

Supporting Information

Single Collision Events of Conductive Nanoparticles Driven by Migration

Jun Hui Park, Aliaksei Boika, Hyun S. Park, Heung Chan Lee, Allen J. Bard*

Center for Electrochemistry, Department of Chemistry and Biochemistry, The University of

Texas at Austin, Austin, TX 78712, USA. Fax: 512-471-0088; Tel: 512-471-3761

E-mail: ajbard@mail.utexas.edu

Numerical Simulation of Mass Transport of Particles to the Working Electrode

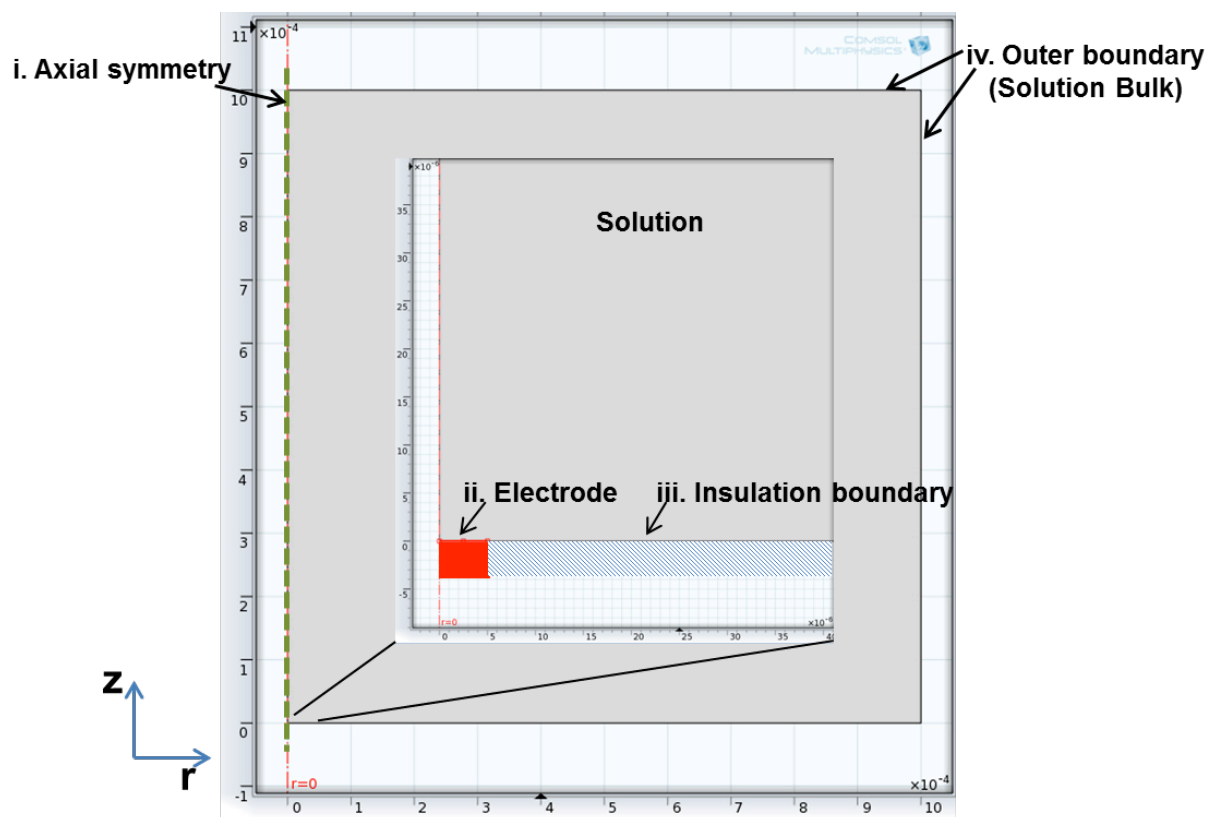
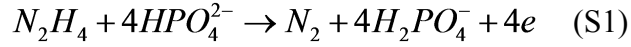


Figure S1. Geometry of the model used in simulations. An electrode disk ($5\ \mu\text{m}$ radius) embedded in a glass sheath.

Simulation details

A hydrazine oxidation reaction in a phosphate buffer solution is assumed as:



To consider both diffusion and migration of every species in solution the Nernst-Planck equation is used.

$$J_i(r, z) = -D_i \nabla C_i(r, z) - u_i C_i(r, z) \nabla V(r, z) \quad (S2)$$

where J_i is the flux of each species, D_i is the diffusion coefficient, C_i is the concentration, u_i is the electrical mobility of the ionic species, F is the Faraday constant, V is the electric potential, every species are indicated by the subscript.

For ions in solution the electrical mobility and diffusion coefficients are directly related:

$$u_i = \frac{z_i F D_i}{RT} \quad (S3)$$

where R is the ideal gas constant, T is temperature.

However, the mobility of the NP was directly measured by the particle analyzer after removing residual surfactant in NP solution as described in the main paper.

Potential V is defined by the Poisson equation.

$$-\nabla \cdot \epsilon_0 \epsilon_r \nabla V = \rho \quad (S4)$$

Charge density (ρ) is defined as

$$\rho = \sum C_i z_i F \quad (S5)$$

We assume an anodic current flow at the working electrode implying the injection of positive charge into the solution in the form of ions. Charge imbalance produces the potential, which affects the motion of all charged species in solution. The initial conditions of the potential V (before current flow) is assumed to be zero everywhere in the system.

The expressions for the boundary conditions used in the simulations are given in Table 1, where C_{bulk} is the bulk concentration, n is the normal vector, ρ_s is the surface charge, and n_e is the number of electrons in reaction (S1).

Table 1. Boundary conditions used in Figure S1.

Boundary selection	Boundary conditions	Quantity	Note
i	Axial symmetry	$r = 0$	symmetry axis
ii	Concentration, Flux, Flux, Flux, Flux, Surface Charge	$C_{NP} = 0,$ $\bar{n} \cdot \bar{J}_{Na^+} = 0,$ $\bar{n} \cdot \bar{J}_{HPO_4^{2-}} = -\frac{i}{n_e F},$ $\bar{n} \cdot \bar{J}_{H_2PO_4^-} = \frac{i}{n_e F},$ $\bar{n} \cdot \bar{J}_{N_2H_4} = -\frac{i}{F},$ $\rho_s = \sum C_i z_i F$	electrode surface
iii	Insulation/Symmetry, Surface Charge	$\bar{n}_i \cdot \bar{J}_i = 0,$ $\rho_s = 0$	insulator
iv	Concentration, Ground	$C_i = C_{bulk},$ $V = 0$	simulation space limit

Finally, the NP collision flux at the disk electrode is obtained by a simple integration:

$$J_{NP} = \int_0^{r_0} 2\pi r \frac{\partial C_{NP}}{\partial z} dr \quad (S6)$$

Where r_0 is the radius of the electrode, $\partial C_{NP}/\partial z$ is the NP concentration gradient at the electrode surface.

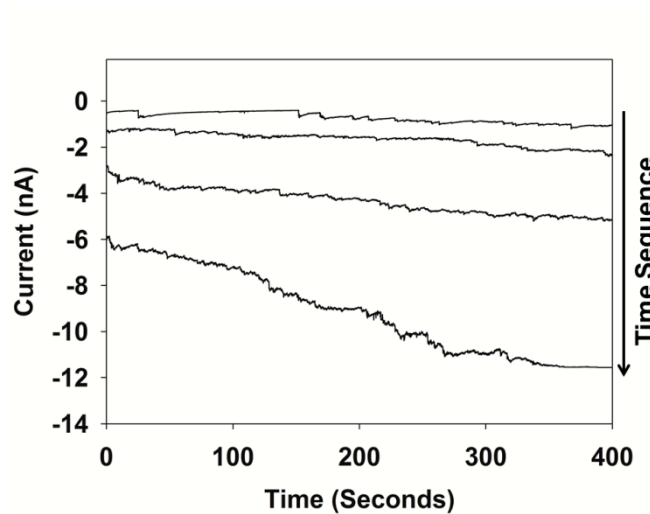


Figure S2. Four consecutive chronoamperometric curves for single Pt NP (radius ~16 nm) collisions at the Au UME (radius 5 μm) in the presence of 7.5 pM Pt NPs, 5 mM phosphate buffer (pH 7.0) and 15 mM hydrazine. Applied potential is -150 mV (vs Ag/AgCl).