Supporting Information
"Nanoparticle Electrocatalysis: Unscrambling Illusory Inhibition and Catalysis"

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S1 Theoretical Model

We consider the cyclic voltammetry of an electrochemically reversible reaction of the two species A and B:

$$A + e \rightleftarrows B \tag{S1}$$

The experiment is conducted at a sufficiently high electrolyte concentration to screen the electric field in solution and to suppress migration. Mass transport is hence solely due to diffusion and can be modelled by diffusion equation:

$$\frac{\partial c_i(\vec{r},t)}{\partial t} = D\frac{\partial^2 c_i(\vec{r},t)}{\partial \vec{r}^{\,2}} \tag{S2}$$

where c_i is the concentration of species i, $\vec{r}$ is the spatial coordinate $r\vec{e_r} + z\vec{e_z}$ in cylindrical coordinates and D_i is the diffusion coefficient of species i. The assumption of equal diffusion coefficients for the oxidised and the reduced species, $D_A = D_B$, further yields:

$$\begin{aligned} c_B(\vec{r},t) &= c_B(\vec{r},t=0) + c_B(\vec{r},t=0) - c_A(\vec{r},t) \\ &= c_A^* + C_B^* - c_A(\vec{r},t) \end{aligned} \tag{S3}$$

where c_A^* and c_B^* are the initial homogeneous concentrations of A and B, respectively. The above equation enables us to solve the entire theoretical model by only evaluating diffusion equation for one of the two species. The electrochemical reaction at the electrode is described by the Nernst equation [1;2]:

$$exp\left(\frac{F}{RT}(E - E_f^0)\right) = \frac{c_A(\vec{r},t)}{c_B(\vec{r},t)} \quad \text{for} \quad r \in [0, r_{max}],\ z = 0 \tag{S4}$$

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where E_f^0 is the formal potential and F, R, and T feature their usual significance. All other boundary conditions are set as indicated in Figure 1 in the main text.

S2 Computational

The theoretical model is solved by means of finite differences and the alternating direction implicit method. For the purpose of this study, custom software that was developed. The simulation code is written in *C++* and utilises the *OpenMP* application programming interface for parallel computing. All further data processing and -visualisation is done in *Python* via the packages *NumPy* and *matplotlib*.

We appreciate the importance of thorough software testing[3] and compare simulation results with theoretical models for peak heights, peak positions, and peak-to-peak separations where possible and as shown in the Figures 2, 3, and 5 in the main text. In addition, we check the conservation of mass in all simulations.

References

[1] R. G. Compton and C. E. Banks. *Understanding voltammetry, second edition.* Imperial College Press, 2011.

[2] A. J. Bard and L. R. Faulkner. *Electrochemical methods: Fundamentals and applications.* John Wiley & Sons, Inc, 2001.

[3] E. Kätelhön and R. G. Compton. Testing and validating electroanalytical simulations. *Analyst*, 140:2592–2598, 2015.