

Supplementary information for:

Meniscus Confined Fabrication of Multidimensional Conducting Polymer Nanostructures with Scanning Electrochemical Cell Microscopy (SECCM)

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S1. Experimental

Solutions. 20 mM aniline hydrochloride (Sigma-Aldrich) in phosphate buffer pH 7.2 (Sigma Aldrich) or 20 mM aniline hydrochloride in Milli-Q water (Millipore Corp.) with 75 μ M HCl (36 %, Sigma-Aldrich) solutions (pH 1.6) were used.

Substrates. Gold electrodes (100 – 200 nm thick) on SiO₂ substrates were created by a lift off process.

Probes. Dual barrel borosilicate glass theta pipettes (o.d. 1.5 mm, i.d. 0.23 mm, Harvard Apparatus) were pulled using a laser puller (Model P-2000, Sutter Instruments) to produce tapered pipettes with an overall diameter between 400 nm and 1 μ m. The following parameters were used: heat : 600; fil: 4; Vel: 30; Del: 150 Pul 20 (400 nm); heat : 550; fil: 4; Vel: 30; Del: 120 Pul 28 (1 μ m). The dimensions were accurately characterized by SEM (*vide infra*).

Electrochemical Instrumentation. Probes were filled with the appropriate electrolyte solution, and Ag/AgCl QRCEs were inserted into each barrel. The QRCEs were connected to a custom potentiostat, and the substrate was connected to a custom current follower, as described in detail previously.^{S1} The probe was mounted on a piezoelectric positioner (P-753

LISA, Physik Instrumente) which was, in turn, mounted on micropositioners (Newport Corp.) and the substrate was mounted on XY piezoelectric positioners (Nano-Bio300, MadCityLabs). This was situated on an optics table (RS2000, Newport Corp.) within a faraday cage. A lock-in amplifier (SR830 DSP, Stanford Research Systems) was used to extract the AC component of the ionic conductance current between the QRCEs. The potentiostat and piezoelectric positioners were controlled, and the currents measured, through a PC running custom Labview2011 (National Instruments) code through a FPGA card (7852R, National Instruments). The procedure used to control the position of the probe, with respect to the substrate, has been described in detail previously.^{S1,S2}

Scanning Electron Microscopy. A Zeiss Supra 55-VP, at acceleration voltage of 1 kV, was used.

S2. CV for Aniline Electropolymerization

Figure S1 shows a typical CV for the electropolymerization of aniline to produce polyaniline (PANI) using a SECCM probe on a gold substrate (see caption for details).

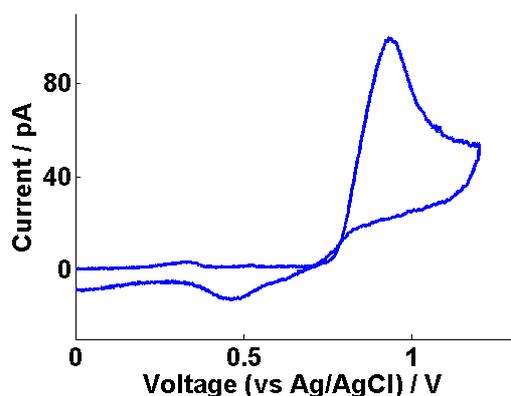


Figure S1. Cyclic voltammogram (200 mV s^{-1}) for the electropolymerization of polyaniline on a gold substrate using a $1 \mu\text{m}$ diameter SECCM probe. The solution in the probe contained 20 mM aniline hydrochloride and $75 \mu\text{L}$ HCl (36%).

S3. PANI Dot Analysis

Individual dot size, extracted from the SEM image in Figure 2 of the main paper, and surface charge, extracted from the integrated area of the surface current, are shown in Figure S2. These data highlight the level of consistency of dot size (area) over the array of dots ($0.37 \pm 0.04 \mu\text{m}^2$), and of the surface charge ($8.0 \pm 0.5 \text{ pC}$). Note that the variation in charge correlates with a similar variation in dot size.

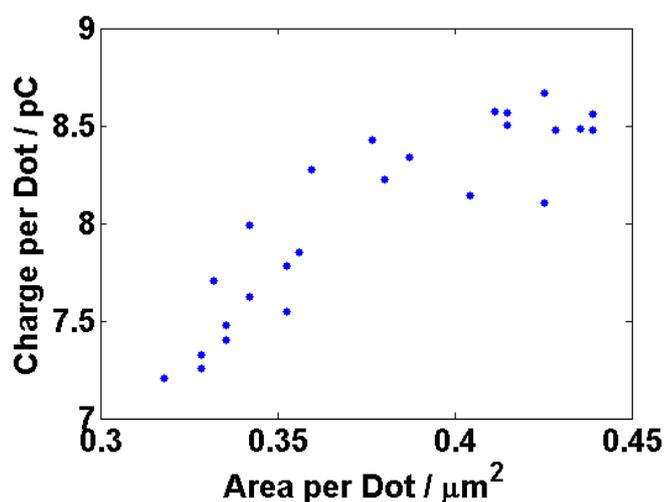


Figure S2. Scatter plot of dot size vs. substrate charge for the array of 25 PANI dots shown in Figure 2 of the main text.

References

- S1. Snowden, M. E.; Güell, A. G.; Lai, S. C. S.; McKelvey, K.; Ebejer, N.; O'Connell, M. A.; Colburn, A. W.; Unwin, P. R. *Anal. Chem.* 2012, 84, 2483–91.
- S2. Ebejer, N.; Schnippering, M.; Colburn, A. W.; Edwards, M. A.; Unwin, P. R. *Anal. Chem.* 2010, 82, 9141–5.