

Supporting Information

Monitoring the Electrophoretic Migration and Adsorption of Single Insulating Nanoparticles at Ultramicroelectrodes

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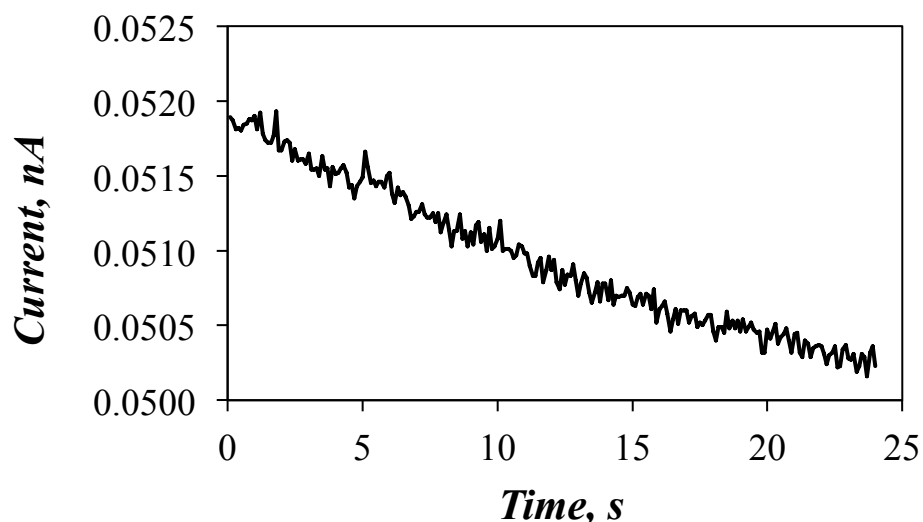


Figure S1. Representative chronoamperogram showing variation in the current (noise) with time in the absence of adsorbing particles. Experimental conditions: 2.5 μm Pt disk UME in 2 mM FcMeOH, 1 mM KCl. The electrode was biased at 0 mV vs Ag|AgCl|KCl(sat.), sampling rate was 10 Hz.

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In Figure S2 one can see a representative collision curve recorded with a 2.5 μm radius Pt disk ultramicroelectrode (UME) in 2 mM FcMeOH, 1 mM KCl solution. At time t a polystyrene particle solution was injected into the cell, the solution was purged with Ar to disperse the particles (indicated by noise spikes) and the electrode potential was stepped to a value corresponding to the steady-state oxidation of FcMeOH (450 mV vs. Ag|AgCl|KCl(sat.)). Upon zooming-in the curve (Figure S2, *inset*), shows individual steps corresponding to the adsorption events. The observed frequency of the steps (0.31 Hz) suggests that particles are not only transported by diffusion, but rather predominantly by migration, as developed in the main paper.

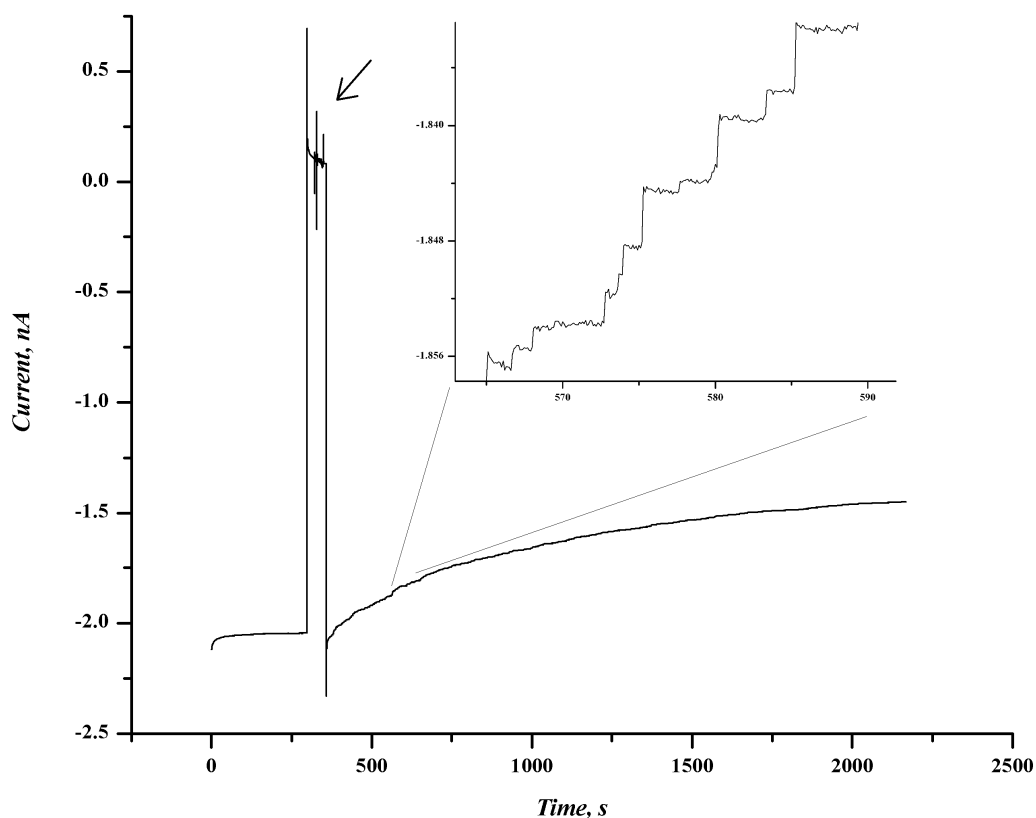


Figure S2. Amperometric collision curve obtained in the experiment with polystyrene spheres (260 nm in radius) in 2 mM FcMeOH, 1 mM KCl solution. Initial region of the curve (*ca.* 0 –

300 s) corresponds to the oxidation of FcMeOH on a radius 2.5 μm Pt disk UME at +450 mV vs. Ag|AgCl|KCl(sat.). The potential was then stepped to 0 mV and an aliquot of particle solution was injected and dispersed in the electrochemical cell by bubbling with Ar (indicated by an arrow and noise on the curve). Then the potential of the electrode was stepped back to +450 mV and the data was recorded for over 30 min. Concentration of spheres in the cell was 50 fM.

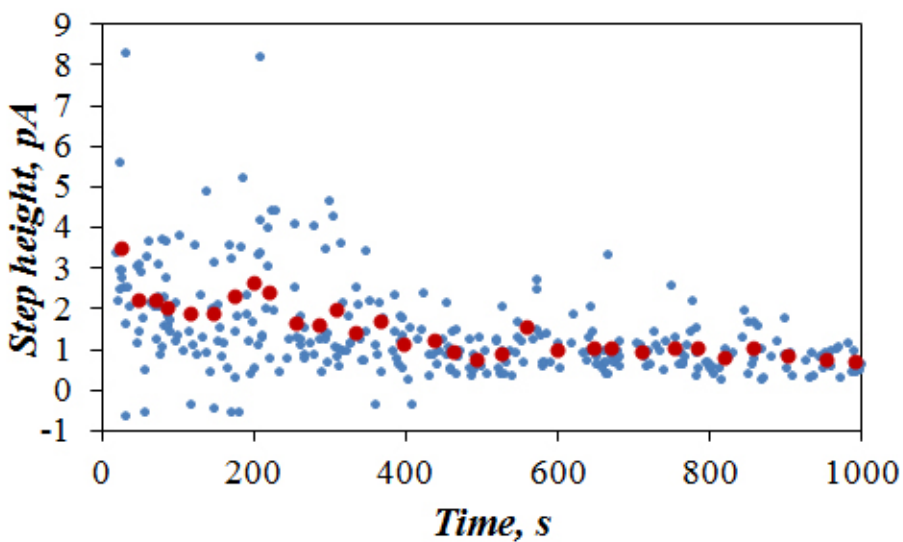


Figure S3. Time map of the results presented in Figure S2. Blue data points correspond to the magnitudes of individual collisions, while each red data point is the average magnitude of ten consecutive collisions.

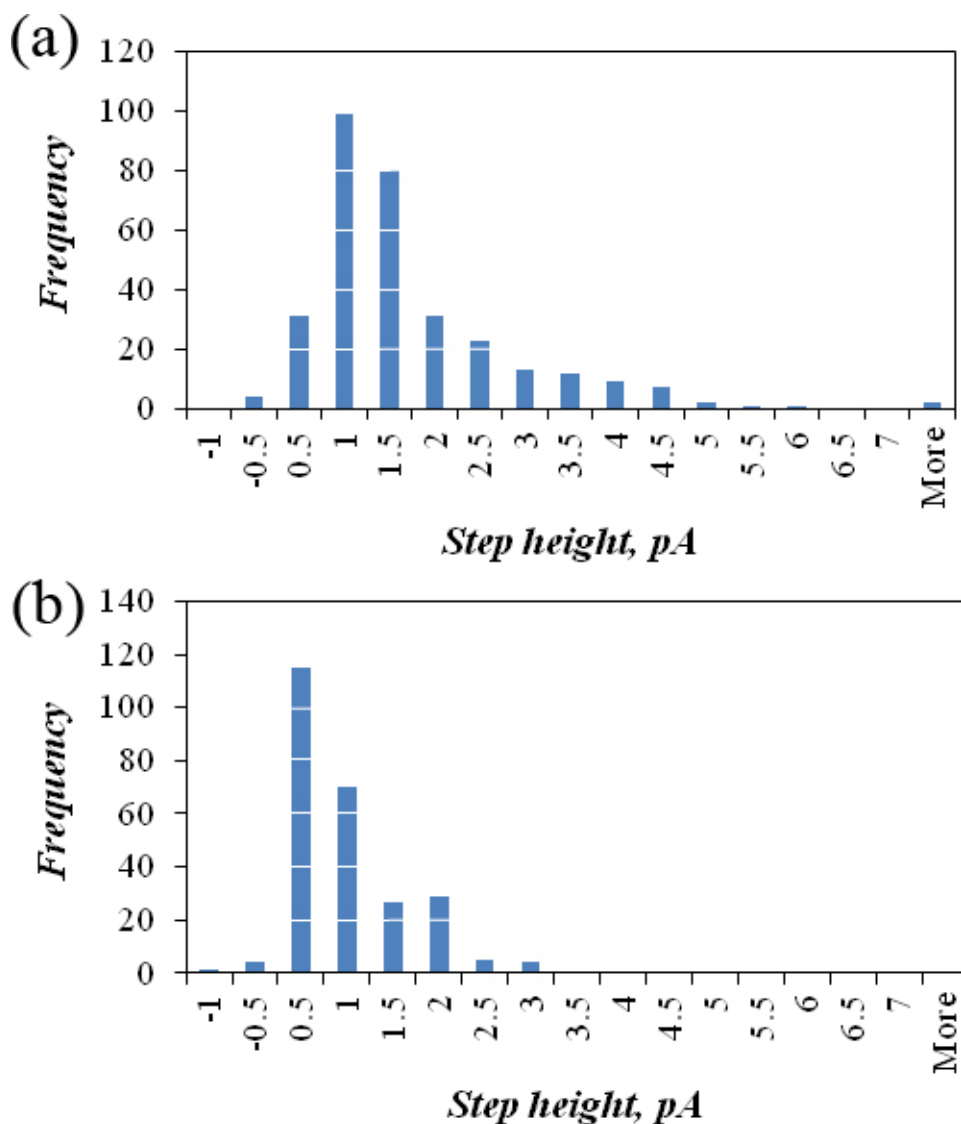


Figure S4. Distribution of current step magnitudes determined from the polystyrene particle collision experiment in (a) 2 mM FcMeOH, 1 mM KCl and (b) 1 mM FcMeOH, 0.5 mM KCl solution. In both cases: particle radius 260 nm, concentration 50 fM; electrode radius 2.5 μm ; electrode potential was held at 450 mV vs Ag|AgCl|KCl(sat.) corresponding to diffusion limited steady-state oxidation of FcMeOH.

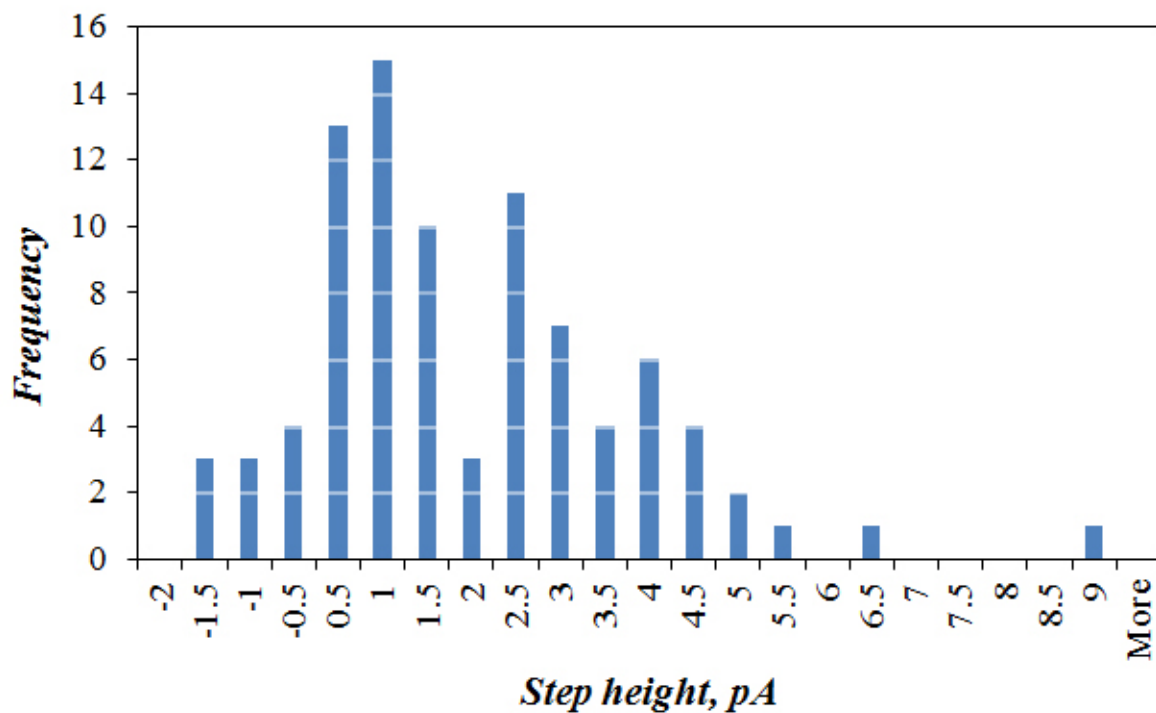


Figure S5. Histogram of current step heights for the adsorption of 310 nm diameter silica spheres on a 2 μm Pt UME in 2.5 mM ferrocenemethanol with 1 mM KCl. The working electrode potential was +0.5 V vs. Ag/AgCl. Steps shown were recorded during the first 1000 s of a 5000 s chronoamperogram, before increasing surface coverage of the spheres caused the heights of the steps to decrease, as explained in the main paper.

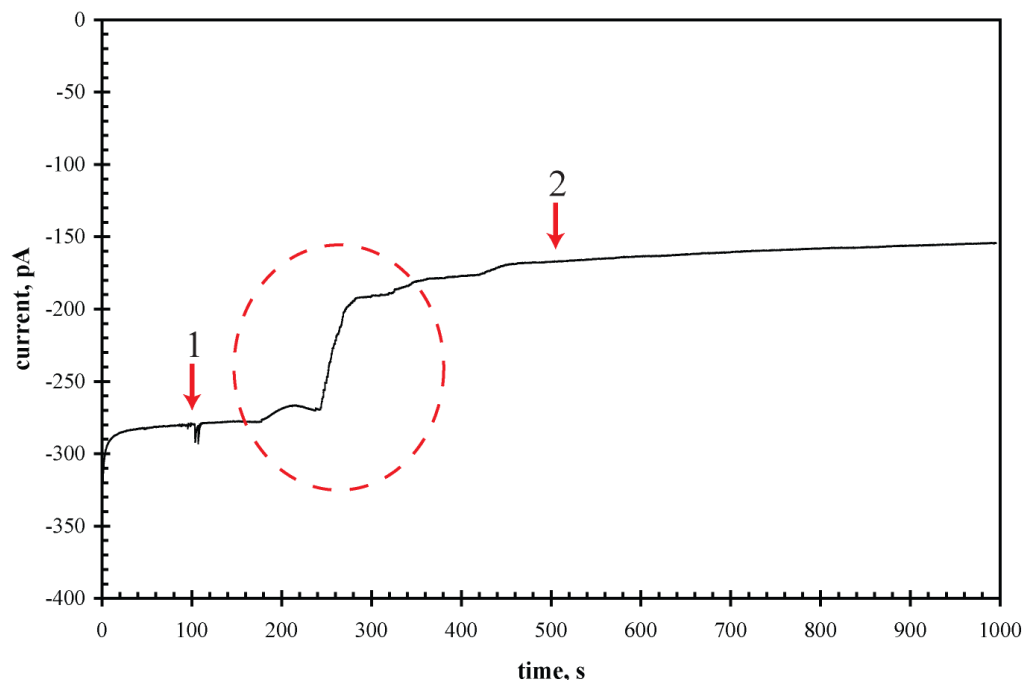


Figure S6. Adsorption of spheres at higher sphere concentration: Chronoamperogram recorded for a 2 μm diameter Pt UME in 1 mM ferrocenemethanol with 1 mM KCl. The working electrode potential was set to +0.5 V (sufficient for diffusion limited oxidation of ferrocenemethanol) for the entire chronoamperogram. At 100 s (red arrow 1), an aliquot of a dilute suspension of polystyrene spheres (390 nm diameter, Bangs Laboratories, Inc., Fishers IN) was injected to the cell sufficient to give a final concentration of 1 pM spheres. The irregular decreases in current highlighted with a dashed line are associated with a sudden increase in concentration of the spheres at the electrode, following injection. Importantly, when the same experiment was performed in 1 mM ferrocenemethanol with 0.1 M KCl, no decreases in current were noted, indicating that the spheres here still arrive and adsorb by an electrophoretic mechanism (as in the main paper), despite the non-uniform concentration of spheres in the cell. After around 500 s (red arrow 2), no further steps and only a small current decay were recognized, indicating an effective maximum surface concentration of the spheres at the electrode, with continued diffusion of FcMeOH through pores in the layer.

Numerical Simulation of Current Steps Due to Blocking of Electrode by Insulating Particles

Particles

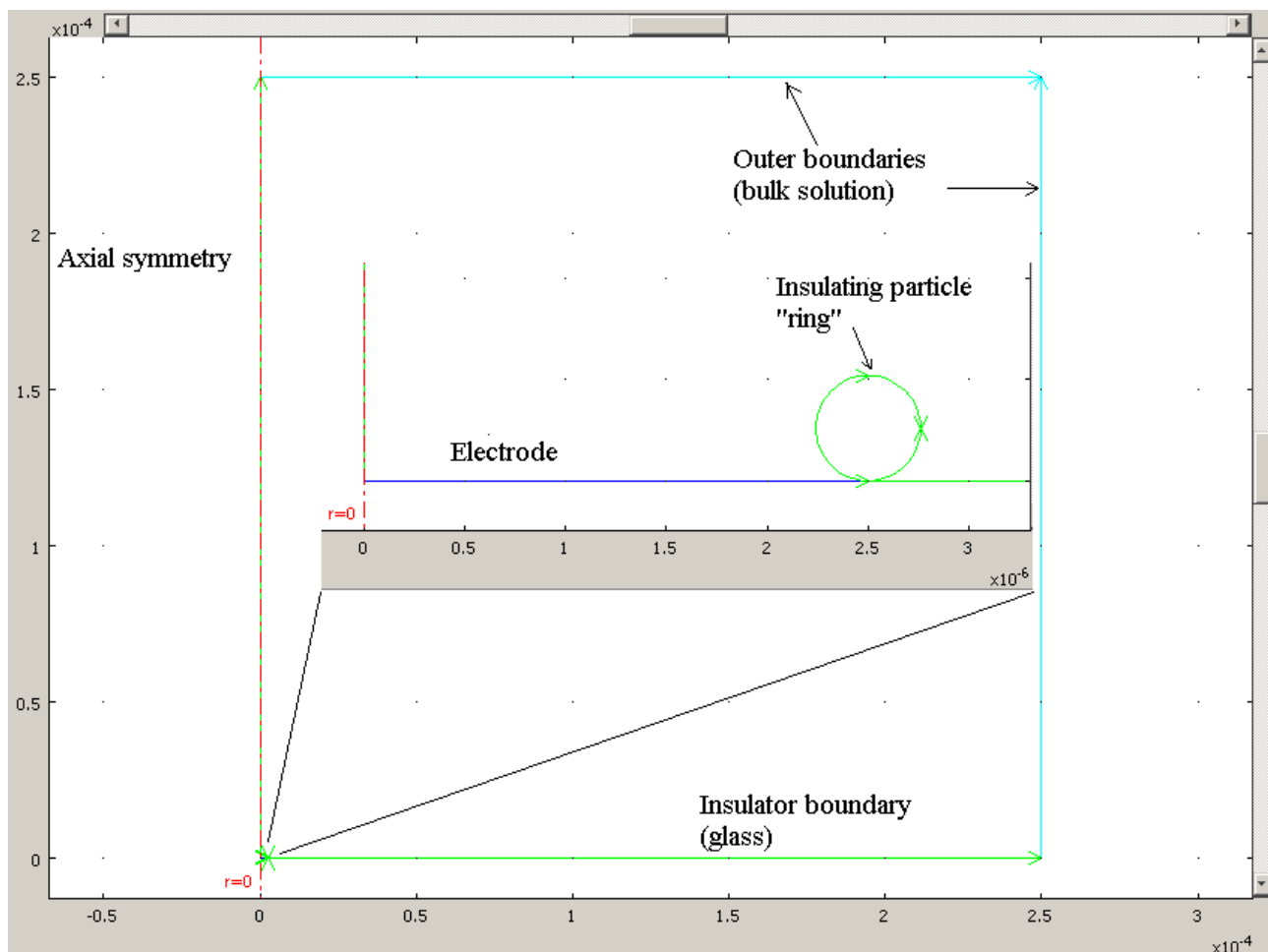


Figure S7. Geometry of the model used in simulations of the magnitude of current steps due to adsorption of insulating particles. An inset shows an electrode disk (2.5 μm radius) embedded in a glass sheath and a spherical ring representing an insulating feature positioned right on top of the disk edge.

The expressions for the boundary conditions used in the simulations are given by eqs 1-3.

For the electrode surface a fully reversible redox process is assumed (ferrocenemethanol oxidation):

$$C = 0 \quad (1)$$

where C is the concentration of FcMeOH.

For the bulk solution boundary:

$$C = C_b \quad (2)$$

where C_b is the bulk concentration of FcMeOH.

For the axial symmetry axis, insulating ring and glass sheath:

$$\bar{n} \cdot \bar{J} = 0 \quad (3)$$

where n is the normal vector and J is the flux of the redox species given by the Nernst-Planck equation (eq. 2 in the main paper).

The initial condition is given by an equation identical to eq. 2.

Finally, the current through the disk is obtained by a simple integration:

$$I = nFD \int_0^{r_0} 2\pi r \frac{\partial C}{\partial z} dr \quad (4)$$

where n is the number of electrons transferred in the electrode reaction (one), F is the Faraday constant, D is the diffusion coefficient of the redox species ($1 \cdot 10^{-5}$ cm²/s), r_0 is the radius of the electrode and $\partial C/\partial z$ is the species concentration gradient at the electrode surface.

Numerical Simulation of Mass Transport of Insulating Particles to the Working Electrode

For the boundary conditions one has to specify the relations that describe concentrations of all the species and the electric (migration) field at all system boundaries. In the bulk solution concentrations of the species are given by their bulk values (similar to eq. 2) and the electric (migration) potential is zero:

$$\varphi = 0 \quad (5)$$

At the electrode surface the flux boundary conditions are used to describe the flux of the redox species (eqs. 6-7), and a no-flux condition is used for the cations of the supporting electrolyte (eq. 8).

$$\bar{n} \cdot \bar{J} = k_f C_A - k_b C_{A^+} \quad (6)$$

$$\bar{n} \cdot \bar{J} = -k_f C_A + k_b C_{A^+} \quad (7)$$

$$\bar{n} \cdot \bar{J} = 0 \quad (8)$$

It should be noted that the concentration of anions of the supporting electrolyte in our model is determined using the electroneutrality condition, so no condition needs to be specified specifically for these ions. The electrode surface boundary condition for the nanoparticle concentration is identical to eq. 1; it means that all particles reaching the surface of the electrode “stick” to it thus leaving the solution phase.

The rate constants k_f and k_b in eqs. 6-7 are given assuming Butler-Volmer kinetics:

$$k_f = k_0 \exp\left[\frac{(1-\alpha)F}{RT}(E - E^0)\right] \quad (9)$$

$$k_b = k_0 \exp\left[\frac{-\alpha F}{RT}(E - E^0)\right] \quad (10)$$

where k_0 is the standard rate constant (assumed 1 cm/s), α is the electron transfer coefficient (assumed 0.5), E is the electrode potential and E^0 is the standard potential of FcMeOH⁺/FcMeOH couple.

For the migration electric field a current inflow boundary condition is used:

$$-\bar{n} \cdot F \sum_i z_i J_i = z_{A^+} F \left(-D_{A^+} \frac{\partial C_{A^+}}{\partial z} - z_{A^+} u_{A^+} F C_{A^+} \frac{\partial \varphi}{\partial z} \right) \quad (11)$$

where u is the mobility of the ionic species indicated by the subscript and all other symbols have their usual meaning. One can see that this current density is proportional to the flux of the hydroxymethylferricinium ions.

All other boundary conditions are given similarly to eq. 3 (insulating boundaries).

For initial conditions it is assumed that the potential φ is zero everywhere in the system and the concentrations of all species are equal to their values in the bulk solution.

Besides the boundary and initial conditions one also has to specify the mobility and charge of all ionic species, as well as the nanoparticles. For ions in solution the mobility and diffusion coefficients are directly related:

$$u_i = D_i \frac{|z_i|F}{RT} \quad (1)$$

where the diffusion coefficient is given by the Einstein-Smoluchowski equation (eq. 13).

$$D_i = \frac{kT}{6\pi\eta a} \quad (2)$$

where k is the Boltzmann constant, η is the viscosity of solution and a is the radius of a species.

However, the behavior of large (compared to ions) colloidal particles is more complex and their mobility is expected to depend, among other parameters in eqs. 12-13, on the concentration of the supporting electrolyte ions in solution.¹ Therefore, the mobility of nanoparticles was calculated using an approximate analytical relation reported by Ohshima et al.² Also, the average charge on nanoparticles z_p was determined from their electrokinetic charge density σ^{ek} , which in turn is related to the zeta potential of the particles ζ in aqueous solutions at 25 °C:³

$$\sigma^{ek} = -11.73\sqrt{C_p} \sinh(0.0195 z_p \zeta) \quad (3)$$

where C_p is the molar concentration of the particles, σ^{ek} has units $\mu\text{C cm}^{-2}$ and ζ is in mV.

The values of the zeta potential (measured experimentally), as well as the comparison between the simulated and experimentally determined values of the collision frequency, are listed in Table 1 of the main text.

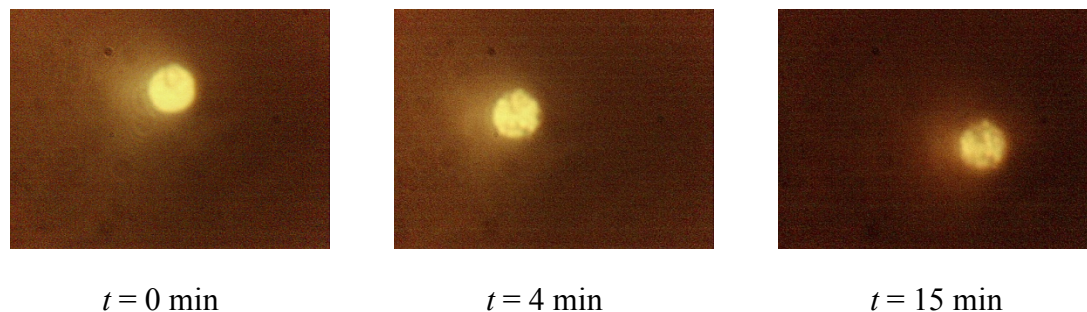


Figure S8. Photographs of a 2.5 μm radius disk Pt UME taken during the recording of a polystyrene particle adsorption chronoamperogram (t indicates the time from the beginning of the experiment when a photograph was taken). The size of particles was 520 nm and the concentration 50 fM. Other experimental conditions were the same as indicated in the caption of Fig. 6.

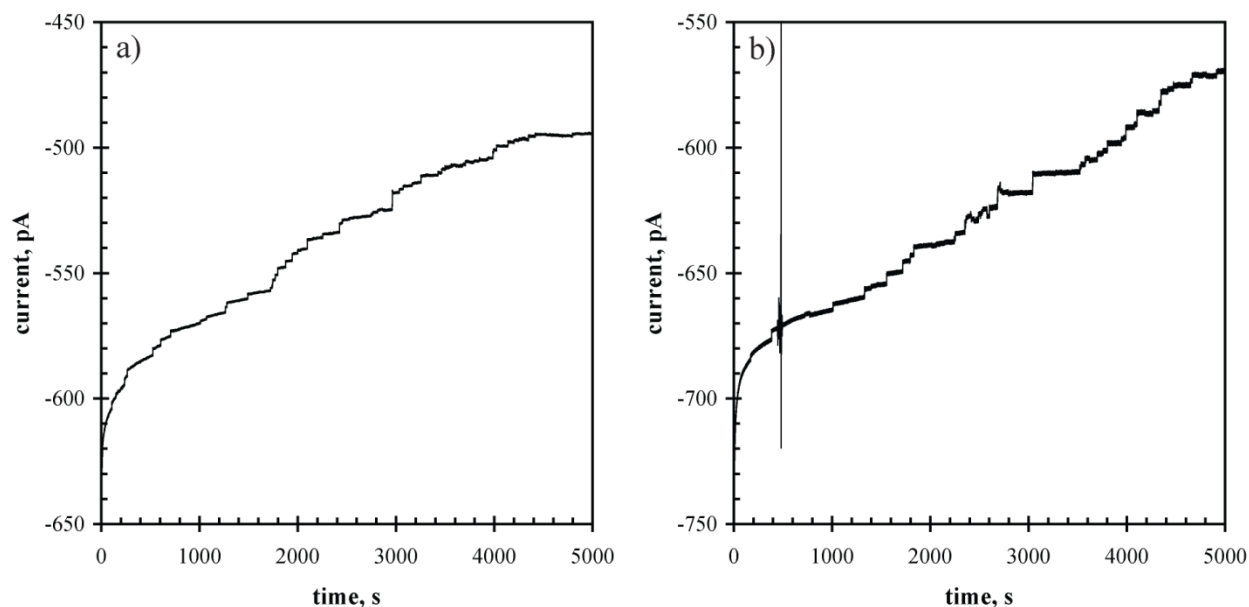


Figure S9. Sphere collision chronoamperograms recorded for a 2 μm diameter Pt UME biased at +0.5 V vs. Ag/AgCl in 2.5 mM FcMeOH with 1 mM KCl and in the presence of 5 fM 310 nm diameter silica spheres, with all other experimental details identical to those described in the main paper. These experiments at low sphere concentration were used to test the occurrence of unlikely “bunches” of steps which may indicate reorganization of spheres on the electrode surface. An example of one such step bunch is shown in Figure 8b, and was drawn from the chronoamperogram shown in panel a) above. The large current spikes occurring near 250 s in the chronoamperogram shown in panel b) above were due to accidental disconnection and reconnection of the Faraday cage ground at the potentiostat instrument panel, and did not coincide with any step features.

References

- ¹ O'Brien, R. W.; White, L. R. *J. Chem. Soc., Faraday Trans. 2*, **1978**, 74, 1607.
- ² Ohshima, H.; Healy, T. W.; White, L. R. *Chem. Soc., Faraday Trans. 2*, **1983**, 79, 1613.
- ³ Lyklema, J. *Fundamentals of Interface and Colloid Science, vol. II*. Academic Press, London, 1995, pp. 3.21.