

SUPPLEMENTARY MATERIAL

Aryldiazonium reduction mechanism deciphered by scanning electrochemical microscopy through an EC' process.

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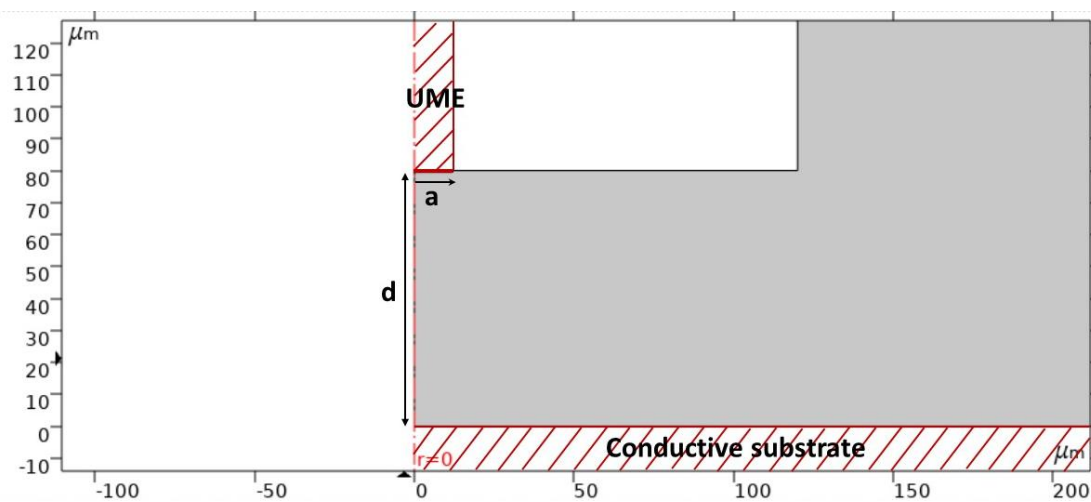


Figure S1: Geometry of the SECM configuration used in the Comsol model. The radius of the conductive substrate considered herein is 1000 μm , to ensure a planar diffusion process.

Table S1: Parameters used in the simulation model

Parameter symbol	Value	Note
a_{UME}	12 μm	UME radius
d	0.1-80 μm	UME-substrate distance
t	100 s	time of the experiment
$C_{0,\text{Ch}}$	2 mM	Initial concentration of-chloranil
$C_{0,\text{Diazo}}$	2 mM	Initial concentration of 4-NBD
$k_{\text{sc, GC}}$	$3 \times 10^{-2} \text{ cm} \cdot \text{s}^{-1}$	Heterogeneous electron transfer rate for the redox mediator
$k_{\text{sd Au}}$	$3 \times 10^{-2} \text{ cm} \cdot \text{s}^{-1}$	Heterogeneous electron transfer rate for the 4-NBD electroreduction
k_{f}	varying $\text{M}^{-1} \cdot \text{s}^{-1}$	rate constant associated to the reaction between the reduced form of chloranil and 4-NBD
k_{d}	varying s^{-1}	First order dissociation rate constant of the diazenyl
$k_{\text{f}'}$	varying $\text{M}^{-1} \cdot \text{s}^{-1}$	reaction rate constant associated to the reaction between the aryl radical and 4-NBD
$k_{\text{f}''}$	varying $\text{M}^{-1} \cdot \text{s}^{-1}$	reaction rate constant associated to the reaction between the aryl radical and the and chloranil
D_{ch}	$7 \times 10^{-6} \text{ cm}^2 \cdot \text{s}^{-1}$	Diffusion constant of chloranil and its reduced counterpart
D_{diazo}	$1 \times 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$	Diffusion constant of 4-NBD and its reduced counterpart

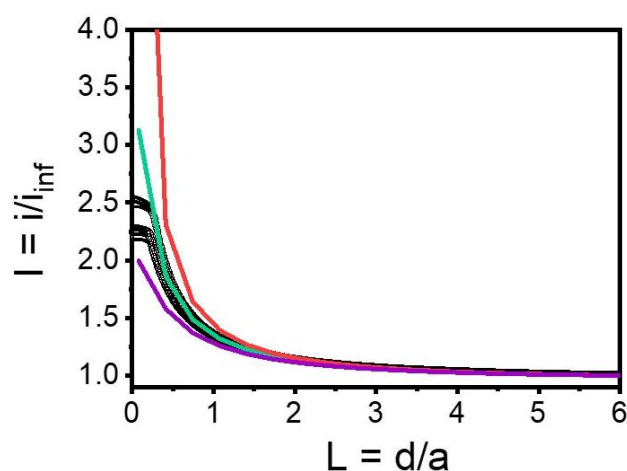


Figure S2: Experimental vs simulated approach curves with 2 mM of chloranil at a conducting GC substrate in DMF solutions in the presence of 0.1 M TBAPF₆, applying -0.3 V vs Ag pseudo reference at a 25 μm diameter gold UME at 1 μm.s⁻¹. The experimental approach curves (□) were recorded at random positions of the substrate. The different simulated curves correspond to a $k_{sc} = 0.3 \text{ cm s}^{-1}$ (—), 0.03 cm s⁻¹ (—) and 0.015 cm s⁻¹ (—).

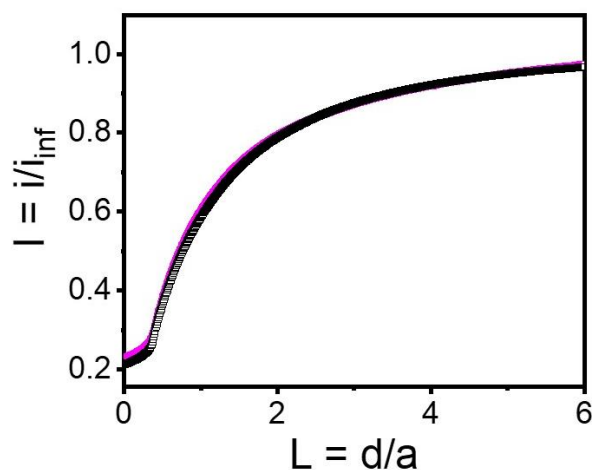


Figure S3: Approach curves recorded with 2 mM of chloranil at a glass substrate without (□) and with (□) addition of 2 mM of 4-nitrobenzenediazonium. The experiments were performed in DMF solutions in the presence of 0.1 M TBAPF₆, applying -0.3 V vs Ag pseudo reference at a 25 μm diameter gold UME at 1 μm.s⁻¹.

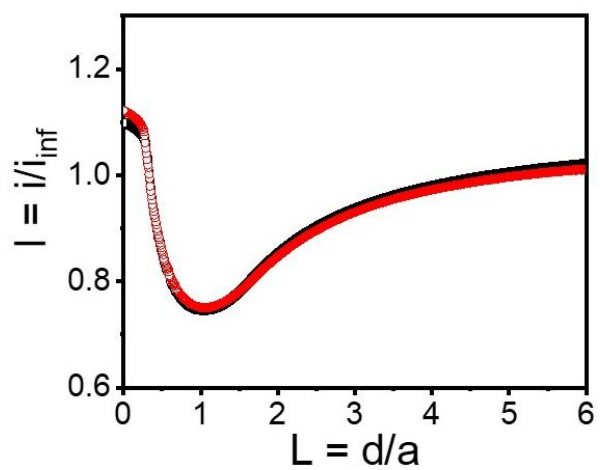


Figure S4: Successive approach curves (first, \square , and second, \square) recorded at a GC substrate with 2 mM of chloranil and 2 mM of 4-nitrobenzenediazonium. The experiments were performed in DMF solutions in the presence of 0.1 M TBAPF₆, applying -0.3 V vs Ag pseudo reference at a 25 μm diameter gold UME at $1 \mu\text{m}\cdot\text{s}^{-1}$.

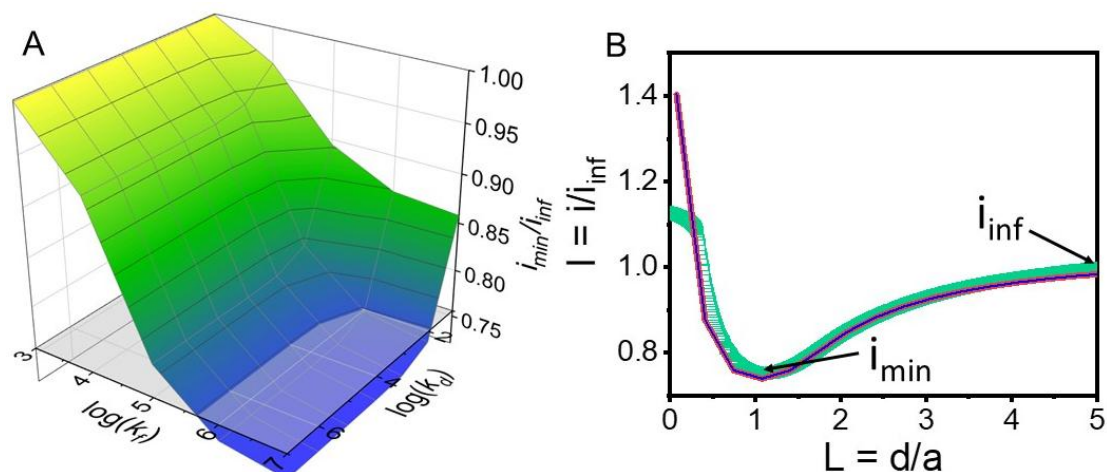


Figure S5: (left) 3D diagram showing the variation of the simulated depletion current over the simulated infinite current as a function of log of the homogeneous electron transfer rate constant (k_f) and the dissociation rate constant of the diazenyl (k_d). The values examined were $10^3, 10^4, 10^5, 10^6, 10^7 \text{ M}^{-1} \cdot \text{s}^{-1}$ and $10, 10^2, 10^4, 10^5, 10^6, 10^7 \text{ s}^{-1}$ for k_f and k_d respectively. (right) Experimental approach curves recorded with 2 mM of chloranil at a 3 mm diameter glassy carbon substrate with 2 mM of 4-nitrobenzenediazonium(\square) in DMF solutions in the presence of 0.1 M TBAPF₆, applying -0.3 V vs Ag pseudo reference at a 25 μm diameter gold UME at 1 μm.s⁻¹. Lines correspond to the simulated curves for $k_f = 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$ and $k_d = 0$ (—) and for $k_f = 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$ and $k_d = 10^4 \text{ s}^{-1}$ (—); other parameters from Table S1.

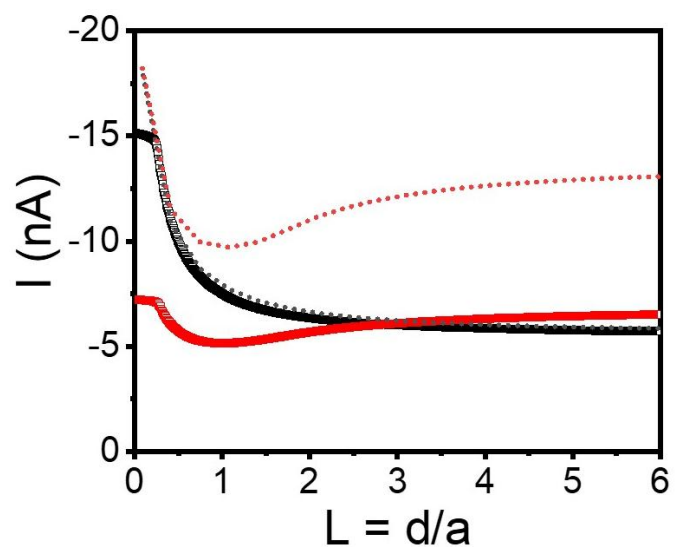


Figure S6: Experimental approach curves recorded with 2 mM of chloranil at a 3mm diameter glassy carbon substrate with 2mM of 4-NBD (□) or 0 mM (□) in DMF solutions in the presence of 0.1 M TBAPF₆, applying -0.3 V vs Ag pseudo reference at a 25 μm diameter gold UME at 1 μm.s⁻¹. Red and black dotted lines correspond to the simulated curves with 2 mM (red) or 0 mM (black) of diazonium, for $k_f = 10^6 \text{ M}^{-1} \cdot \text{s}^{-1}$ and $k_d = 10^4 \text{ s}^{-1}$; other parameters from Table S1.

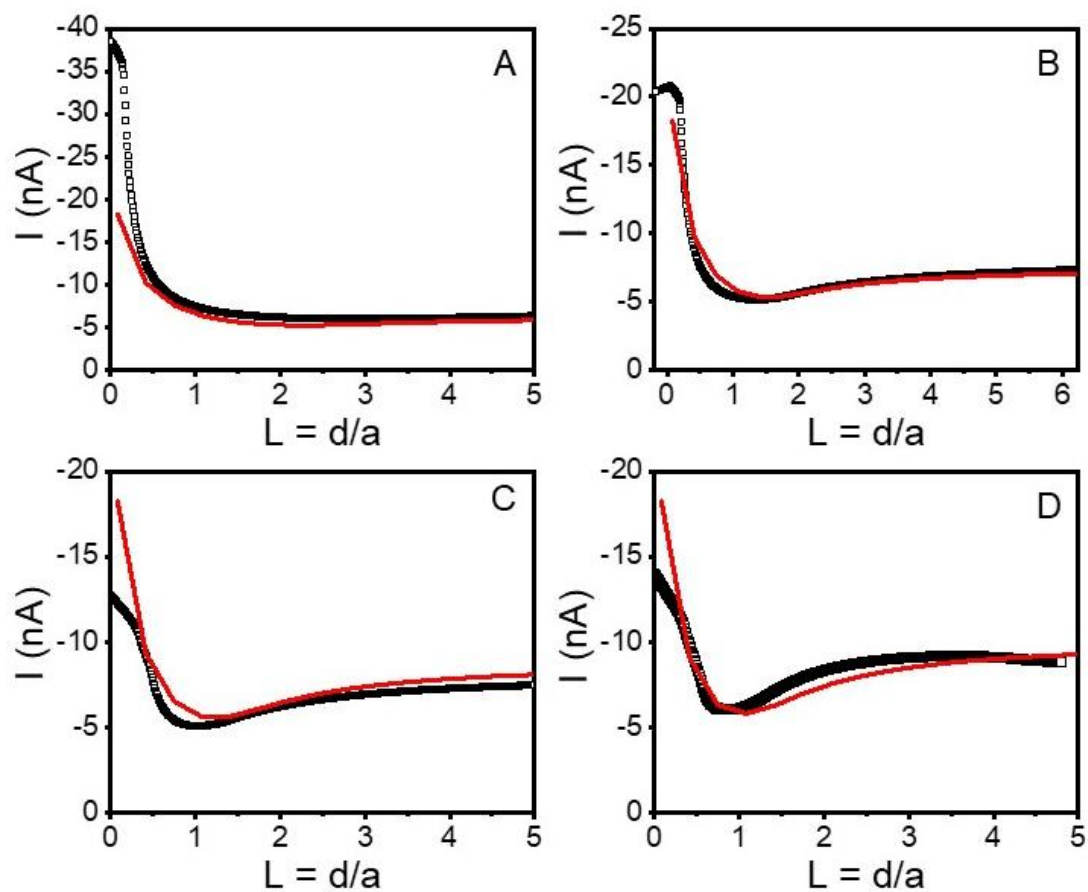


Figure S7: Experimental(\square) vs simulated ($-$) approach curves with 2 mM of chloranil at a 3mm diameter glassy carbon substrate with A) 0.5, B) 1, C) 3 and D) 4 mM of 4-nitrobenzenediazonium in DMF solutions in the presence of 0.1 M TBAPF₆, applying -0.3 V vs Ag pseudo reference at a 25 μm diameter gold UME at $1 \mu\text{m}\cdot\text{s}^{-1}$. For the simulations the following parameters were used $k_f = 6.6 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$, $k_f'' = 4.2 \times 10^4 \text{ M}^{-1} \text{ s}^{-1}$; other parameters from Table S1.