Supplementary Information (SI) for Nanoscale.

Supplementary Information

Facet-Controlled Electrosynthesis of Nanoparticles by Combinatorial Screening in Scanning Electrochemical Cell Microscopy

Heekwon Lee[1,†], Jesús Alberto Muñoz-Castañeda[1,†], Hang Ren[1, 2, 3,*]

1. Department of Chemistry, University of Texas at Austin, Austin, Texas 78712, United States

2. Texas Materials Institute, University of Texas at Austin, Austin, Texas 78712, United States

3. Allen J. Bard Center for Electrochemistry, University of Texas at Austin, Austin, Texas 78712, United States

[†]Authors contributed equally

[*]Corresponding author: hren@utexas.edu

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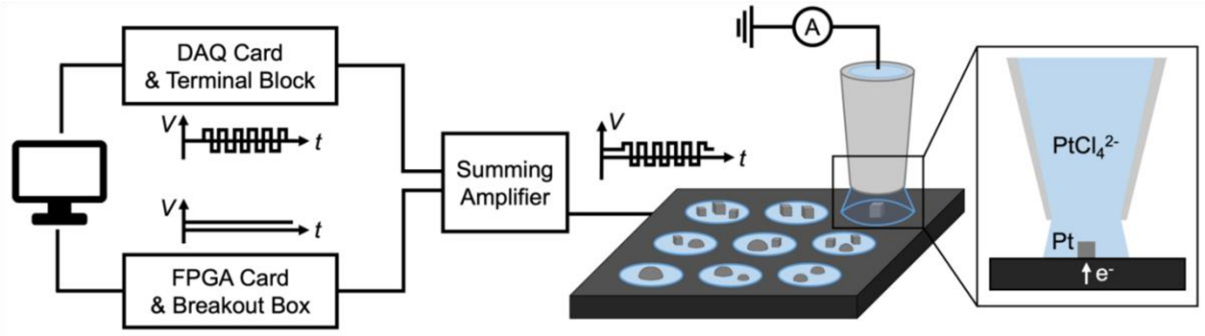
S1. Experimental setup for square-wave voltammetry in SECCM

The experimental setup integrates an FPGA card (NI PCIe-7846, attached to a breakout box) with a DAQ-card (NI PCIe-6361, attached to a terminal block), as illustrated in **Scheme S1**. This system enables synchronization between the FPGA-based WEC-SPM software with waveforms generated by the DAQ system, allowing varying the pulse potential conditions within a SECCM map in one experiment. The system operates by monitoring a command potential from the FPGA, which triggers the output of the DAQ to select one of the preset potential pulse waveforms based on the potential values. This potential is then combined with the DC potential channel (from the FPGA) via a summing amplifier, which is sent to the potential command input of the amplifier (Dagan Chem-Clamp). Note that the pulse potential channel is turned off during pipette approaching to avoid false detection of the surface by the capacitive current. By varying the DC potentials or potential pulses by row, it is possible to probe multiple conditions within a single SECCM map. In our experiment, each condition is repeated along each row, while the condition is changed between the rows. This repletion helps to assess the experimental variability.



Scheme S1. Schematic illustration of shaped controlled electrodeposition of a metal nanoparticle array by SECCM.

S2. SEM image of a nanopipette

The opening radius of the nanopipette was measured by scanning electron microscope (FEI Quanta 650 SEM, Thermo Fisher Scientific) under 20 kV with a 10 mm working distance. The pipette has 420 nm radius openings as shown in **Figure S1**.

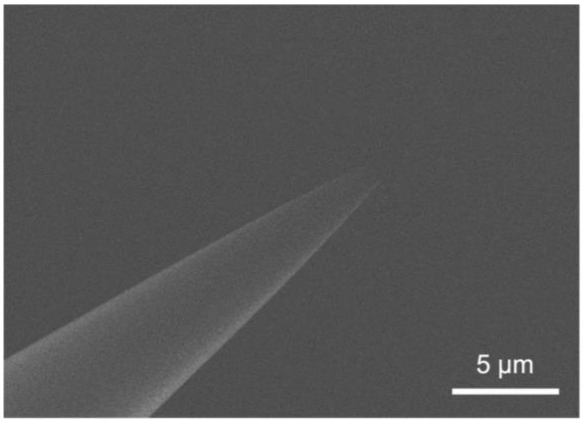
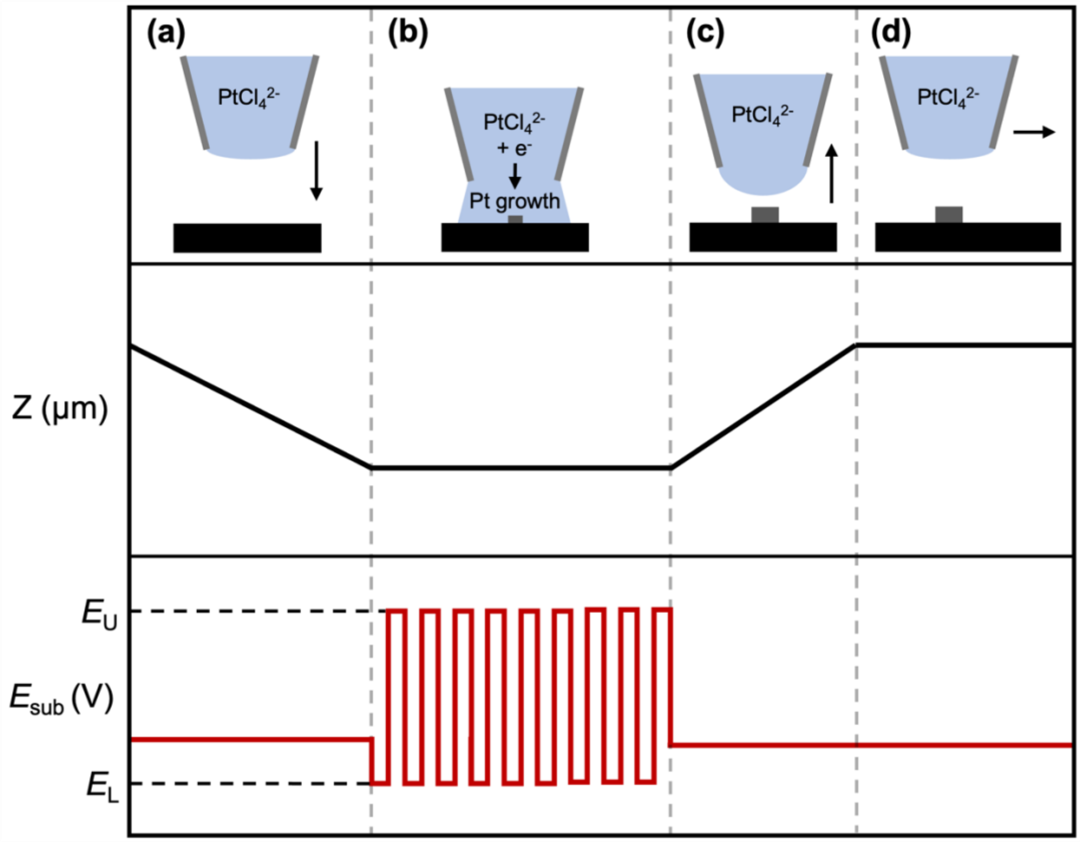


Figure S1. SEM image of a pipette with an opening radius of 420 nm.

S3. Experimental sequence of shape-controlled electrodeposition of nanoparticles

The electrodeposition of shape-controlled nanoparticles is carried out in 4 steps. Firstly, the probe is positioned approximately 50 µm away from the substrate. During the approach (**Scheme S2a**), 0.5 V is applied on the substrate (E_{sub}), which is chosen to avoid a Faradaic reaction even when the circuit is complete. Once the droplet contacts the substrate surface, square wave potentials are applied, during which Pt nanoparticles are formed (**Scheme S2b).** The waveform is defined by the upper potential (E_U), lower potential (E_L), frequency, and deposition time (t_d). When the deposition process is completed, the probe is retracted (**Scheme S2c**) and then moves to the next position (**Scheme S2d**).



Scheme S2. Experimental sequence of shape-controlled electrodeposition of Pt nanoparticles by SECCM. (a) approach and contact (b) Pt deposition with square wave potential waveforms (d) retraction (e) X-Y move to the next position.

S4. Cyclic voltammetry of Pt deposition in SECCM

Cyclic voltammograms for Pt deposition and the hydrogen evolution reaction (HER) were obtained using a solution of 0.5 mM Na_2PtCl_4 and 100 mM H_2SO_4, with a Ag/AgCl reference electrode and a glassy carbon substrate in SECCM. As shown in **Figure S2**, two reduction peaks appear, attributed to Pt reduction at -0.09 V and HER at -0.15 V (vs. Ag/AgCl).

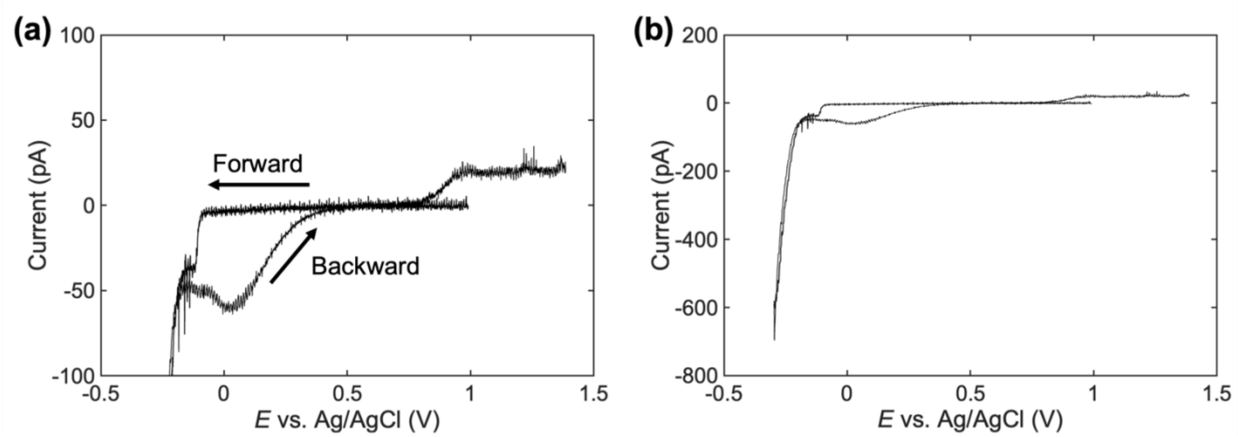


Figure S2. Pt cyclic voltammetry in SECCM (solution: 0.5 mM Na_2PtCl_4 + 100 mM H_2SO_4, reference electrode: Ag/AgCl, substrate: glassy carbon)

S5. Pt nanoparticle electrodeposition with constant potential in SECCM

In the constant potential electrosynthesis, Pt nanoparticles were deposited onto the GC substrate using scanning electrochemical cell microscopy (SECCM) by applying a fixed deposition potential *E* varying from -0.1 to -0.275 V as shown in **Figure S3**. Electrodeposition was conducted at two deposition times (t_d): 2.5 seconds and 5 seconds. **Figures S3a-e** show Pt nanoparticles grown at potentials from -0.1 V to -0.275 V with a deposition time of 2.5 seconds, while **Figures S3f-j** represent the same potential range with 5 seconds. Increasing the deposition time from 2.5 to 5 seconds allowed further growth, yielding larger and more densely packed Pt nanoparticles within a single droplet in SECCM. However, as the deposition potential shifted from -0.15 to -0.25 V, the size of each deposited Pt nanoparticle decreased, likely due to the competing nanoparticle growth and the hydrogen evolution reaction (HER) occurring on the deposited nanoparticles spontaneously.

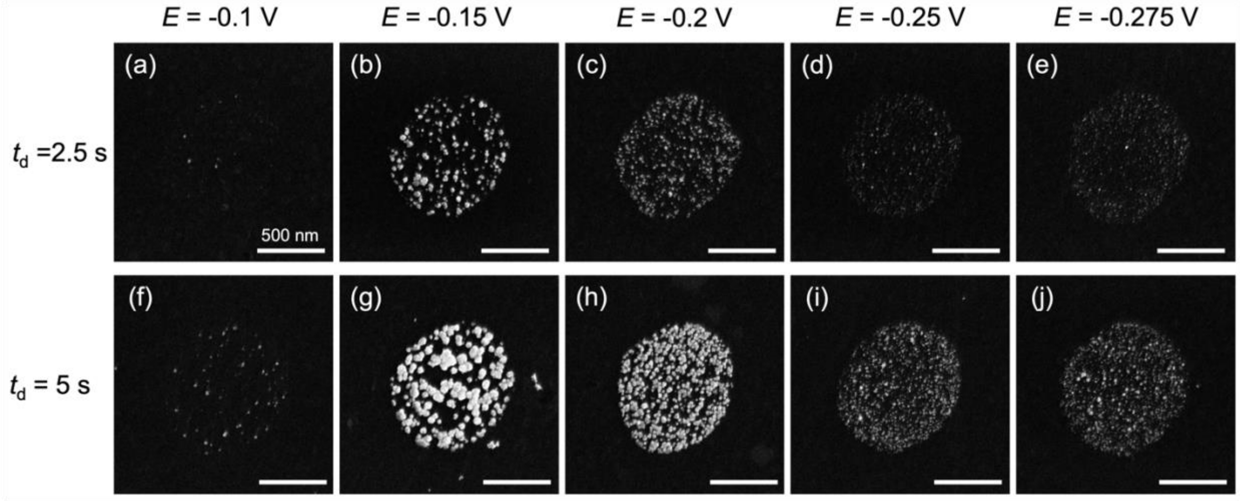


Figure S3. SEM images of electrodeposited Pt nanoparticles by SECCM at varying the deposition potential *E*. *E* was set to (a) -0.1 V, (b) -0.15 V, (c) -0.2 V, (d) -0.25 V, and (e) -0.275 V, with a deposition time (t_d) of 2.5 seconds, and (f) -0.1 V, (g) -0.15 V, (h) -0.2 V, (i) -0.25 V, and (j) -0.275 V with t_d of 5 seconds.

S6. Electrodeposition of Pt nanoparticles with varying E_U

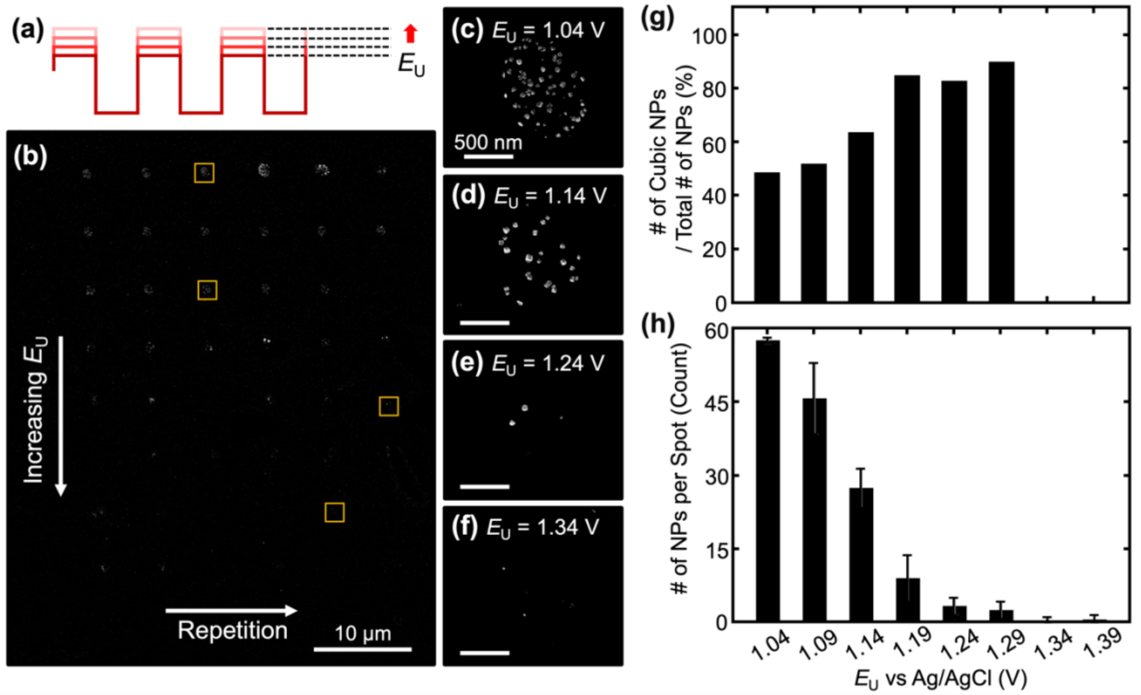


Figure S4. Electrosynthesis of Pt nanoparticle arrays with varying E_U in SECCM. (a) Schematic of the potential waveform. (b) SEM micrographs of SECCM electrodeposition map with varying E_U in each row ranging from 1.04 to 1.34 V, at intervals of 50 mV. The parameters of E_L = -0.275 V, f = 500 Hz, and t_d = 5 s were used. Insets are high-magnification SEM micrographs of individual deposition spots of E_U from (c) 1.04, (d) 1.14, (e) 1.24, to (f) 1.34 V. (g) Ratio of cubic nanoparticles to total nanoparticles as a function of E_U from 1.04 to 1.39 V with an increment of 0.05 V. Note that the ratios for E_U of 1.34 and 1.39 are not plotted due to the limited number of nanoparticles. (h) number of nanoparticles per spot as a function of E_U.

S7. TEM sample preparation for imaging Pt nanoparticles deposited in SECCM

The cross-section lamella sample of the electrodeposited Pt nanoparticles (**Figure S5a**) was prepared using a focused ion beam (FIB) in a scanning electron microscopy system (Scios2 DualBeam, Thermo Fisher). A 0.5-µm-thick carbon layer and a 2-µm-thick Pt layer were deposited to cover the top of the Pt nanoparticles deposited in SECCM for protection during the milling process (**Figure S5b**). The areas at the top and bottom of the protection region were milled by the Ar ion at 30 kV and 5 nA. The lamella was then attached to a FIB lift-out grid followed by milling under 30 kV with 0.5 nA and 0.1 nA current. The final thickness of the lamella was around ~150 nm (**Figures S5c-d**).

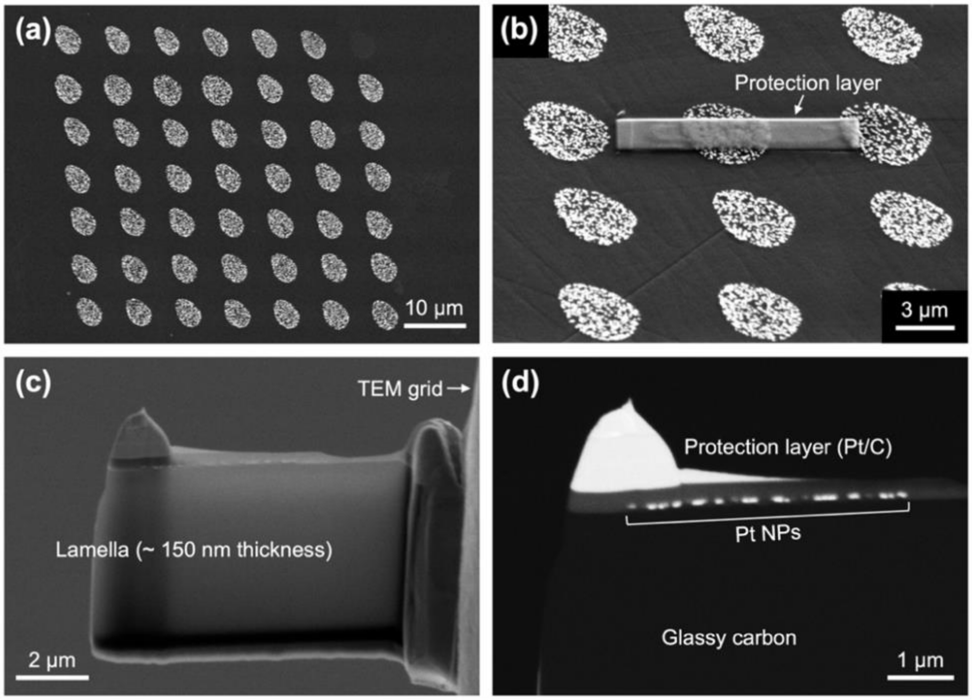


Figure S5. Preparation of Pt nanoparticles for TEM analysis. (a) SEM image of Pt nanoparticle deposits on GC substrate prepared by SECCM (E_L = -0.275 V, E_U = 1.24 V, f = 500 Hz, t_d = 5 s, and pipette diameter = 3 µm) and (b) deposition of protection layer (carbon then Pt) on Pt nanoparticle s. (c) SEM image of the FIB sample and (d) dark-field image of the sample showing protection layers of Pt/C with Pt nanoparticles on GC. Figures S5b and d are the same figures as Figures 3a-b in the main text.

S8. Supplementary SEM images of Pt nanoparticles deposited with varying frequency

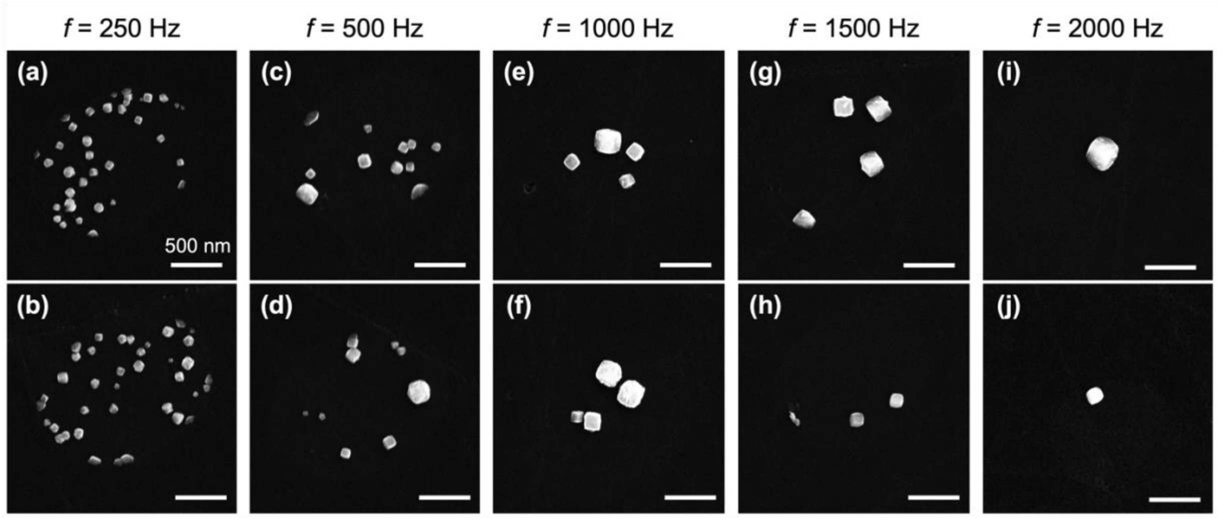


Figure S6. SEM images of electrodeposited Pt nanoparticle s at varying frequencies from (a, b) 250, (c, d) 500, (e, f) 1000, (g, h) 1500, to (i, j) 2000 Hz. E_U = 1.24 V, E_L = -0.275 V, and t_d of 5 s were used. Note that all Pt nanoparticles are from the same sample presented in Figure 4.

S9. RC time constant calculation

The upper limit of the frequency accessible in SECCM was determined by estimating the RC time constant. First, the overall capacitance (which includes the double-layer capacitance) in SECCM was measured using cyclic voltammetry at different scan rates, which yields 25 pF (**Figure S7**). The solution resistance (R_s) was calculated using eq 1, resulting in 1.5 MΩ.[1] These values result in a RC time constant (τ) of 38 μs, corresponding to a cutoff frequency (f_c) of 4.2 kHz (eq. 3),

$$R_s = \frac{h}{\kappa \pi r^2} + \frac{1}{\kappa \pi r \tan(\theta)} \qquad \text{(eq. 1)}$$

In eq 1, h is the droplet height, κ = 29.4 mS/cm is the solution conductivity,[2] r = 420 nm is the pipette radius and θ = 11° is the half-cone angle of the nanopipette. The droplet height is assumed to be equal to the pipette radius r.

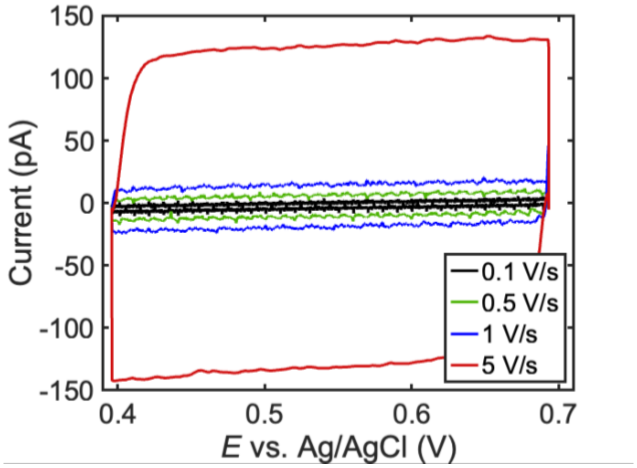


Figure S7. Cyclic voltammograms in SECCM with varying the scan rate from 0.1 to 5 V/s. (solution: 0.5 mM Na_2PtCl_4 + 100 mM H_2SO_4, reference electrode: Ag/AgCl, substrate: glassy carbon)

S10. Quantitative analysis of electrodeposited nanoparticle distribution

Firstly, the droplet contact area was quantitatively evaluated to ensure consistency in the nanoparticle distribution analysis. As shown in **Figure S8**, the droplet areas remain relatively stable over deposition times from 1 s to 15 s. Each condition includes measurements from five independent samples.

Pair correlation function analysis is used to assess the spatial distribution of electrodeposited Pt nanoparticles and determine whether the locations are dispersed or clustered. In the analysis, pair correlation function $g(r)$ quantifies the chance of finding a nanoparticle at a distance r from a reference point. **Figures S9a-b** show a scatter plot of experimentally electrodeposited Pt nanoparticles and the calculated $g(r)$ from (a), indicating no significant spatial correlation. To verify this random distribution, two additional randomized scenarios are presented. **Figures S9c-d** exhibit 120 randomly generated locations within a defined circular boundary, which follows a droplet geometry, with its corresponding $g(r)$. In **Figures S9e-f**, random points are restricted to a radial distance range between 0.7 and 0.8 µm with its $g(r)$. The similarity between the $g(r)$ plots for both experimental and randomly generated data supports that our electrodeposition falls into random distribution, characteristic of bulk electrodeposition.

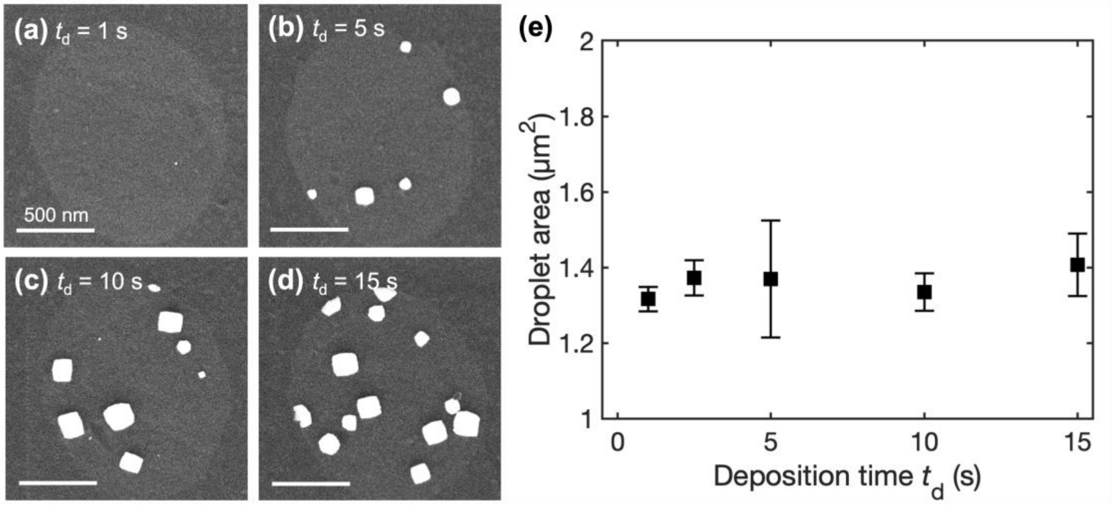


Figure S8. Droplet area analysis as a function of deposition time t_d. (a-d) SEM images of Pt nanoparticles deposited with t_d of (a) 1 s, (b) 5 s, (c) 10 s, and (d) 15 s. (e) Measured droplet area plotted as a function of t_d. Panels a-d are the same as Figures 5a and c-e in the main text.

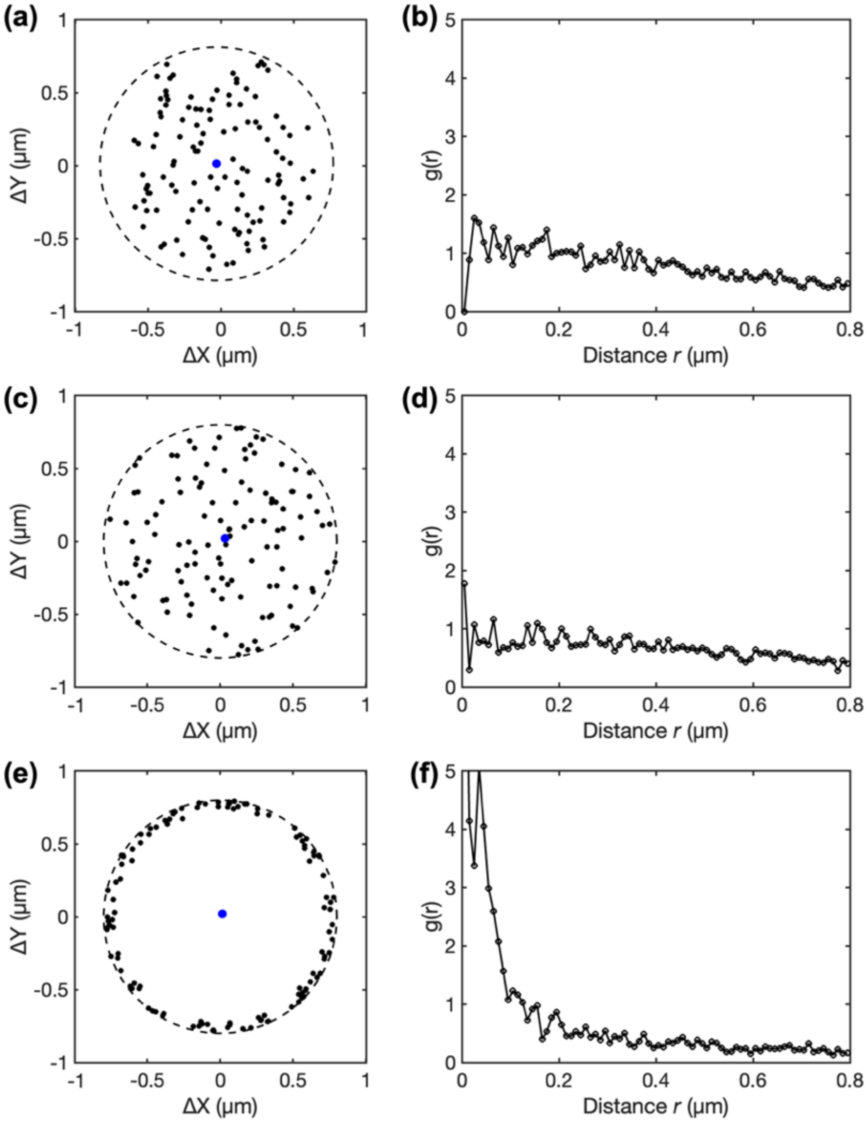


Figure S9. Pair correlation function analysis of nanoparticle distribution. (a) Scatter plot of electrodeposited Pt nanoparticles (same data as Figure 5h), and (b) corresponding $g(r)$ calculated from (a). (c) Scatter plot of 120 randomly generated locations within a dashed circle, with (d) its corresponding $g(r)$. (e) Scatter plot of 120 randomly generated locations with radii ranging from 0.7 to 0.8 μm, and (f) corresponding $g(r)$. A blue dot is the centroid of all locations, which serves as a reference center for the analysis.

S11. References

(1) Blount, B.; Juarez, G.; Wang, Y.; Ren, H. *iR* Drop in Scanning Electrochemical Cell Microscopy. *Faraday Discuss.* **2022**, *233*, 149–162. https://doi.org/10.1039/D1FD00046B.

(2) Xiao, C.; Tian, N.; Tang, J.-X.; Chen, L.-F.; Zhou, Z.-Y.; Sun, S.-G. Electrolyte Effects on the Shape-Controlled Synthesis of Pt Nanocrystals by Electrochemical Square-Wave Potential Method. *J. Electroanal. Chem.* **2023**, *935*, 117344. https://doi.org/10.1016/j.jelechem.2023.117344.