Supporting Information

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A Joint Experimental and Computational Search for Authentic Nano-electrocatalytic Effects: Electrooxidation of Nitrite and L-Ascorbate on Gold Nanoparticle-Modified Glassy Carbon Electrodes

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Supporting Information

1. Simulation Details

1.1. Electrode Kinetics

For the one-electron oxidation:

\[ A \xrightleftharpoons{\kappa^0, \alpha, \beta^0} \overset{\alpha}{\rightarrow} B + e^- \]  

the flux of species 'A' normal to the electrode surface at a given applied potential \( E \) is described by the Butler-Volmer equation:

\[
D \frac{\partial [A]_0}{\partial x} = \kappa^0 \left[ \exp \left( \frac{1 - \alpha}{RT} \left( E - E_r^0 \right) \right) \left[ A \right]_0 - \exp \left( -\alpha \frac{F}{RT} \left( E - E_r^0 \right) \right) \left[ B \right]_0 \right]
\]  

where \( F \) is the Faraday constant, \( R \) is the gas constant, \( T \) is the temperature, \( x \) is a Cartesian coordinate normal to the electrode surface and \( \left[ i \right]_0 \) refers to the concentration of the species \( i \) at the electrode surface (\( x = 0 \)). Given that \( E_r^0 \) is dependent on the redox couple and the surrounding medium, the use of different electrodes can result in a change in the rate constant \( \kappa^0 \) and the transfer coefficient \( \alpha \) for the electrode reaction.

1.2. Numerical Simulation

Modelling the entire 3-dimensional ensemble of nanoparticles directly is not a realistic possibility, but certain assumptions and simplifications can be employed to give a highly accurate approximation. First it is assumed that for a given electrode, all of the nanoparticles are of the same size and are regularly distributed over the GC substrate. Now since the substrate is large and there are a large number of particles, differences due to the altered local environment at the edge of the disc can be considered negligible\(^1\) and so the GC surface may
be treated as though it is composed of a vast array of identical unit cells, each centred around a single nanoparticle. Since each cell is identical, only one need be simulated with the results simply being scaled by the total number of nanoparticles on the GC surface. This is still a 3-dimensional problem (albeit much smaller) and is thus highly computationally demanding. Through the use of the ‘diffusion domain approximation’ each unit cell is approximated as a cylindrical cell of the same radius, \( r \) (see Figure S1):

\[
r = \sqrt{\frac{r_e^2}{\Theta}} \quad (3)
\]

where \( \Theta \) is the surface coverage and \( r_e \) the radius of a single nanoparticles.

Previous studies have demonstrated that simulations employing the diffusion domain approximation show very good agreement with experiments\(^{[4]}\) and that there is little difference between the simulated voltammetry of arrays of regular and random distribution in most cases, the differences being only significant when very slow scan rates are employed (less than 10 mV s\(^{-1}\))\(^{[5]}\).

The use of the diffusion domain approximation renders the cell cylindrically symmetric and therefore allows it to be represented in a 2-dimensional cylindrical polar coordinate system as depicted in Figure S1, which is computationally tractable. The simulation space is therefore a 2D ‘slice’ of the unit cell with radial coordinate \( r \) and axial coordinate \( z \).

The simulation model is normalized using the dimensionless parameters shown in Table S1. The \((R,Z)\) coordinate system is defined relative to the hemisphere radius while the dimensionless time, \( T \), is defined in terms of the radius and the diffusion coefficient. In this normalized space, the surface of the hemispherical nanoparticle is described by:

\[
R^2 + Z^2 = 1 \quad \text{where } R, Z \geq 0 \quad (4)
\]
The 2-dimensional continuous space is discretized by dividing it up into a finite grid of spatial points as shown in Figure S2. The distribution of spatial points in the region of the nanoparticle is determined by specifying an angular increment $\Delta \phi$, where $\phi$ is the angle in radians measured from the $R$ axis, and calculating the values of $R$ and $Z$ at each increment\(^{[6]}\), from:

$$
R = \cos \phi \\
Z = \sin \phi
$$

This allows grid points to fit precisely to the curved surface of the spherical particle. The grid spacing expands exponentially from the surface of the nanoparticle in both directions and contracts again in the $R$ direction as the outer boundary of the unit cell is approached, in order to ensure simulation accuracy.

### 1.2.1 Mass transport

As an excess of supporting electrolyte is added in each experiment, the effects of migration may be ignored, and the movement of chemical species in solution is attributed solely to diffusion down a concentration gradient. Diffusion may be modelled by Fick's second law in 2D cylindrical polar coordinates using our normalized coordinate system:

$$
\frac{\partial C_i}{\partial T_{\text{diff}}} = \delta_i \left( \frac{\partial^2 C_i}{\partial R^2} + \frac{1}{R} \frac{\partial C_i}{\partial R} + \frac{\partial^2 C_i}{\partial Z^2} \right)
$$

where $C_i$ is the normalized concentration of species $i$, $T$ is the normalized time and $\delta_i$ the normalized diffusion coefficient of the species in question.

Homogeneous chemical reactions can be accounted for in the mass transport equation by introducing an additional term for each species involved in a chemical step. Therefore at some point in the solution $(R, Z)$, at some arbitrary time, $T$, the rate of change of concentration of each chemical species is given by the sum of the diffusional and reaction terms:

**Nitrite electrooxidation**
\[
\frac{\partial \text{C}_{\text{NO}_3}}{\partial T} = \delta_{\text{NO}_3} \left( \frac{\partial^2 \text{C}_{\text{NO}_3}}{\partial R^2} + \frac{1}{R} \frac{\partial \text{C}_{\text{NO}_3}}{\partial R} + \frac{\partial^2 \text{C}_{\text{NO}_3}}{\partial Z^2} \right) + K_{\text{disp}} \text{C}_{\text{NO}_3}^2 \quad (7)
\]

\[
\frac{\partial \text{C}_{\text{NO}_2}}{\partial T} = \delta_{\text{NO}_2} \left( \frac{\partial^2 \text{C}_{\text{NO}_2}}{\partial R^2} + \frac{1}{R} \frac{\partial \text{C}_{\text{NO}_2}}{\partial R} + \frac{\partial^2 \text{C}_{\text{NO}_2}}{\partial Z^2} \right) - 2K_{\text{disp}} \text{C}_{\text{NO}_2}^2 \quad (8)
\]

\[
\frac{\partial \text{C}_{\text{NO}_3}}{\partial T} = \delta_{\text{NO}_3} \left( \frac{\partial^2 \text{C}_{\text{NO}_3}}{\partial R^2} + \frac{1}{R} \frac{\partial \text{C}_{\text{NO}_3}}{\partial R} + \frac{\partial^2 \text{C}_{\text{NO}_3}}{\partial Z^2} \right) + K_{\text{disp}} \text{C}_{\text{NO}_3}^2 \quad (9)
\]

**L-ascorbate electrooxidation**

\[
\frac{\partial \text{C}_{\text{AH}^-}}{\partial T} = \delta_{\text{AH}^-} \left( \frac{\partial^2 \text{C}_{\text{AH}^-}}{\partial R^2} + \frac{1}{R} \frac{\partial \text{C}_{\text{AH}^-}}{\partial R} + \frac{\partial^2 \text{C}_{\text{AH}^-}}{\partial Z^2} \right) \quad (10)
\]

\[
\frac{\partial \text{C}_{\text{A}^-}}{\partial T} = \delta_{\text{A}^-} \left( \frac{\partial^2 \text{C}_{\text{A}^-}}{\partial R^2} + \frac{1}{R} \frac{\partial \text{C}_{\text{A}^-}}{\partial R} + \frac{\partial^2 \text{C}_{\text{A}^-}}{\partial Z^2} \right) \quad (11)
\]

\[
\frac{\partial \text{C}_{\text{DHA}}}{\partial T} = \delta_{\text{DHA}} \left( \frac{\partial^2 \text{C}_{\text{DHA}}}{\partial R^2} + \frac{1}{R} \frac{\partial \text{C}_{\text{DHA}}}{\partial R} + \frac{\partial^2 \text{C}_{\text{DHA}}}{\partial Z^2} \right) - K_1 \text{C}_{\text{DHA}} \quad (12)
\]

\[
\frac{\partial \text{C}_{\text{HDHA}}}{\partial T} = \delta_{\text{HDHA}} \left( \frac{\partial^2 \text{C}_{\text{HDHA}}}{\partial R^2} + \frac{1}{R} \frac{\partial \text{C}_{\text{HDHA}}}{\partial R} + \frac{\partial^2 \text{C}_{\text{HDHA}}}{\partial Z^2} \right) + K_1 \text{C}_{\text{DHA}} \quad (13)
\]

To perform simulations, the mass transport equation for each species is discretized to the grid of \((R, Z)\) spatial points using the well-known alternating direction implicit (ADI) method\(^7\). The resulting set of partial differential equations is non-linear, and so it is solved for each species at each successive time step using the iterative Newton-Raphson method\(^7\), subject to the boundary conditions described below. Note that internally, these equations are represented in terms of a conventional set of normalised parameters which reduces the number of solutions by amalgamating parameters that act as scaling factors into parameters that do not.
At the beginning of the simulation (i.e. \( T=0 \)), the concentration of the starting species (\( \text{NO}_2^- \) and \( \text{AH}^- \)) is uniform and equal to its bulk value across the whole simulation space, and that of every other species is 0. In the Z direction, the simulation space extends as far as \( Z_{\text{max}} = 6\sqrt{T_{\text{max}}} \) where \( T_{\text{max}} \) is the length of time that the simulated experiment will run for. This distance exceeds the maximum extent of the diffusion layer by the Einstein equation\(^8\), and so the concentration at this point is set to its bulk value. As the system has mirror symmetry about the Z-axis, there can be no material flux through this boundary \((R=0)\) and so the boundary condition is simply one of zero flux \((\partial \theta / \partial R = 0)\). Similarly, as each unit cell is identical, the boundary between them must also have zero flux of material across it.

Finally, both the surface of the Au nanoparticle and at the planar GC surface, a normalized version of the Butler-Volmer equation, described in Section 1, is used as a boundary condition, with different values of dimensionless rate constant, \( K_0 \), for each material:

**Nitrite electrooxidation**

\[
D_{\text{NO}_2^-} \frac{\partial \theta}{\partial N} = -D_{\text{NO}_2^-} \frac{\partial \theta}{\partial N} = K_0 \left( C_{\text{NO}_2^-} e^{\theta} - C_{\text{NO}_2^-} e^{-\theta} \right) \quad (14)
\]

**L-ascorbate electrooxidation**

\[
D_{\text{AH}^-} \frac{\partial \theta}{\partial N} = K_0 \left( C_{\text{AH}^-} e^{\theta} - C_{\text{AH}^-} e^{-\theta} \right) \quad (15)
\]

\[
D_{\text{A}^-} \frac{\partial \theta}{\partial N} = -K_1 \left( C_{\text{A}^-} e^{\theta} - C_{\text{A}^-} e^{-\theta} \right) + K_2 \left( C_{\text{A}^-} e^{\theta} - C_{\text{DHA}^-} e^{-\theta} \right) \quad (16)
\]

\[
D_{\text{DHA}^-} \frac{\partial \theta}{\partial N} = -K_2 \left( C_{\text{A}^-} e^{\theta} - C_{\text{DHA}^-} e^{-\theta} \right) \quad (17)
\]

where \( N \) is the spatial coordinate normal to the particle surface.
To simulate cyclic voltammetry, the dimensionless potential, $\theta$, is swept from some initial value, $\theta_{\text{initial}}$, to a more oxidising potential, $\theta_{\text{final}}$, followed by a reverse sweep. At any time, $T$, the value of $\theta$ is given by:

Forward
$$\theta = \theta_{\text{initial}} + \sigma T$$  \hspace{1cm} (18)

Backward
$$\theta = \theta_{\text{final}} - \sigma (T - T_{1/2})$$  \hspace{1cm} (19)

where $\sigma$ is the normalized scan rate and $T_{1/2}$ is the time at which the sweep direction is reversed. The value of $\theta$ is then used in a normalized version of the Butler-Volmer boundary condition. The boundary conditions are summarized in Table S2.

1.2.3 Current Calculations

The normalized current of a single unit cell is the sum of the contributions from the Au nanoparticle and from the planar GC surface:

$$J_{\text{cell}} = 2\pi (J_{\text{Au}} + J_{\text{GC}})$$  \hspace{1cm} (20)

where $J_{\text{Au}}$ and $J_{\text{GC}}$ are related to the rate of consumption of electroactive material at the Au and GC surfaces respectively (see below). The factor of $2\pi$ is necessary because the simulation space is a 2D slice of the cylindrically symmetric unit cell. The total normalized current is equal the current of a single unit cell multiplied by the number of such cells, $N$. The real current may be obtained according to the relation shown in Table S1.

As the simulation grid is rectangular, the flux at each point on the surface of the nanoparticle is found by summing its components in the $R$ and $Z$ directions. The $J_{\text{Au}}$ value is then found by integrating over the surface:

$$J_{\text{Au}} = \delta \int_0^{\pi/2} \left( \frac{\partial C_i}{\partial R} \cos \phi + \frac{\partial C_i}{\partial Z} \sin \phi \right) \cos \phi \, d\phi$$  \hspace{1cm} (21)
The $J_{Au}$ value is similarly found by integrating the particle flux over the whole surface:

$$J_{GC} = \delta \int_{1}^{R_{max}} \frac{\partial C_i}{\partial Z} R \ dR$$

(22)

The fact that the current response from each material of this composite electrode may be tracked individually can be very useful analytically.

1.2.4 Computation

Simulations were written in C++ with OpenMP for multithreading support and compiled using MSVC++. They were performed with a Dell Precision T5500 with two quad-core hyper-threaded Intel Xeon E5520 processors (16 logical cores, 2.23 GHz). The alternating direction implicit (ADI) method used for simulations in 2-dimensional space is particularly amenable to parallelization: at each time step, multiple calculations may be carried out simultaneously (provided the machine has multiple processor cores), which can decrease runtime considerably. A convergence study was run to determine optimum parameters for spatial and temporal grid densities which gave a good compromise between runtime and simulation accuracy. Typical simulation runtime was in the range 10-20 mins on the machine specified above.
Table S1. Dimensionless parameters.

<table>
<thead>
<tr>
<th>Dimensionless Parameters</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Radial Coordinate</td>
<td>$R = \frac{r}{r_e}$</td>
</tr>
<tr>
<td>Normal Coordinate</td>
<td>$Z = \frac{z}{r_e}$</td>
</tr>
<tr>
<td>Time</td>
<td>$T = \frac{D_A t}{r_e^2}$</td>
</tr>
<tr>
<td>Butler-Volmer Rate Constant</td>
<td>$K^0 = k^0 \frac{r_e}{D_A}$</td>
</tr>
<tr>
<td>Concentration of species $i$</td>
<td>$C_i = \frac{c_i}{C_{A_{bulk}}}$</td>
</tr>
<tr>
<td>Diffusion Coefficient of species $i$</td>
<td>$\delta_i = \frac{D_i}{D_A}$</td>
</tr>
<tr>
<td>Potential</td>
<td>$\theta = \frac{F}{RT} \left( E - E^0_f \right)$</td>
</tr>
<tr>
<td>Scan Rate</td>
<td>$\sigma = \frac{F}{RT D_A} \frac{r_e^2}{V}$</td>
</tr>
<tr>
<td>First Order Rate Constant</td>
<td>$K_1 = \frac{k_r r_e^2}{D_A}$</td>
</tr>
<tr>
<td>Second Order Rate Constant</td>
<td>$K_{disp} = \frac{k_{disp} r_e^2 c_{A_{bulk}}}{D_A}$</td>
</tr>
<tr>
<td>Current</td>
<td>$J = \frac{1}{FD_A c_{A_{bulk}} r_e}$</td>
</tr>
</tbody>
</table>
**Table S2.** Boundary conditions.

<table>
<thead>
<tr>
<th>Initial conditions</th>
<th>$T \leq 0, \text{all } R, Z$</th>
<th>$C_{NO_2} = C_{AH} = 1; \ C_{\text{others}} = 0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>$Z = Z_{\text{max}}$</td>
<td></td>
</tr>
<tr>
<td>Domain boundary</td>
<td>$R = R_{\text{domain}}$</td>
<td>$\frac{\partial C}{\partial R} = 0$</td>
</tr>
<tr>
<td>Axial symmetry</td>
<td>$R = 0, \ Z &gt; 1$</td>
<td></td>
</tr>
<tr>
<td>Substrate surface (active)</td>
<td>$Z = 0, R &gt; 1$</td>
<td>Butler - Volmer</td>
</tr>
<tr>
<td>Particle surface (active)</td>
<td>$Z^2 + R^2 = 1, \ Z,R &gt; 0$</td>
<td></td>
</tr>
<tr>
<td>Substrate surface (inactive)</td>
<td>$Z = 0, R &gt; 1$</td>
<td></td>
</tr>
<tr>
<td>Particle surface (inactive)</td>
<td>$Z^2 + R^2 = 1, \ Z,R &gt; 0$</td>
<td>$\frac{\partial C}{\partial Z} = \frac{\partial C}{\partial R} = 0$</td>
</tr>
</tbody>
</table>
Figures S1. Coordinate system of simulation space. The space is angularly isotropic so the coordinate \( \phi \) may be ignored, reducing the space to 2 coordinates: the radial coordinate, \( r \), and the axial coordinate, \( z \).
Figure S2. Discretization of the simulation space. Note the greater density of points at finite spatial boundaries (electrode surface and diffusion domain boundaries).
References


2. XPS results

Figure S3. XPS spectra corresponding to the glassy carbon electrode before (bottom) and after (top) immersion in a 0.1 M CTAB solution for 30 minutes.
Figure S4. XPS spectra corresponding to the gold electrode before (bottom) and after (top) immersion in a 0.1 M CTAB solution for 30 minutes.
3. Effect of the bromide adsorption

**Figure S5.** Effect of the adsorption of bromide on the gold electrode for the electrooxidation of nitrite (A) and L-ascorbate (B). White points correspond to the bare electrodes and black points to the electrodes after 30 min immersion in a 0.1 M NaBr solution and rinse with water.

Scan rate: 25 mV s\(^{-1}\). Nitrite solution: 2 mM NaNO\(_2\), 0.3 M Na\(_2\)SO\(_4\), pH 4.6. L-ascorbate solution: 0.1 mM L-ascorbic acid, 0.1 M PBS, pH 6.8