Supplementary Methods and Figures for

A digital microfluidic device with integrated nanostructured microelectrodes for

electrochemical immunoassays

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Surface area and plating current correlation

Nanostructured microelectrodes (NMEs) were prepared on DMF top plates by the electrodeposition method described in the main text, but instead of a current-setpoint, plating potential was applied for durations of 200, 250, or 300 s, recording the current at the final time point. Figure S1 summarizes the data obtained for five batches of six NMEs each generated with plating durations of 300s; the intra-batch precisions range from 6.8% to 10.6% relative standard deviation (RSD), and the inter-batch precision is 17.2 % RSD.

Electroactive surface areas of NMEs formed with a range of plating currents were estimated by cyclic voltammetry in 0.5 M $H_2SO_{4\ (aq)}$, scanning from 0.2 to 1.5 V (vs Ag/AgCl) at 100 mV s^{-1}. The observed oxide reduction peak (0.66 V) was used to estimate the surface area of the working electrode by the oxygen adsorption method according to equation 1:

$$A = \frac{Q}{Q_{ref}}$$
(1)

where A is the surface area, Q is the reduction charge and Q_{ref} is the reference charge for polycrystalline gold of 386 µC cm^{-2} (R. Woods, *Electroanalytical Chemistry: A Series of Advances,* New York, Dekker, 1980). Figure S2 shows the measured surface area as a function of the final plating current. A line of regression was fit to the data (y=0.1227 x – 0.2966) with R^2=0.9655.
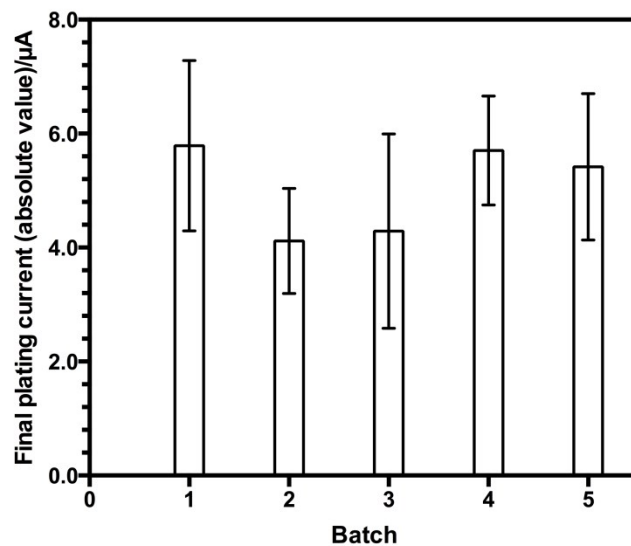
Figure S1 Final plating currents (absolute values) i measured at t = 300 s at 0 V vs. Ag/AgCl. Each batch included six NMEs, and error bars represent ± 1 s.d.
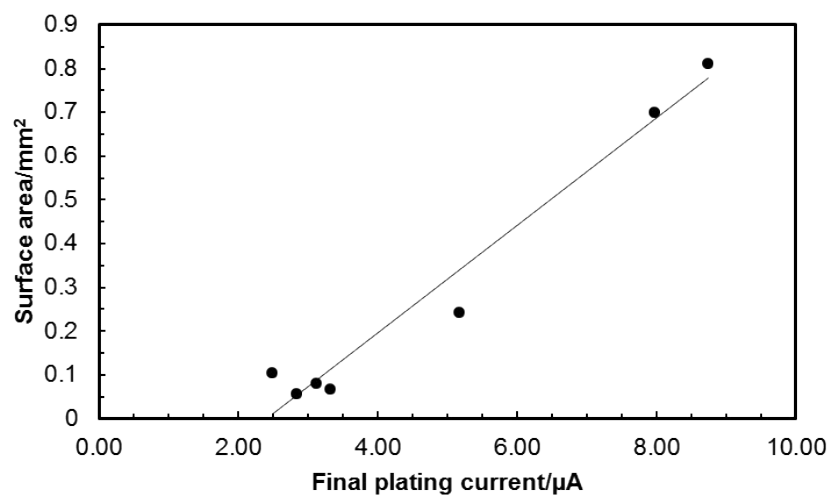

Figure S2 Surface area of NMEs measured by oxygen desorption relative to the absolute value of the final plating current.