueous electrolyte, a cathodic current pulse of 200 μs was applied for 10 seconds. This corresponds to a cathodic charge of 2 mC, which is twice the maximum injected charge of ~1 mC, as reported above. The voltage response of the Pt foil is reported in panel c). It can be appreciated that the voltage excursion falls well inside the cathodic safe window for water reduction even if the injection was twice the highest charge used in our experiments. These evidences confirm that CE size does not limit the amount of charge supplied, and therefore it is not limiting PEDOT:PSS capacitance.
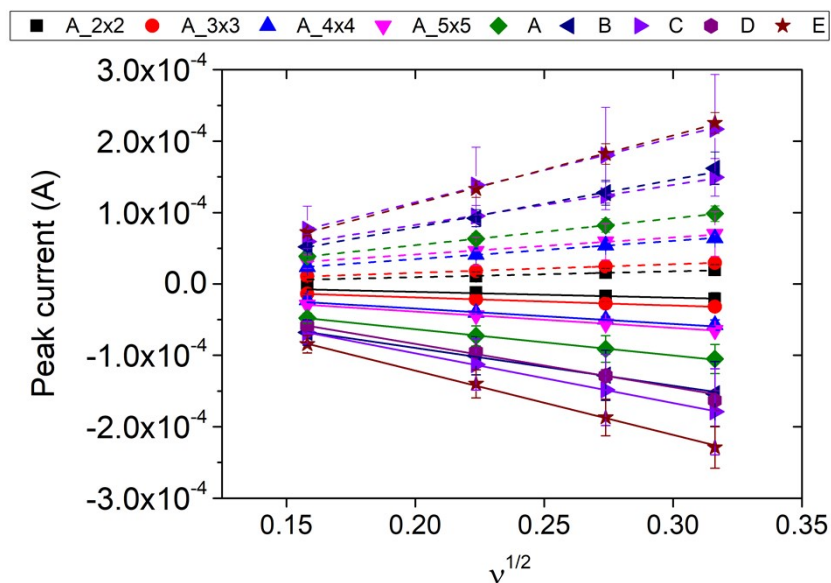
**Figure S5**. Anodic and cathodic peak current vs $\nu^{1/2}$ for all the investigated groups; solid and dashed lines represent the best linear fit ($R^2 > 0.989$ for all the linear fits) used for the anodic and cathodic currents, respectively.
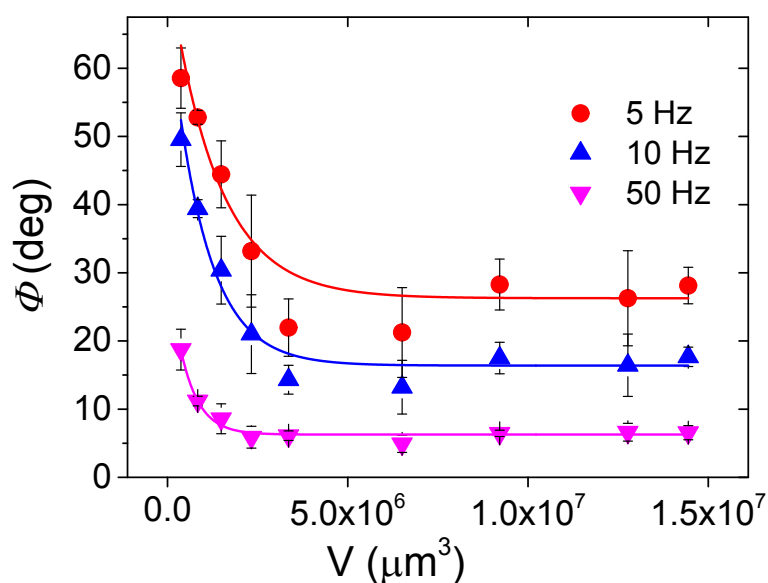


**Figure S6**. Phase angle $\phi$ (at 5, 10 and 50 Hz) scaling plots vs PEDOT:PSS volume. Continuous lines are the guide-for-the-eye lines obtained by fitting phase angle data with an exponential fit ($R^2$=0.97, 0.96 and 0.97 for 5, 10 and 50 Hz, respectively).
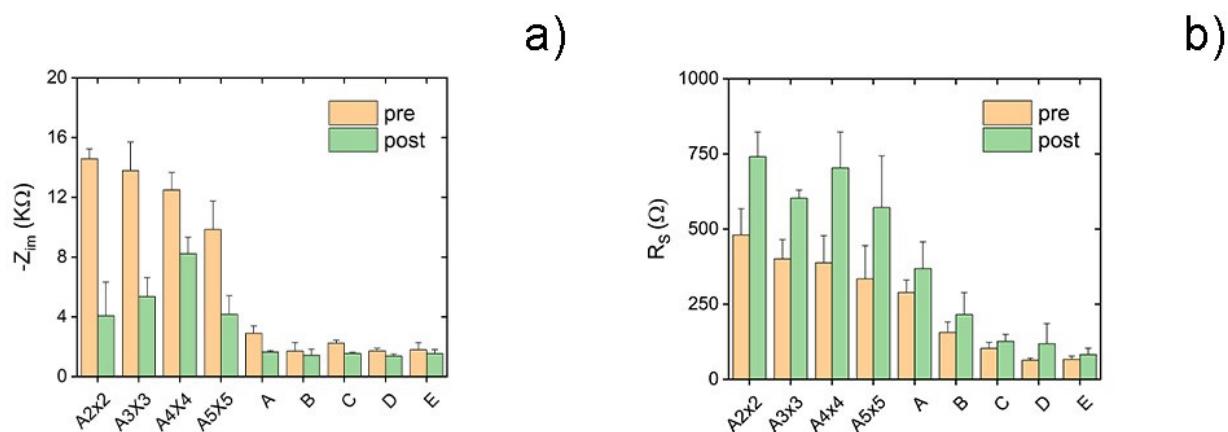
**Figure S7**. a) Imaginary impedance $Z_{im}$ (at 0.1 Hz) and b) solution resistance $R_s$ before and after the EIS and CVs measurements used to calculate ESA.
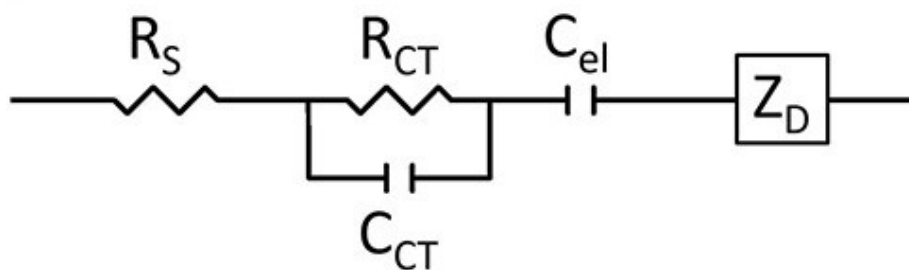


**Figure S8**. Equivalent electrical circuit providing the best fitting of EIS data. $R_s$: solution resistance, $R_{CT}$: charge transfer resistance; $C_{CT}$: charge transfer capacitance; $C_{el}$: electronic capacitance, $Z_d$: finite-length Warburg diffusion impedance
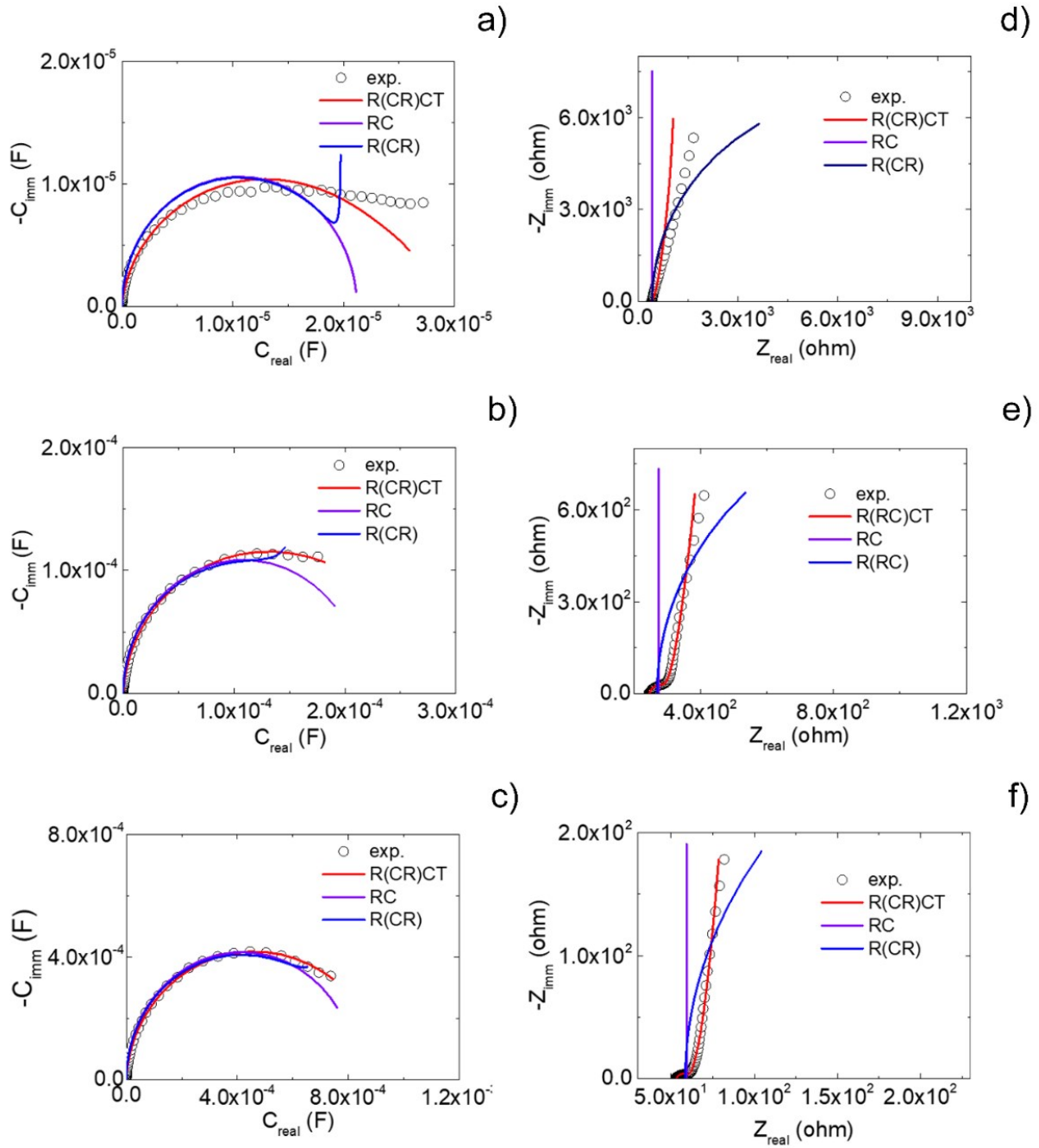
**Figure S9**. EIS data fitting using different equivalent electrical circuits. a-c) Complex plane capacitance and d-f) Nyquist plots for groups A_2x2 (a, d), A (b, e) and E (c, f). R(CR)CT is the circuit element used in this study; RC is a simple series of a solution resistance R and a double layer capacitance C; R(CR) is a series connection of the resistance R with the parallel connection of a charge transfer resistance a and a double layer capacitance.
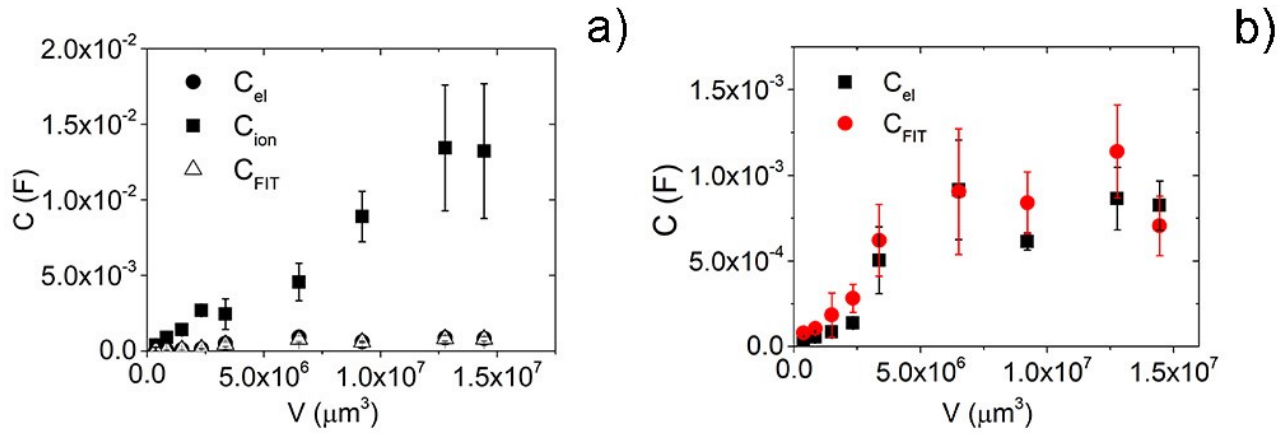
**Figure S10.** a) Plot of electronic capacitance $C_{el}$, ionic capacitance $C_{ion}$ and total capacitance $C_{FIT}$ vs PEDOT:PSS volume. b) detail of a) highlighting $C_{el}$ and $C_{FIT}$ scaling. The saturation of $C_{FIT}$ at large volumes is driven by the saturation of $C_{el}$.

| Group | Volume [μm³] 10⁶ | $R_s$ [ohm] | $R_{CT}$ [ohm] | $C_{CT}$ [F] 10⁻⁵ | $\tau_{CT}{}^a$ [s] 10⁻⁴ | $C_{el}$ [F] 10⁻⁴ | $C_{ion}$ [F] 10⁻⁴ | $\tau_D$ [s] | $C_{CV}{}^b$ [F] 10⁻⁴ |
|---|---|---|---|---|---|---|---|---|---|
| A_2x2 | 0.37 ± 0.04 | 454 ± 132 | 0.2 ± 0.1 | 6.3 ± 0.2 | 0.1 ± 0.08 | 0.4 ± 0.1 | 4 ± 2 | 1.1 ± 0.1 | 0.8 ± 0.3 |
| A_3x3 | 0.84 ± 0.08 | 401 ± 64 | 0.2 ± 0.05 | 0.8 ± 0.15 | 0.02 ± 0.004 | 0.5 ± 0.1 | 9 ± 1 | 1.3 ± 0.1 | 1.1 ± 0.3 |
| A_4x4 | 1.5 ± 0.1 | 390 ± 89 | 0.2 ± 0.06 | 0.8 ± 0.07 | 0.02 ± 0.007 | 0.8 ± 0.1 | 15 ± 1 | 1.45 ± 0.02 | 1.9 ± 1.3 |
| A_5x5 | 2.3 ± 0.2 | 335 ± 110 | 17 ± 3 | 0.8 ± 0.6 | 1.3 ± 0.8 | 1.4 ± 0.2 | 27 ± 1 | 1.5 ± 0.1 | 2.8 ± 0.8 |
| A | 3.4 ± 0.3 | 289 ± 41 | 25 ± 9 | 2.8 ± 0.9 | 6.6 ± 1.7 | 5.0 ± 1.9 | 24 ± 10 | 1.6 ± 0.1 | 6.2 ± 2.1 |
| B | 6.5 ± 0.6 | 155 ± 35 | 11 ± 6 | 1.1 ± 0.3 | 1.3 ± 0.9 | 9.1 ± 2.9 | 46 ± 12 | 1.59 ± 0.04 | 9.1 ± 3.7 |
| C | 9.2 ± 0.5 | 103 ± 20 | 11 ± 5 | 8.4 ± 2.7 | 8.4 ± 2.1 | 6.1 ± 0.5 | 89 ± 17 | 1.62 ± 0.04 | 8.4 ± 1.8 |
| D | 12.4 ± 0.6 | 64 ± 7 | 8 ± 4 | 8.2 ± 3.9 | 5.5 ± 0.4 | 8.6 ± 1.8 | 134 ± 41 | 1.7 ± 0.1 | 11.4 ± 2.7 |
| E | 14.4 ± 0.9 | 67 ± 11 | 12 ± 5 | 2.6 ± 0.3 | 3.6 ± 1.4 | 8.2 ± 1.4 | 132 ± 44 | 1.6 ± 0.1 | 7.1 ± 1.7 |

[a]obtained by CV analysis

**Table S1**: List of relevant parameters obtained through EIS fitting.